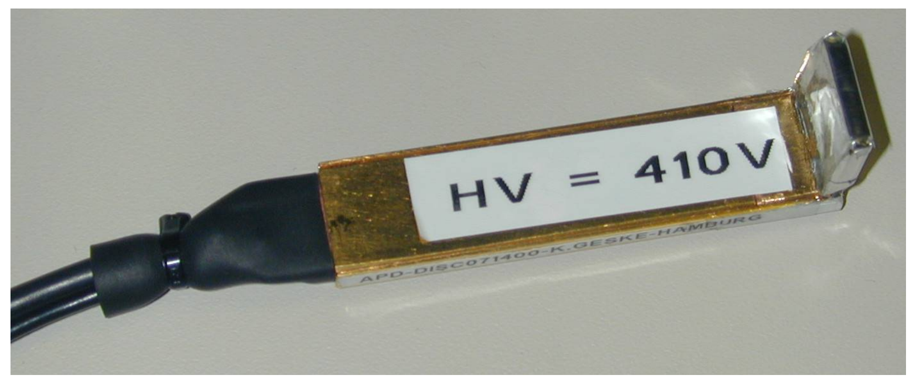
Synchrotron Mössbauer Spectroscopy (SMS)



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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

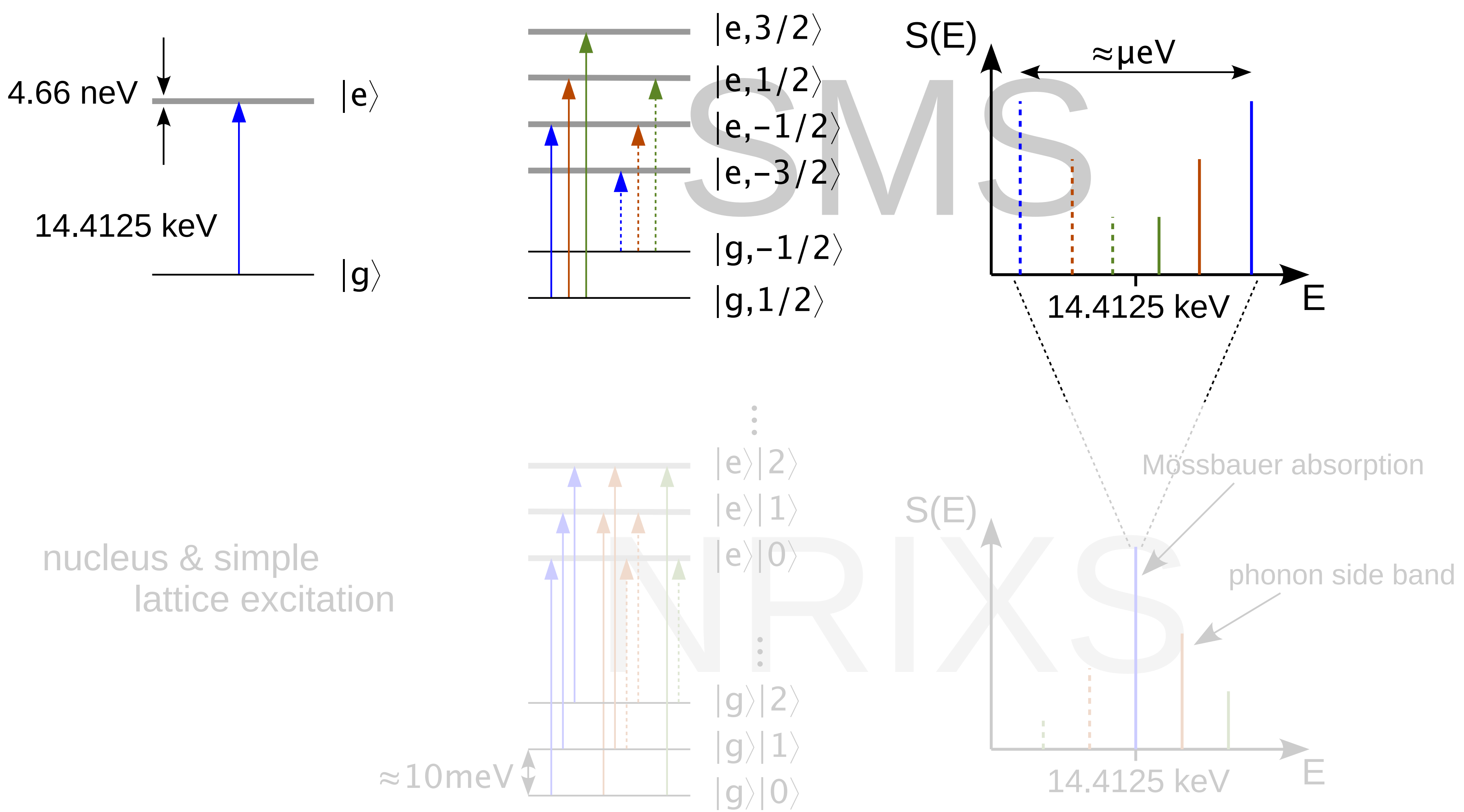
recent reviews of Nuclear Resonant Spectroscopy:

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:

fixed, isolated nucleus

nucleus & electronic interaction or external fields



Scattering channels:

initial state → intermediate state → final state

$$|\gamma_i\rangle|\Psi_i\rangle \quad \longrightarrow \quad |\Psi_n\rangle \quad \longrightarrow \quad |\gamma_f\rangle|\Psi_f\rangle$$

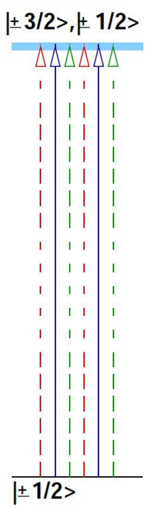
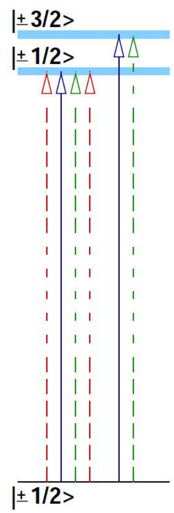
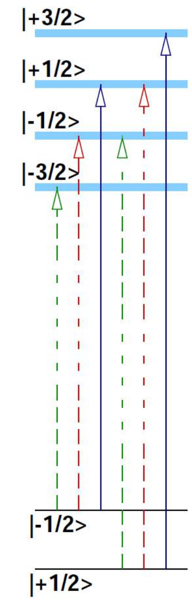
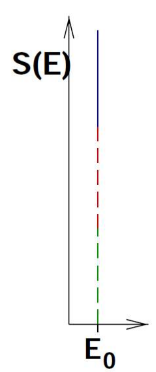
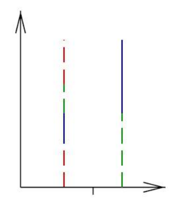
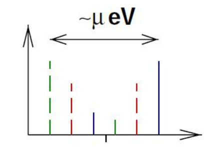
$$|\Psi_i\rangle = |\chi_i\rangle\Pi_j|\phi_j^{(i)}\rangle \qquad\qquad |\Psi_f\rangle = |\chi_f\rangle\Pi_j|\phi_j^{(f)}\rangle$$

lattice — nucleus & core electrons

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

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

Nuclear level splitting:

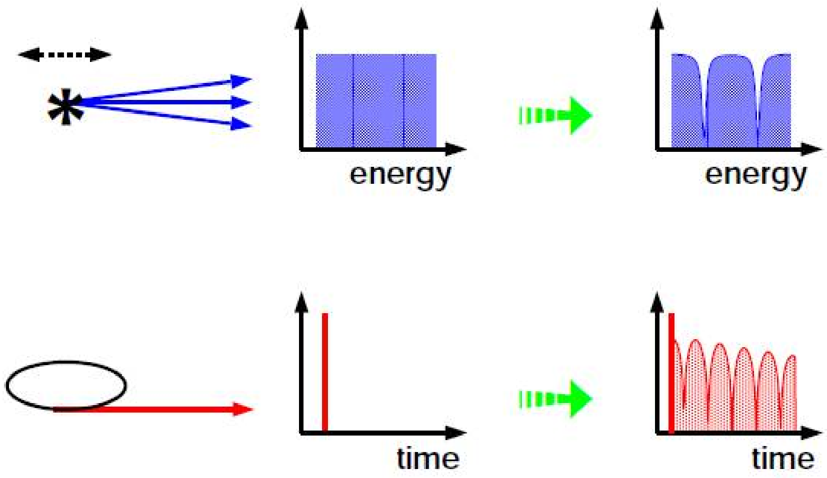
	isomer shift	electric field gradient	magnetic field
level scheme			
energy spectrum			

isomer shift:
- all materials
- electron density

electric field gradient:
- atomic electrons
- crystal field contribution
- vanishes for cubic symmetry

magnetic field:
- magnetic ordering

NRS 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)

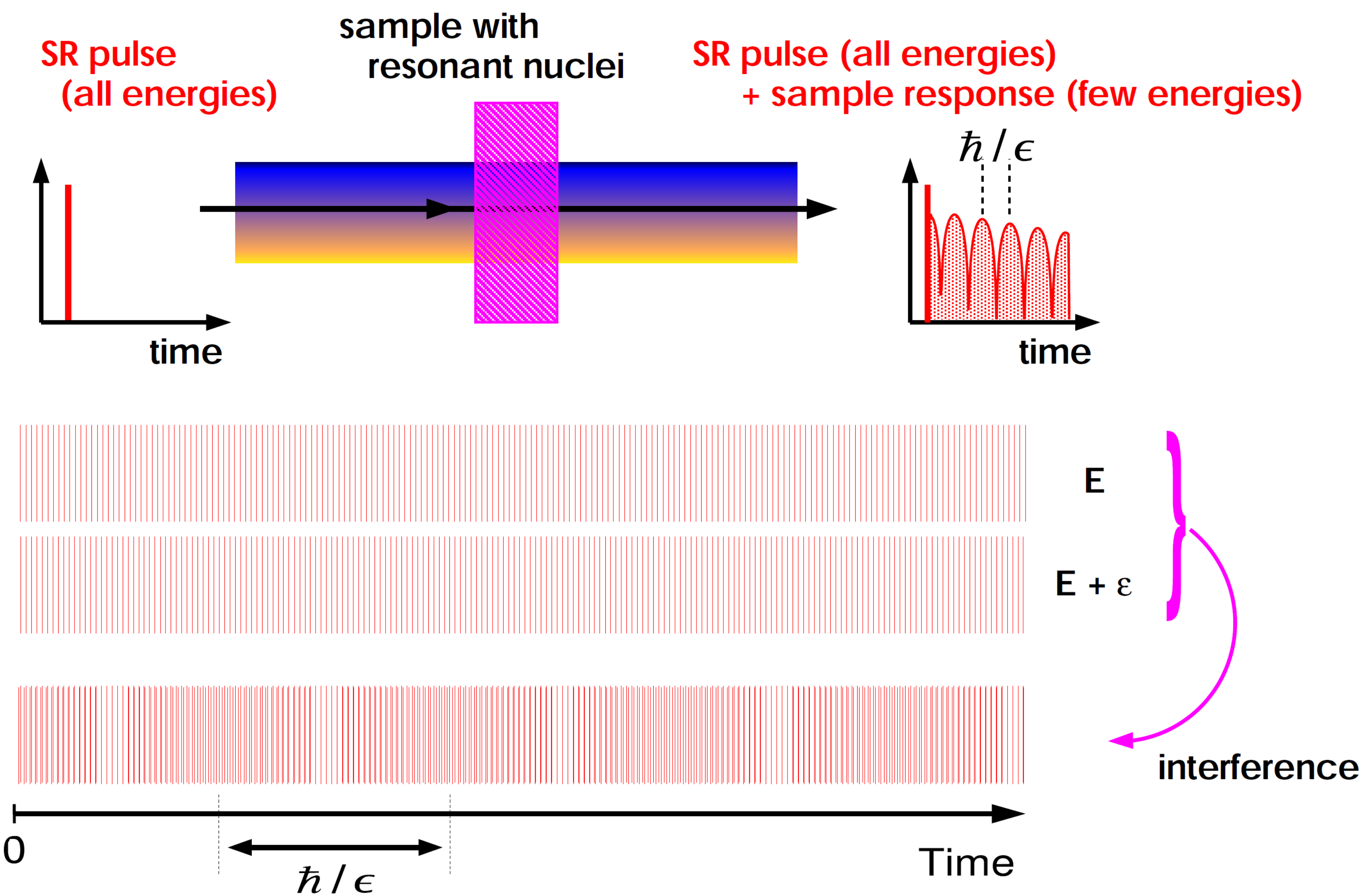
SMS advantages

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

Potential SMS difficulties

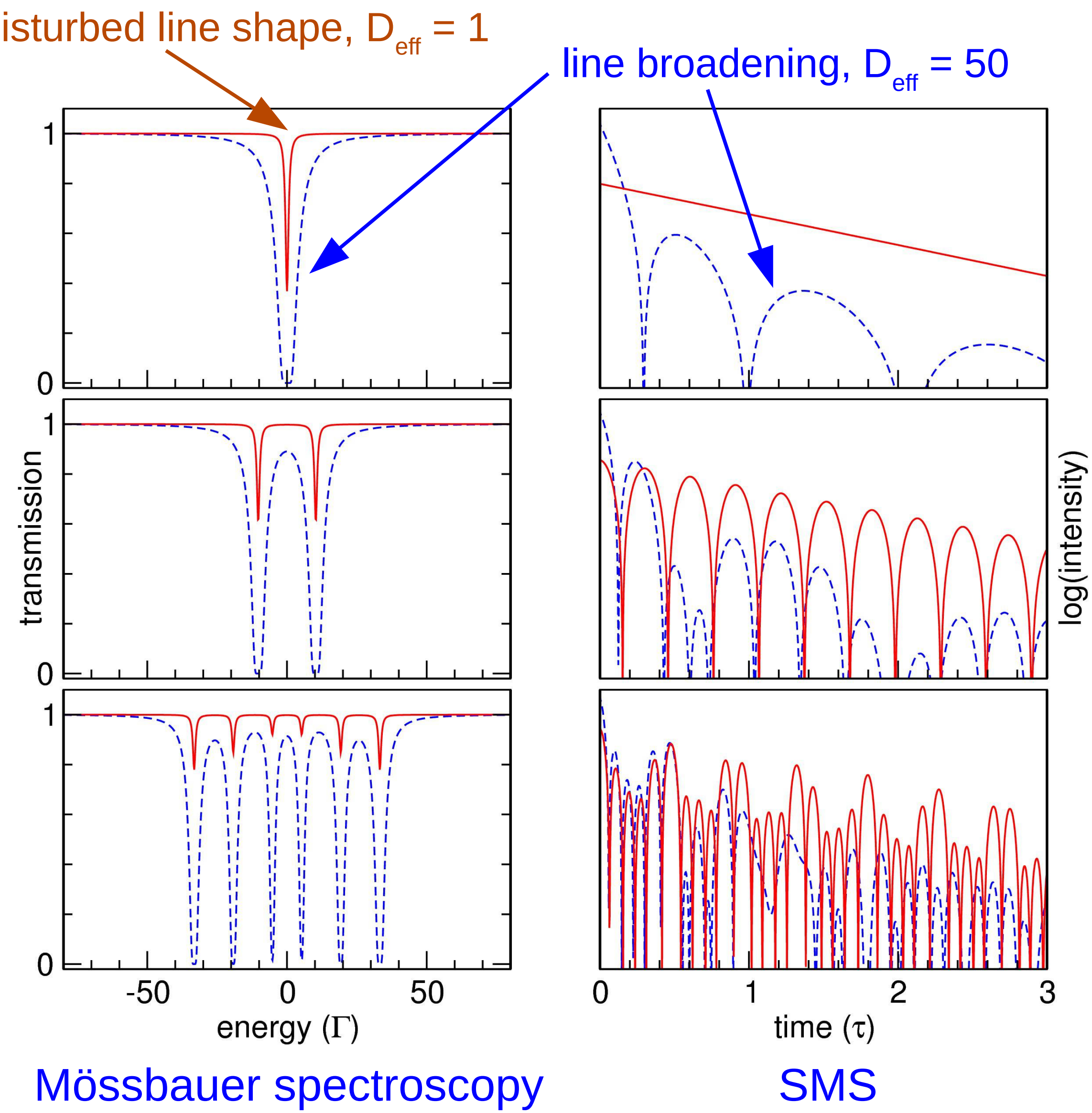
- accessibility
- data evaluation

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

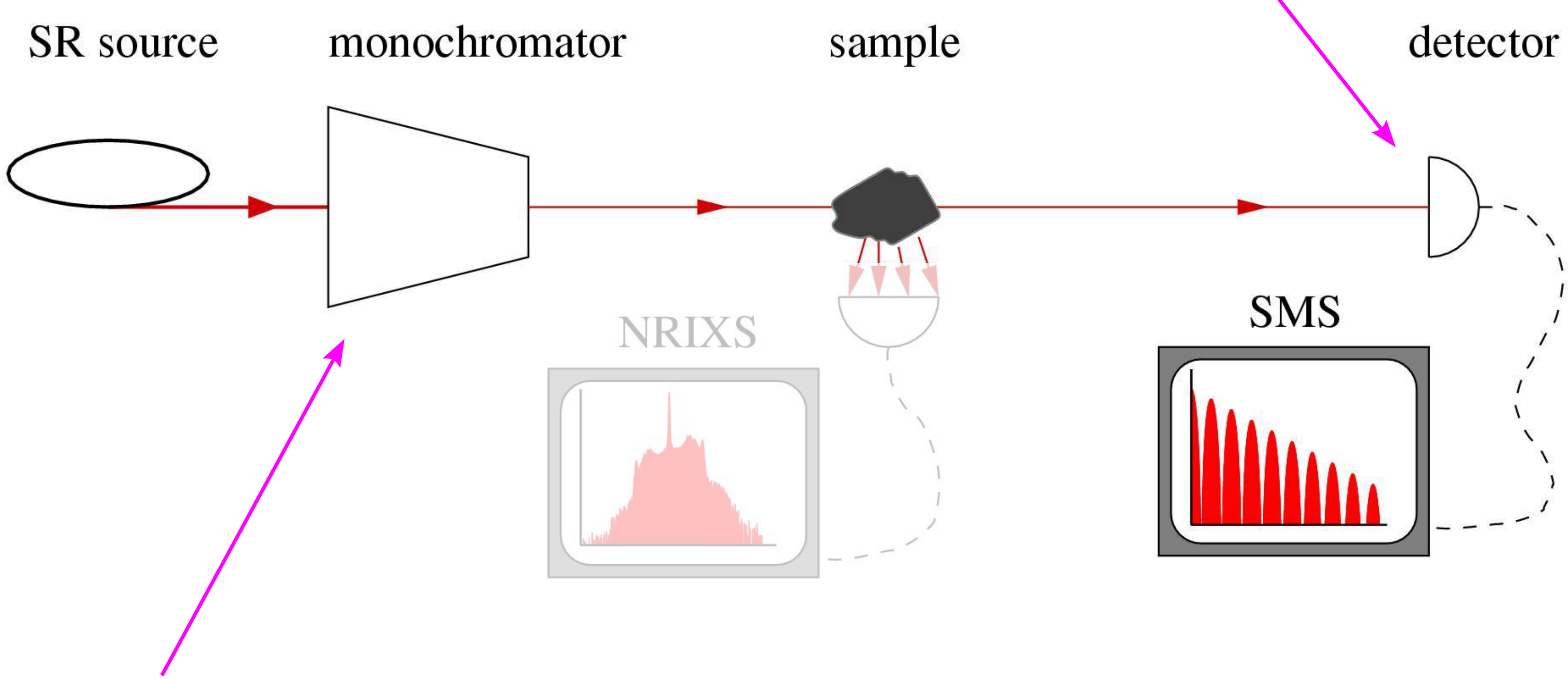
nuclei per area

geometric thickness

California Institute of Technology

Experimental setup for SMS:

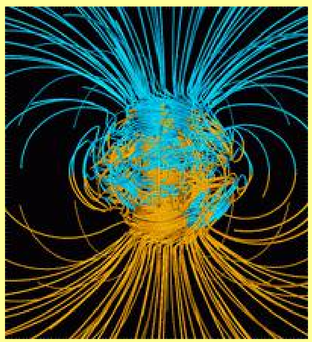
- x-ray pulses must be sufficiently separated in time
- detectors must have good time resolution and excellent dynamic range



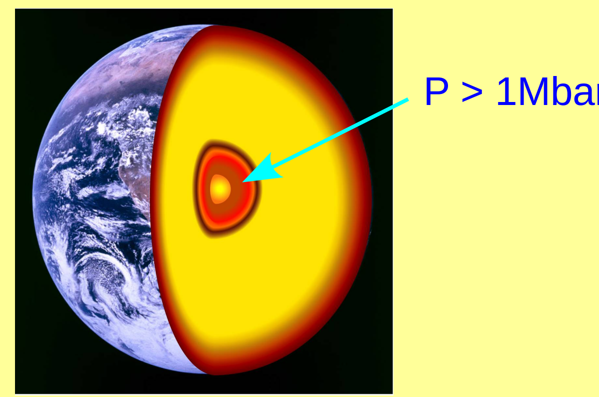
- monochromatization to meV-level required to protect detector
- energy is tuned to the nuclear transition

Target applications:

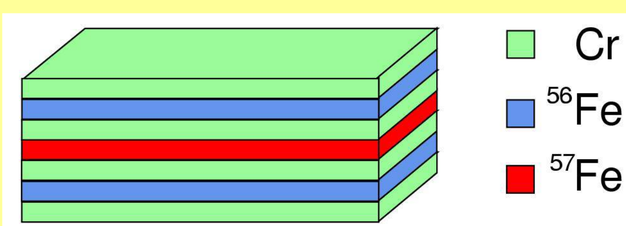
- perfect isotope selectivity & complete suppression of nonresonant signals
- excellent sensitivity (10^{12} nuclei in the focused beam)



☆ magnetism



☆ materials under high pressure

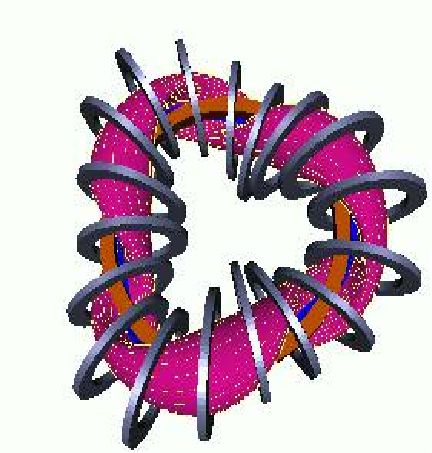


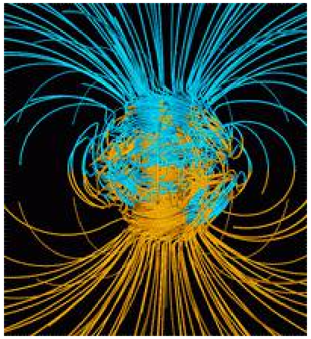
☆ nano-structures

Magnetism:

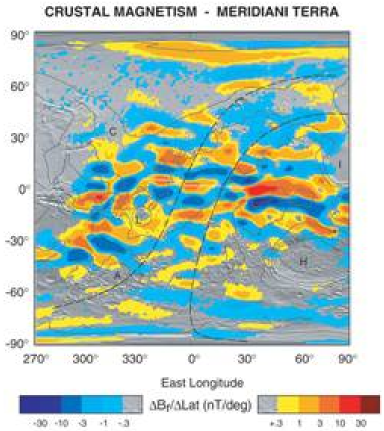
- magnetism is of great importance in science and technology.

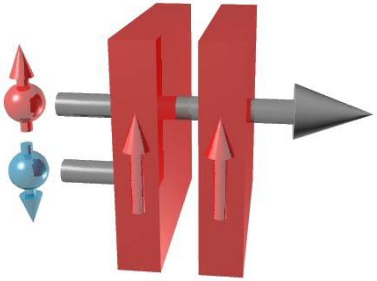
magneto-hydrodynamics





planetary magnetism & magnetic records





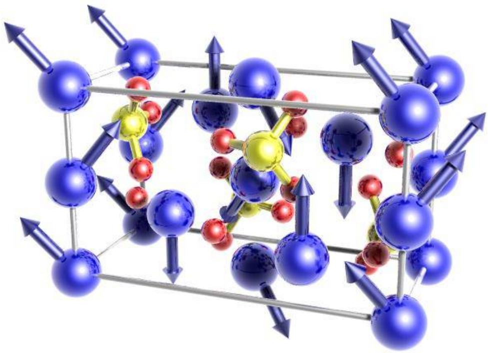
spintronics

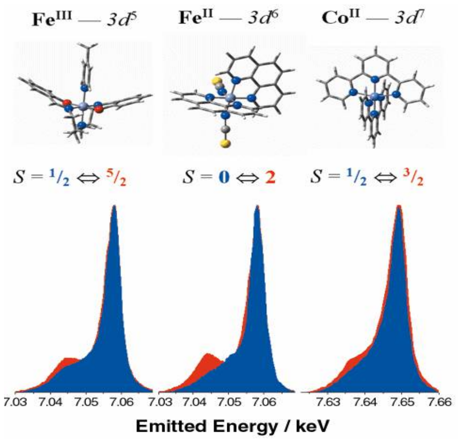
storage devices

- 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:

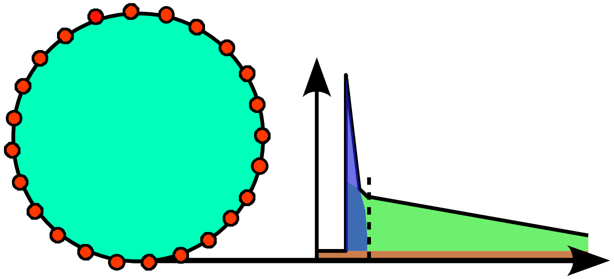
- spatially coherent, snapshot in time
  - ☆ magnetic neutron diffraction
  - ☆ magnetic x-ray diffraction



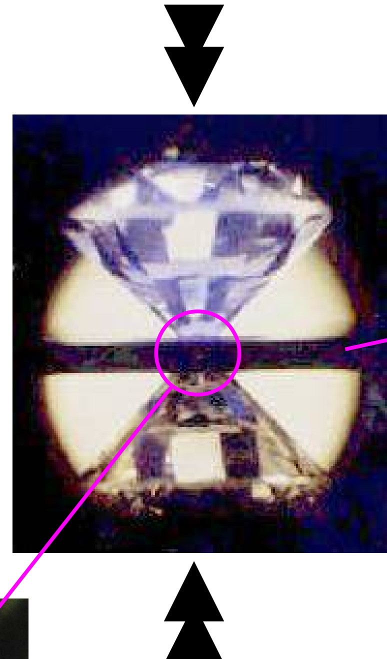


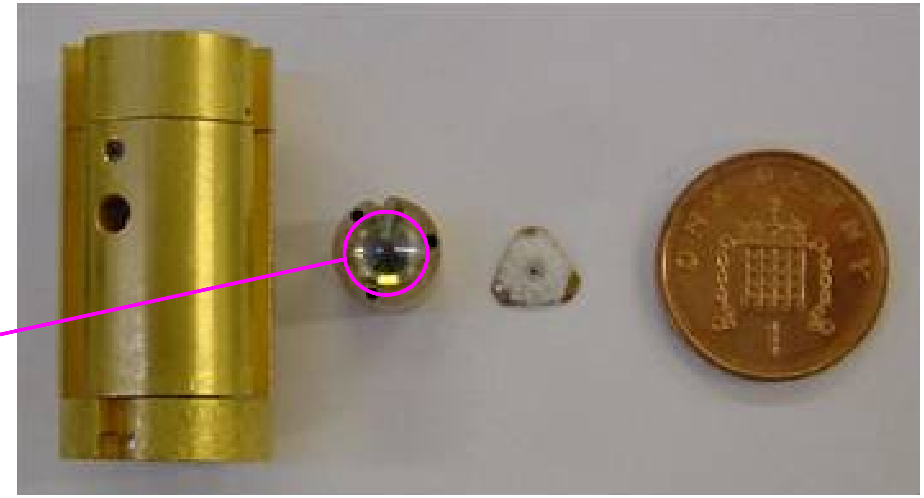
- local in space, snapshot in time
  - ☆ polarization-dependent x-ray absorption such as XMCD
  - ☆ x-ray emission spectroscopy (XES)

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

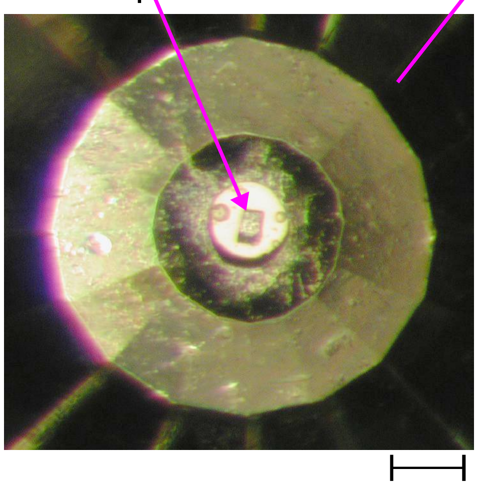


Diamond anvil cells for Mbar pressures:



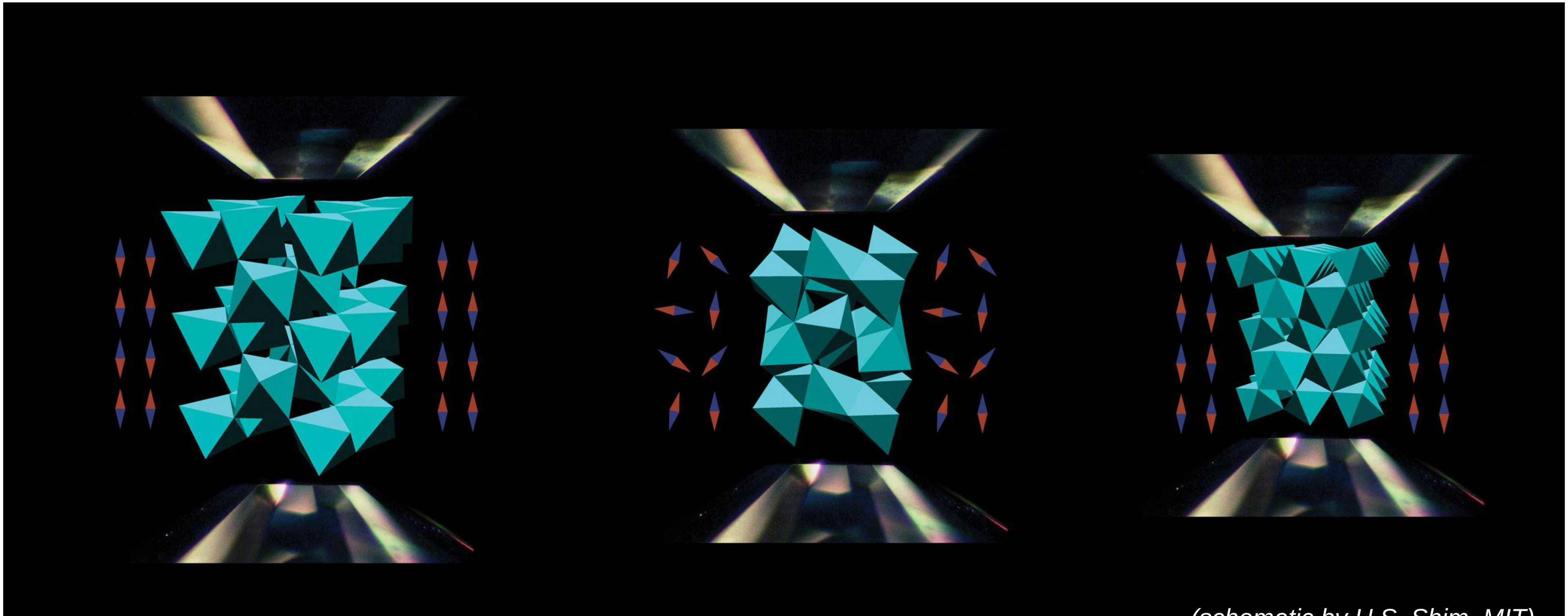


☆ A force applied to the diamond anvils can produce extreme pressures in a small sample chamber.



Re-entrant magnetism in Fe_2O_3:

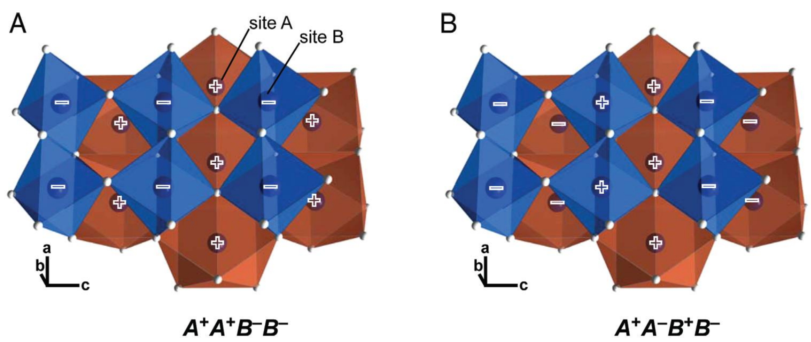
- ✰ canted anti-ferromagnet at low pressures (α–Al_2O_3 structure)
- ✰ loss of magnetic order at intermediate pressures (Rh_2O_3–II structure)
- ✰ complex magnetic order at high pressures (post-perovskite structure)



(schematic by H.S. Shim, MIT)

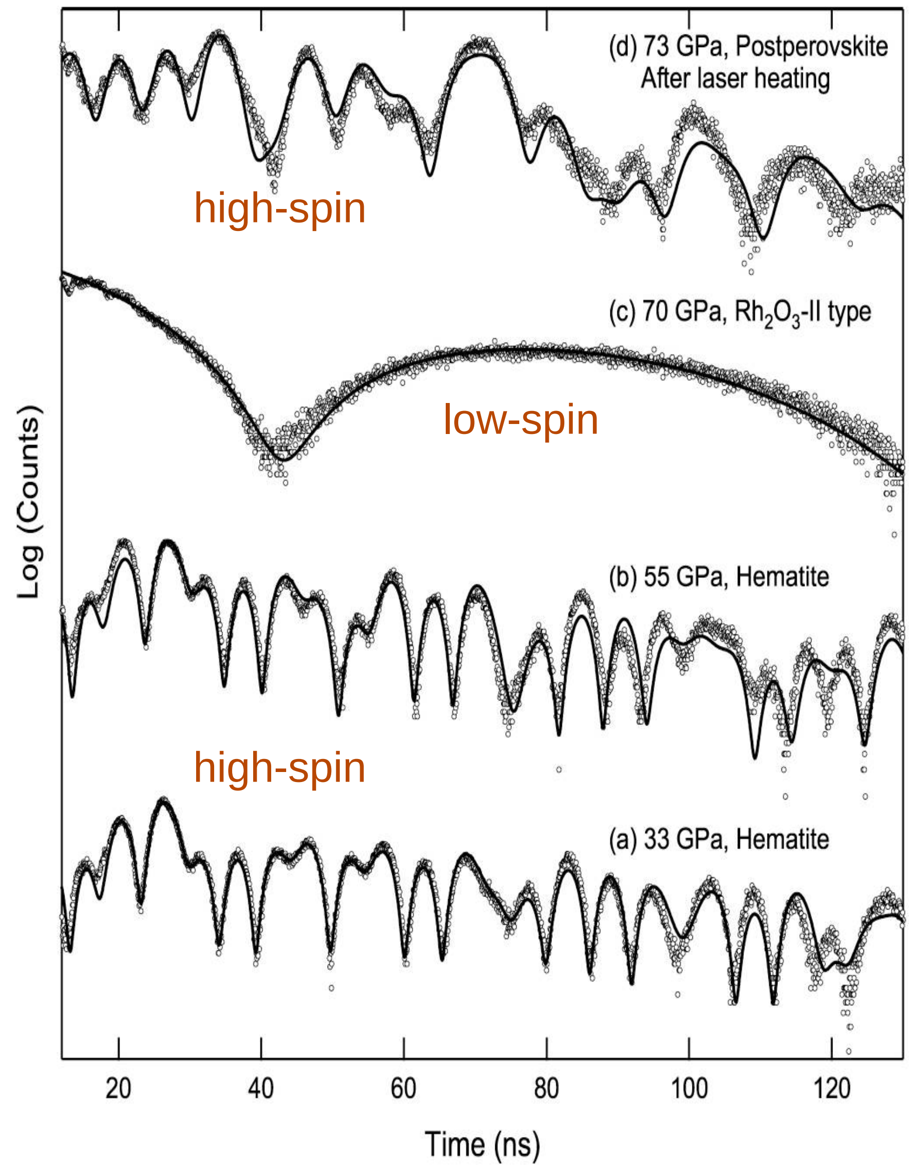
Re-entrant magnetism in Fe_2O_3:

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



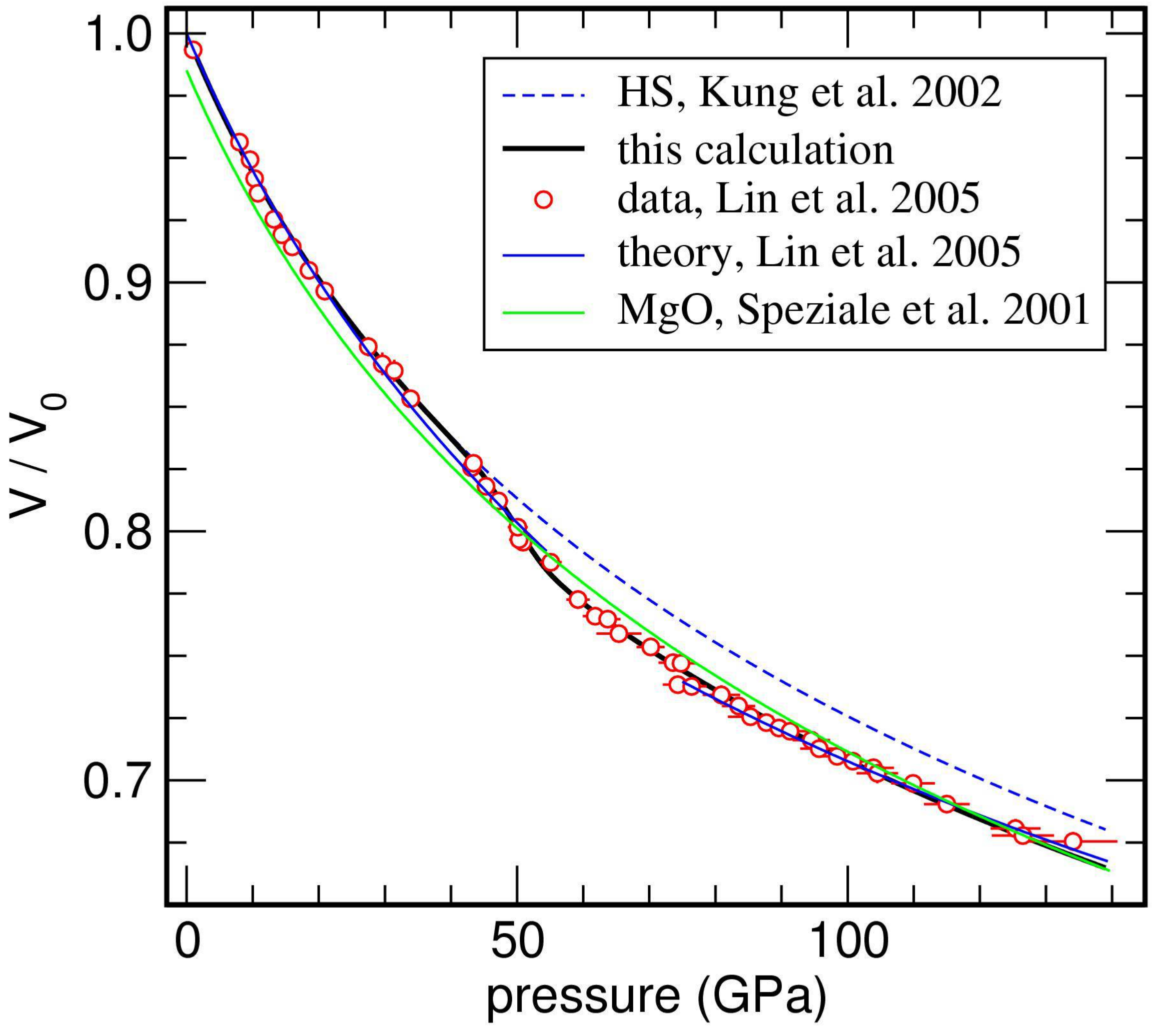
- ✰ but the actual magnetic structure has not been determined yet

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



Compression of $(Mg_{0.83}Fe_{0.17})O$ periclase:

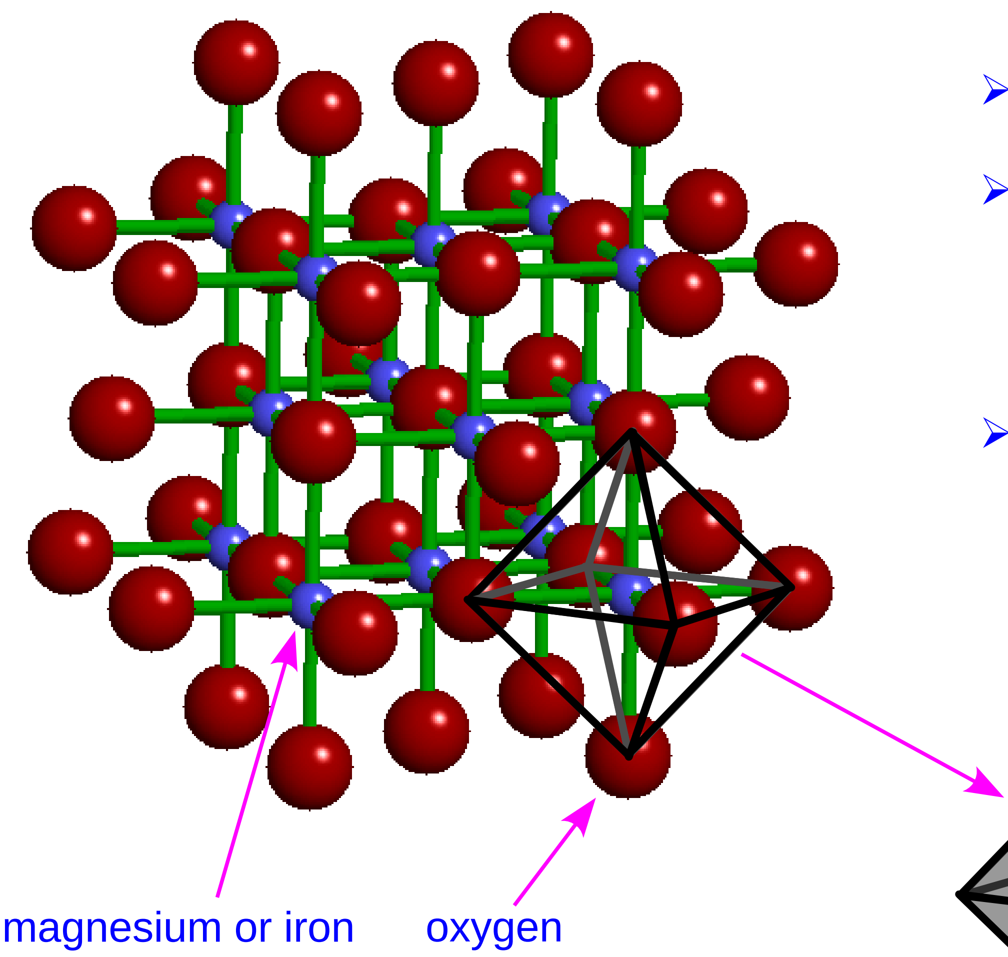
Data from: J.-F. Lin et al., Nature 436 (2005)

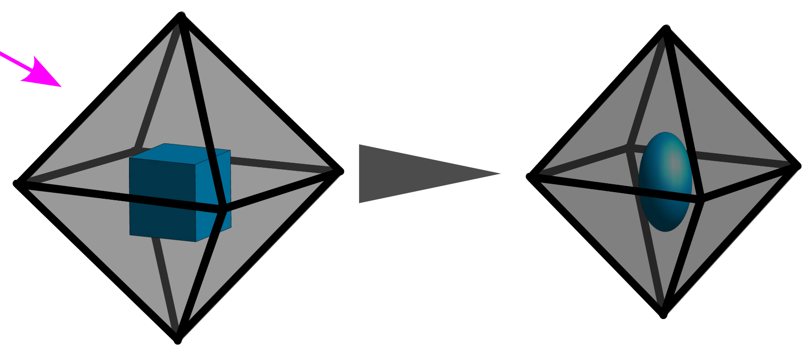


- Kung et al., 2002 (p < 10 GPa):
  K_{0T} = 164 GPa K_0' = 4.2
- Lin et al., 2005:
  HS: K_{0T} = 161 GPa K_0' = 3.28
  LS: K_{0T} = 245 GPa K_0' = 4
  V_{0LS}/V_{0HS} = 0.904
- this calculation:
  HS: K_{0T} = 150 GPa K_0' = 4.5
  LS: K_{0T} = 158 GPa K_0' = 4.5
  P_{HSLS} = 51 GPa
  V_{0LS}/V_{0HS} = 0.95

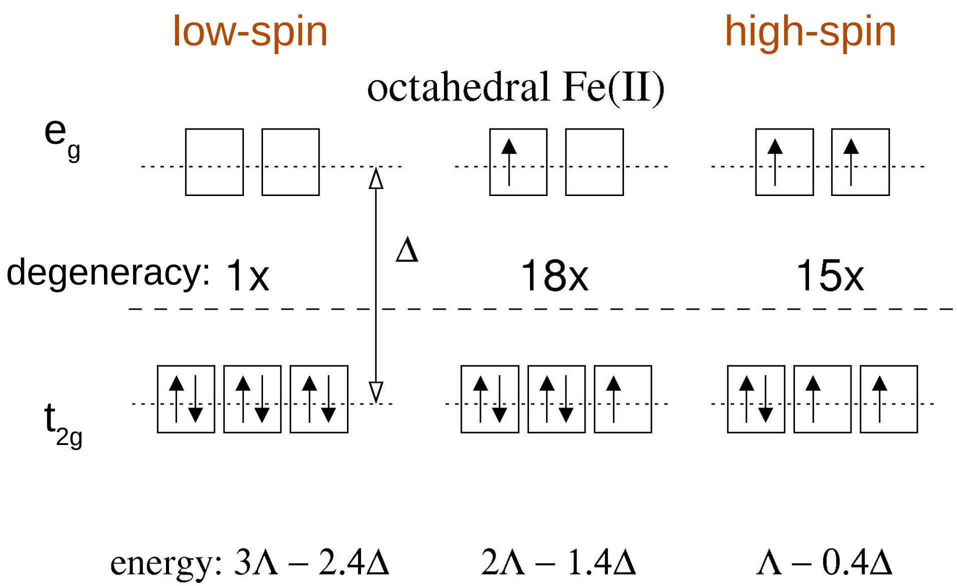
Structure of Periclase:

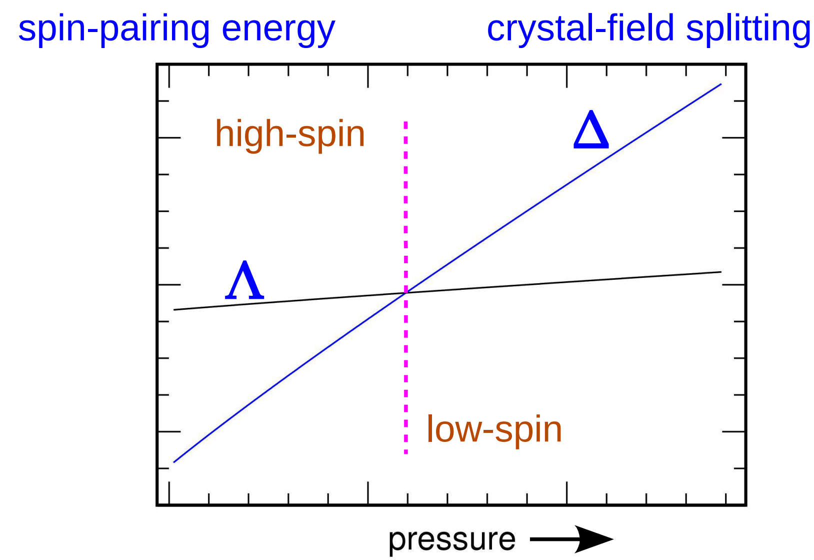
- halite (rocksalt) structure; cubic unit cell
- MgO and FeO form a solid solution
- Mg and Fe atoms are surrounded by six oxygen atoms that form a slightly distorted octahedron
- upon compression the localized (non-binding) 3d electrons of Fe can change configuration

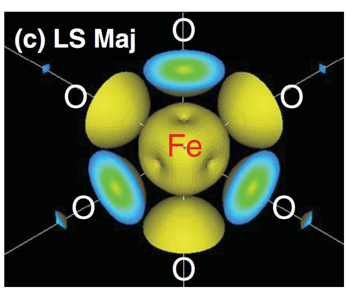


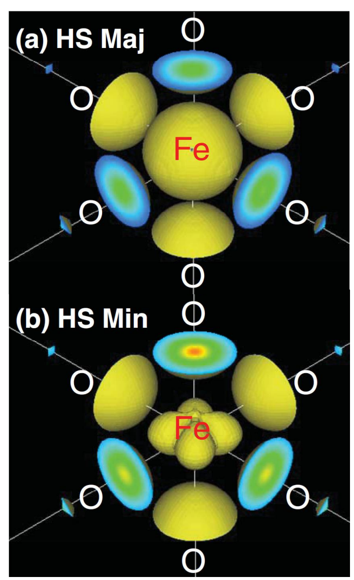


3d-electrons for Fe(II), (Ar)$3d^6$:







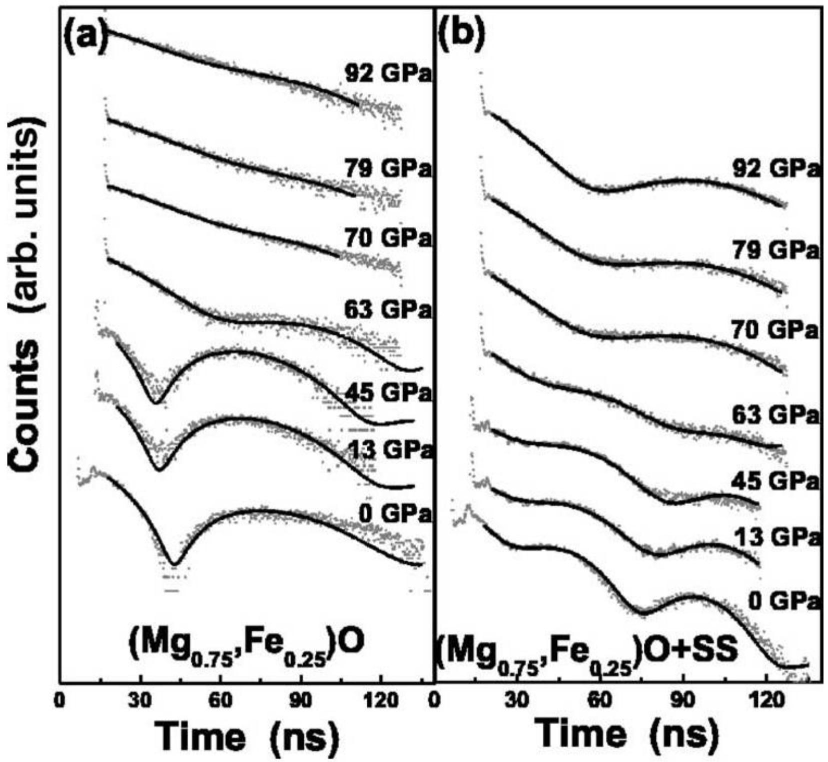


3d-electron pseudo-charge density surfaces at 0.3 e/Å^3
from T.Tsuchiya et al., PRL 96 (2006)

- the minimum-energy state will change for
  $\Lambda = \Delta$
- this identifies a spin transition

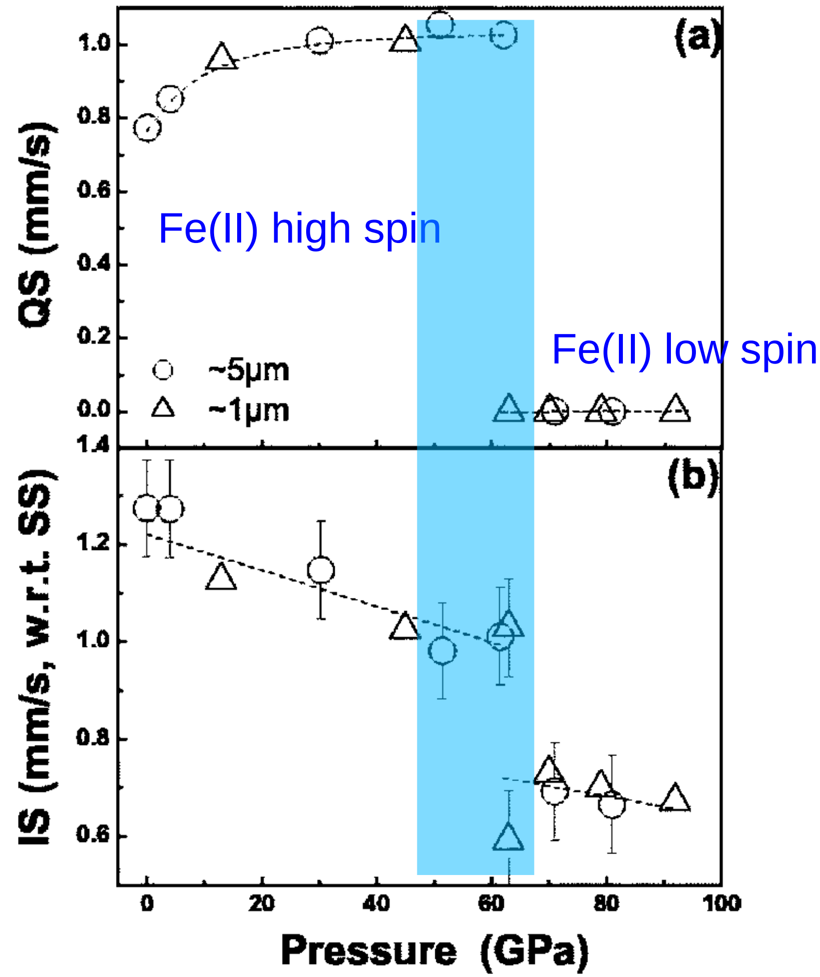
SMS analysis of spin crossover in periclase:

- time spectra
  (response of sample following x-ray pulse)



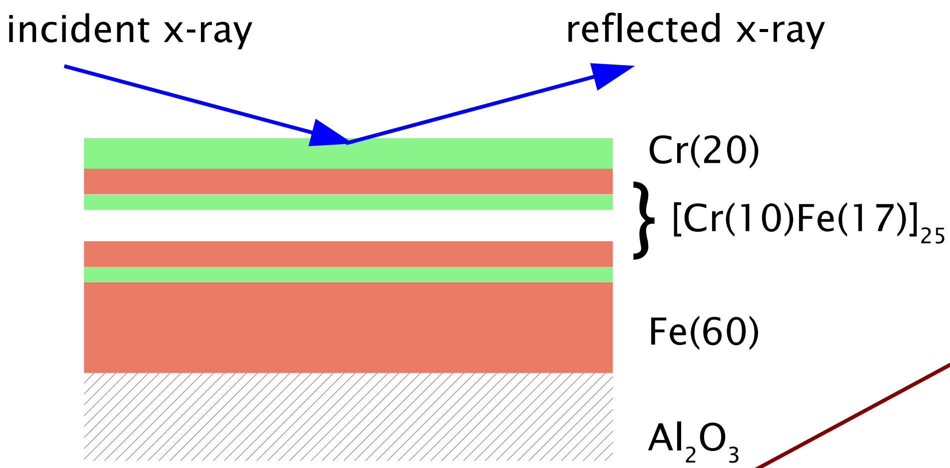
☆ the crossover from a high-spin to low-spin state of Fe significantly affects the density, sound velocities, elastic properties, and transport properties of ferropericlase.

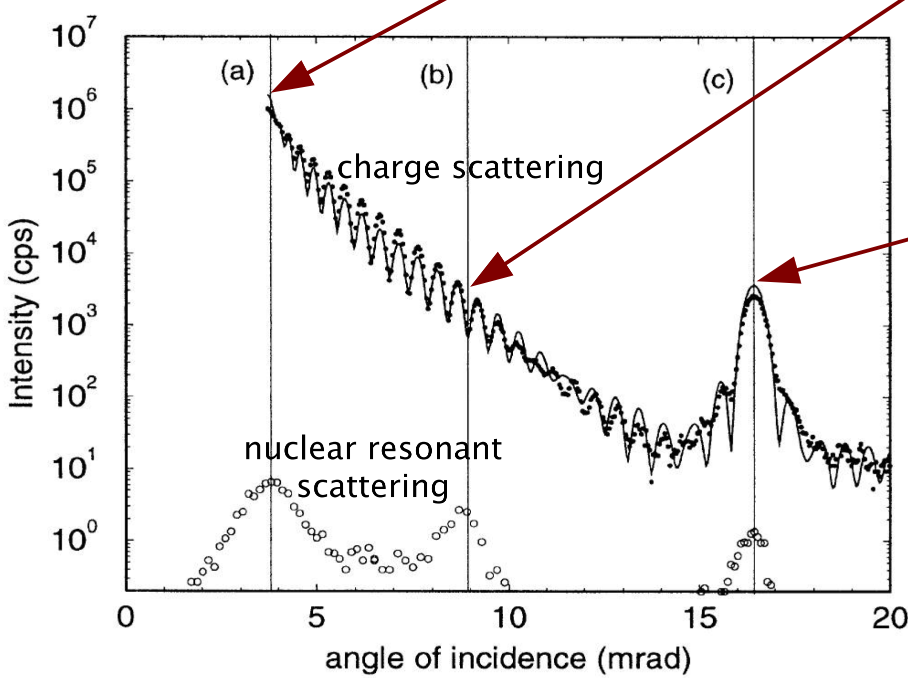
- electric field gradient and isomer shift

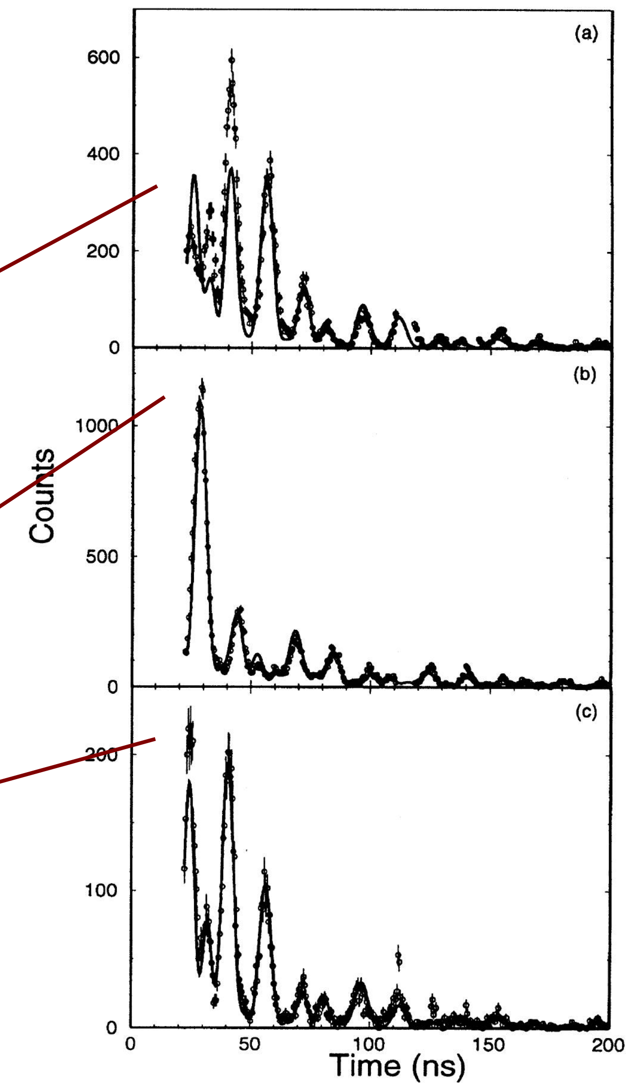


J.-F. Lin, A.G. Gavriliuk, V.V. Struzhkin, S.D. Jacobson, W. Sturhahn, M.Y. Hu, P. Chow, C.-S. Yoo
Phys. Rev. B 73 (2006)

Spin wave in a Fe/Cr multilayer:

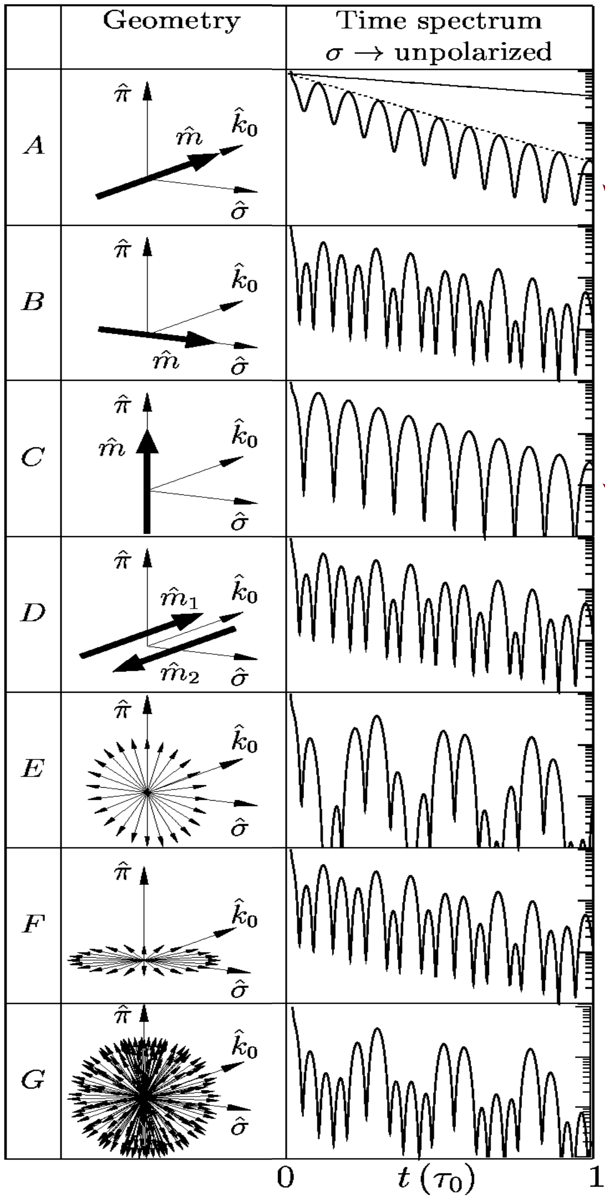


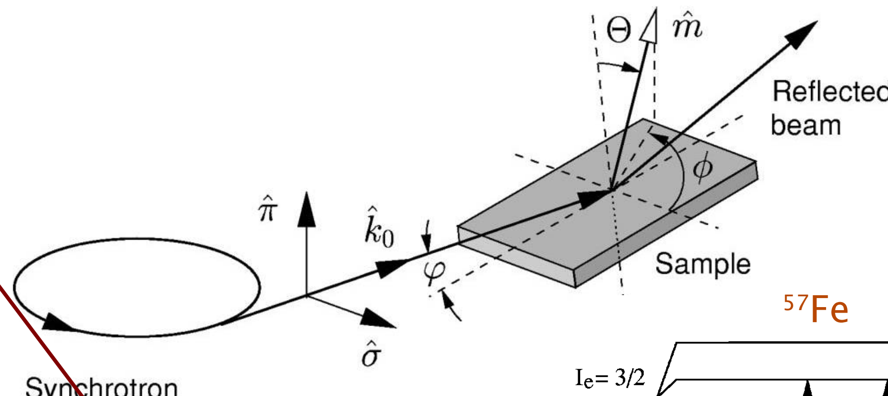


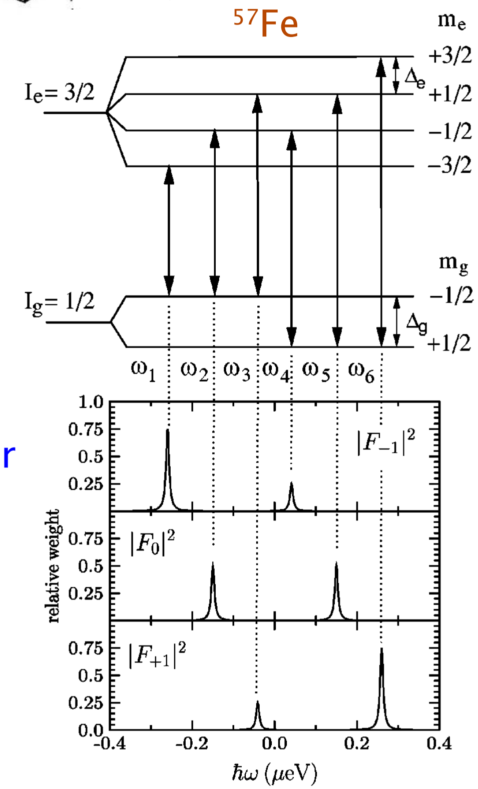


T.S. Toellner, W. Sturhahn, R. Röhlsberger,
E.E. Alp, C.H. Sowers, E. Fullerton,
Phys. Rev. Lett. 74 (1995)

Polarization and direction:







right circular

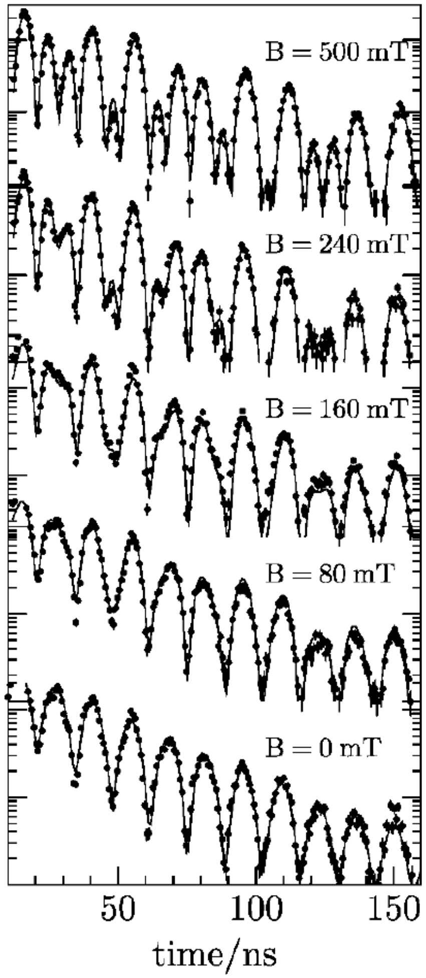
linear π

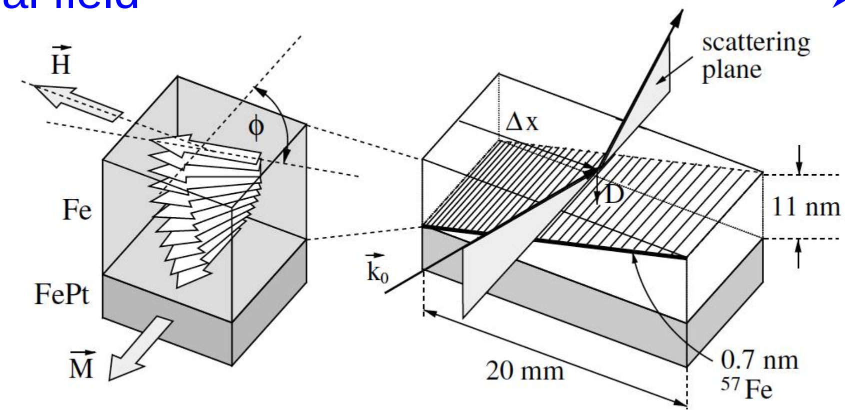
left circular

R. Röhlsberger, J. Bansmann, V. Senz, K.L. Jonas, A. Bettac, K.H. Meiwes-Broer, Phys. Rev. B 67 (2003)

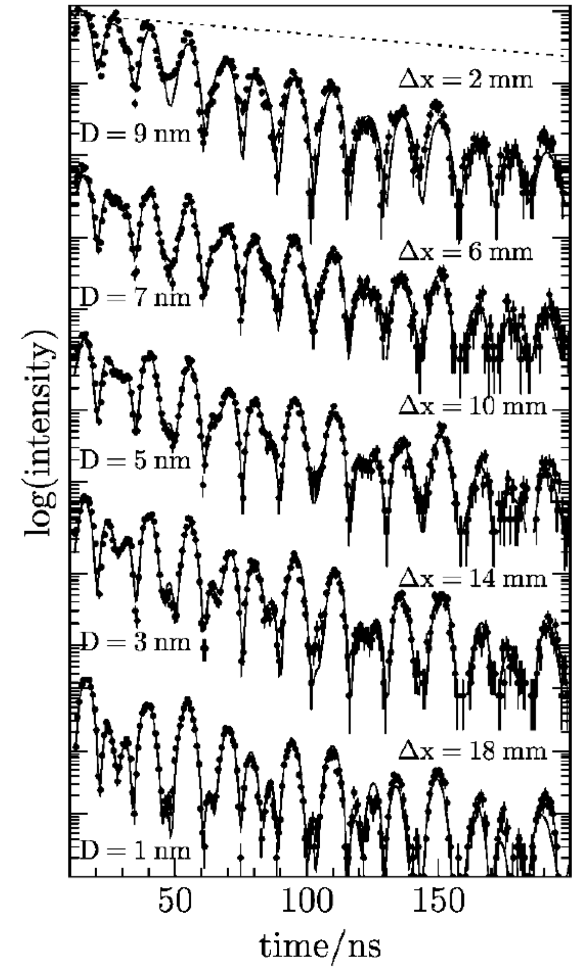
Spin structure in a thin Fe film:

- variation of external field

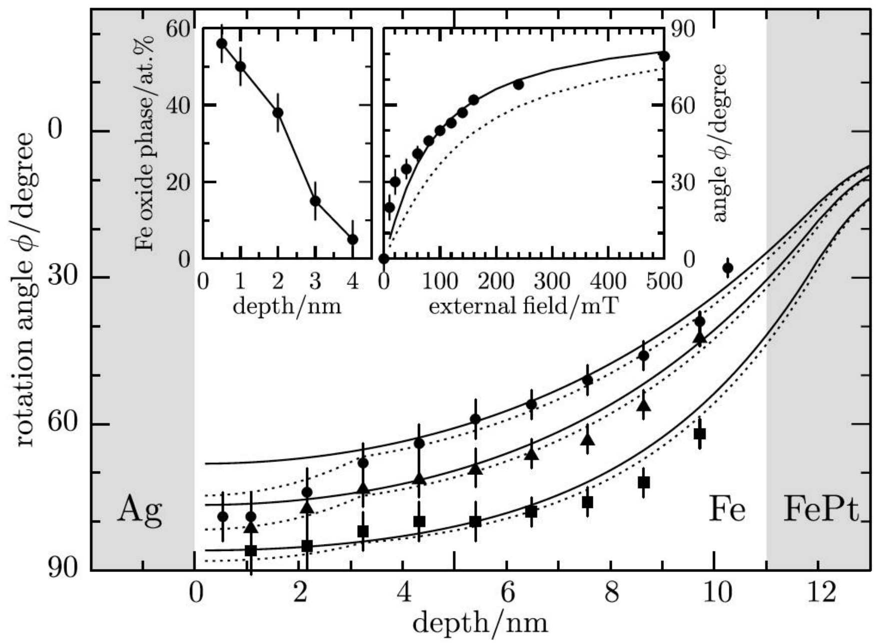




- variation of layer thickness



- results



R. Röhlsberger, H. Thomas, K. Schlage, E. Burkel, O. Leupold, R. Rüffer, Phys. Rev. Lett. 89 (2002)

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
  - ☆ various 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
  - ☆ reliable software required for evaluation of SMS time spectra
  - ☆ some suitable resonant isotopes are ^{57}Fe, ^{119}Sn, ^{151}Eu, ^{161}Dy

Ende