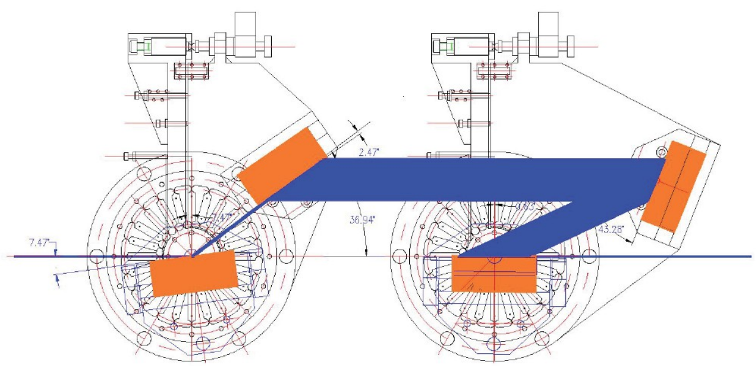
Nuclear Resonant Inelastic X-ray Spectroscopy (NRIXS)



Wolfgang Sturhahn

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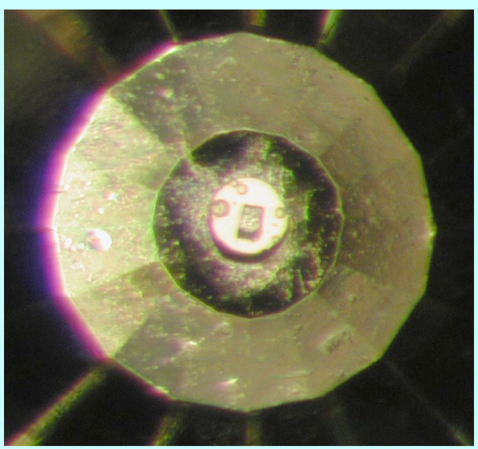
wolfgang@nrixs.net

Dynamical behavior of atoms:

solids

phase transitions
diffusion
nanostructures
rotational excitations
superconductivity



(Fe-sample in DAC)

(levitated Al_2O_3-sample)

liquids

melting processes
viscosity
atomic clusters
glasses

gases

velocity distributions
confined systems

(methane escapes ice-chlathrate)

The nucleus as a probe:

- The nucleus is not at rest
  - ✰ energy/momentum conservation ⇒ recoil energy shift
  - ✰ velocity in gases ⇒ Doppler shift
  - ✰ vibrations in solids ⇒ phonon excitation/annihilation, recoilless absorption

- NRIXS – Nuclear Resonant Inelastic X-ray Scattering (a.k.a. NRVS and NIS)
  - ✰ local vibrational density of states
  - ✰ applications include determination of sound velocities and thermodynamic properties

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, Nuclear Condensed Matter Physics with Synchrotron Radiation: Basic Principles, Methodology and Applications, Springer (2004)
W. Sturhahn and J.M. Jackson, GSA special paper 421 (2007)

The two faces of nuclei:

- conventional role of nuclei

☆ majority carrier of the atomic mass

☆ carries the positive electric charge

☆ negligible scattering cross section:

$\sigma(\text{nucleus}) / \sigma(\text{atom}) = (Z\, m/M)^2 \approx 10^{-7}$
(Thomson)

- but in some cases

☆ dynamics of the nucleons results in well-defined resonances with

$\sigma(\text{nucleus}) / \sigma(\text{atom}) \approx 10^3$

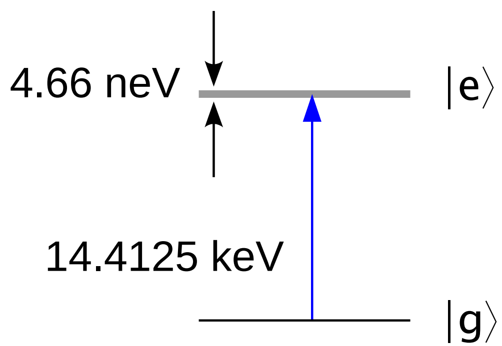
☆ nuclear resonant scattering may dominate

☆ nuclear resonances are extremely narrow

$\Gamma / E \approx 10^{-12}$

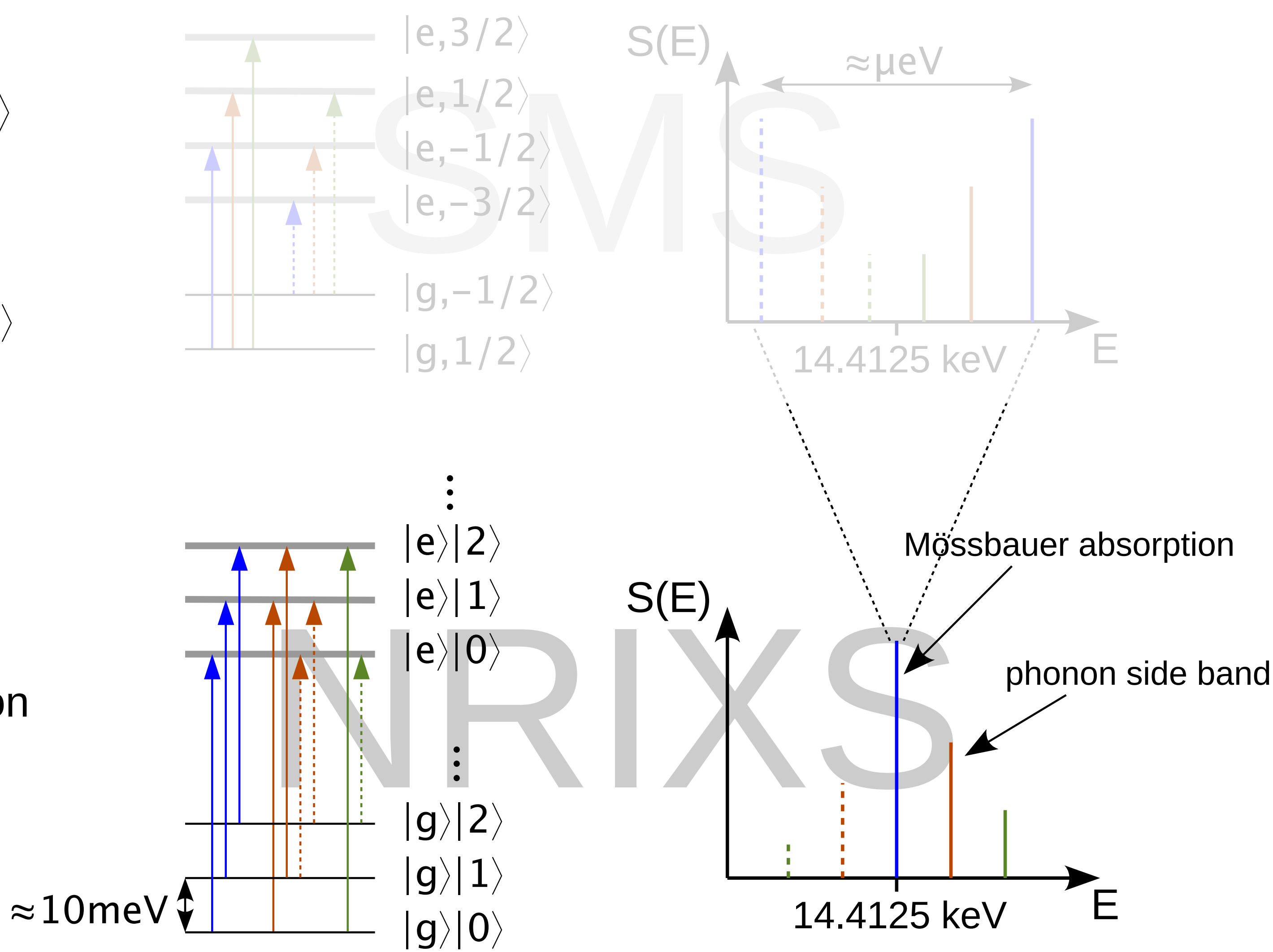
Excitation of the ^{57}Fe nuclear resonance:

fixed, isolated nucleus



nucleus & electronic interaction or external fields

nucleus & simple lattice excitation



Scattering channels:

initial state → intermediate state → final state

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

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

lattice nucleus & core electrons

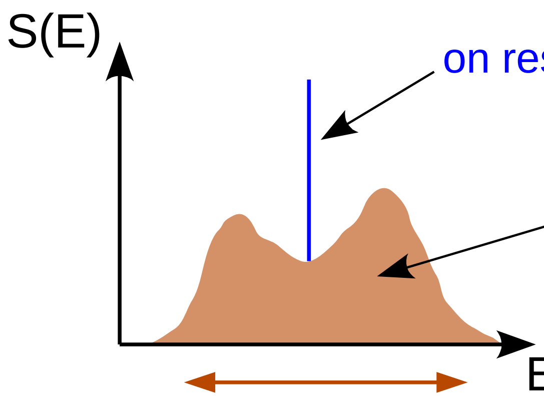
NRIXS	(negligible)	SMS
incoherent	coherent inelastic	coherent elastic
$\|\phi_j^{(i)}\rangle \neq \|\phi_j^{(f)}\rangle$	$\|\phi_j^{(i)}\rangle = \|\phi_j^{(f)}\rangle$ $\|\chi_i\rangle \neq \|\chi_f\rangle$	$\|\Psi_i\rangle = \|\Psi_f\rangle$

W.Sturhahn and V.Kohn
Hyperfine Interact. 123-124 (1999)

Cross section for nuclear excitation:

$$\boxed{\sigma(E) = \frac{\pi}{2}\,\sigma_0\,\Gamma\,S(E)}$$

σ_0 ~ nuclear resonant cross section
Γ ~ width of the nuclear resonance
$S(E)$ ~ probability density for phonon excitation



on resonance: $\Gamma\,S(0) = f$ (0.1 < f < 0.9)

off resonance: $\Gamma\,S(E) \propto (1-f)\,\dfrac{\Gamma}{\Theta}$

Θ ~ Debye energy

iron metal:

$\sigma(0) = 560\ \sigma_{pe}$

$\sigma(E) \approx 0.0002\ \sigma_{pe}$

σ_{pe} ~ photoelectric cross section

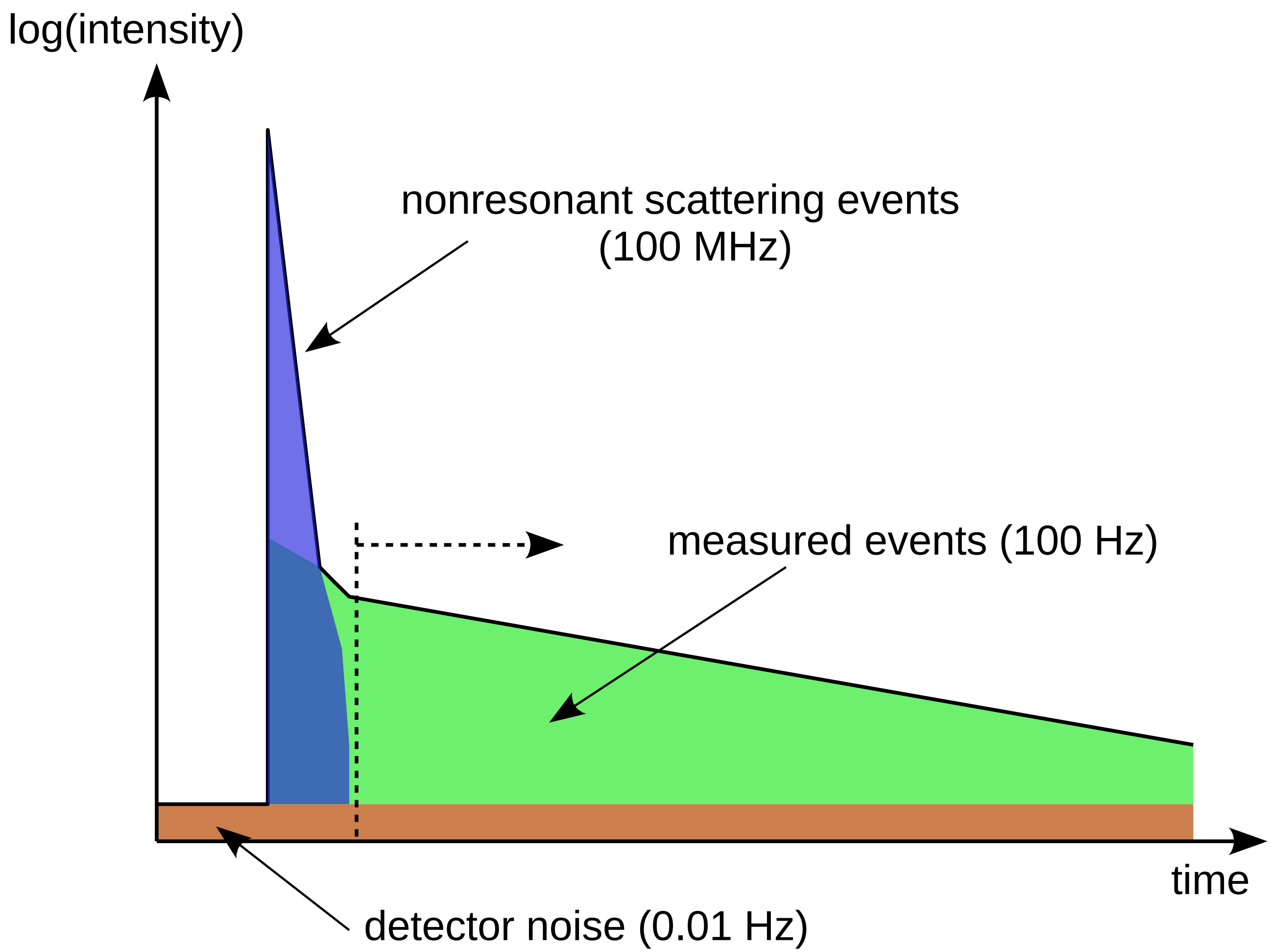
W.Sturhahn, J.Phys.: Condens. Matter 16 (2004)

The time discrimination trick:

The excited nucleus decays incoherently with its natural life time τ.

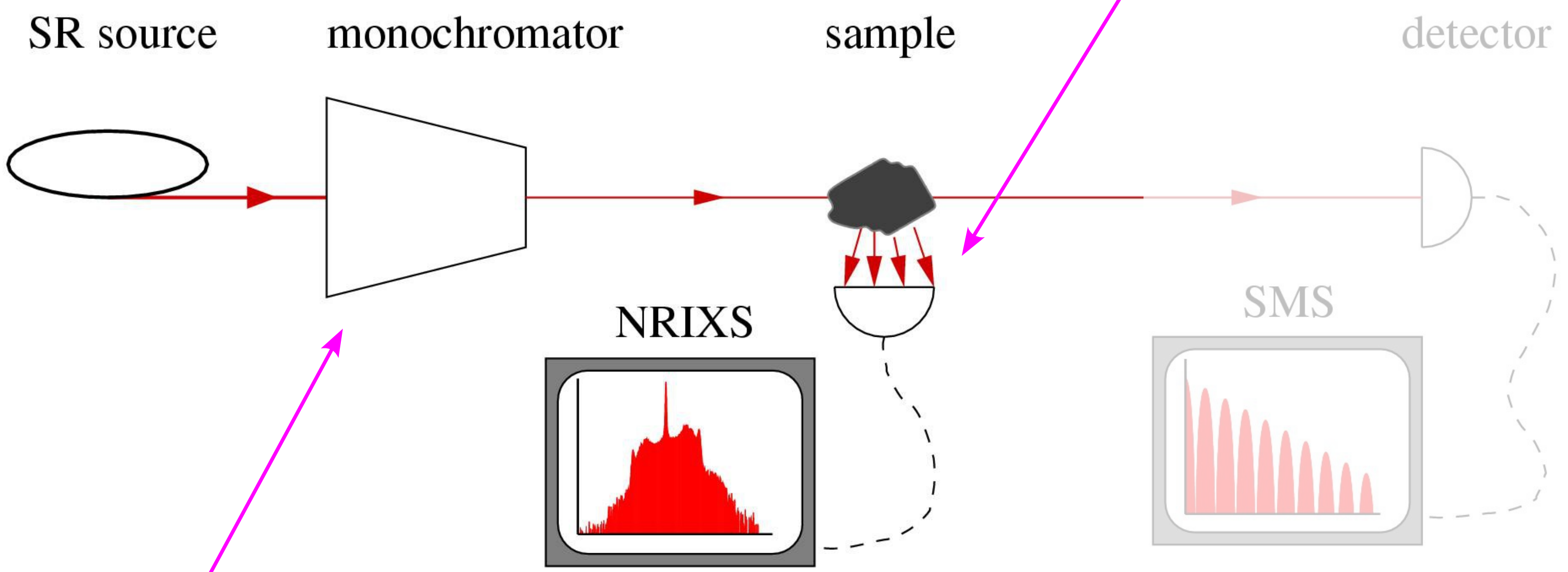
$\tau = \hbar \, / \, \Gamma$

141 ns for ^{57}Fe



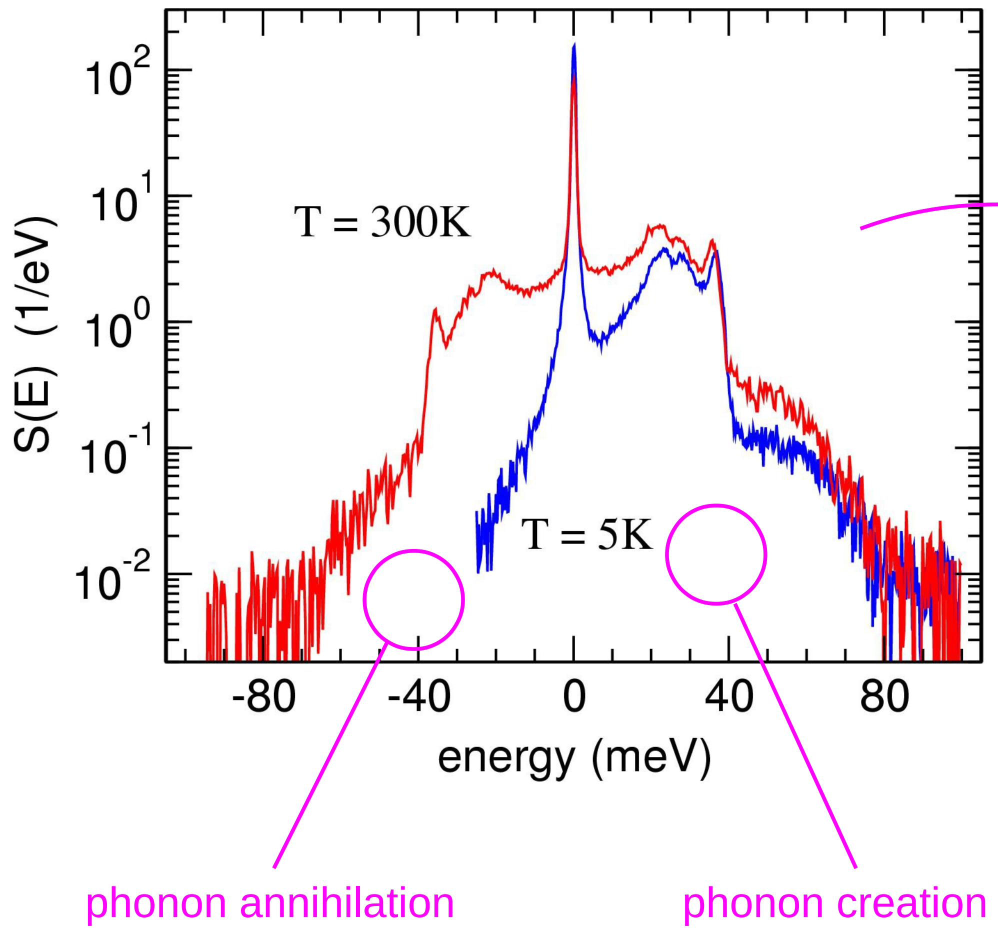
NRIXS, experimental setup:

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



- monochromatization to meV-level required
- energy is tuned around nuclear transition

NRIXS, bcc-Fe:

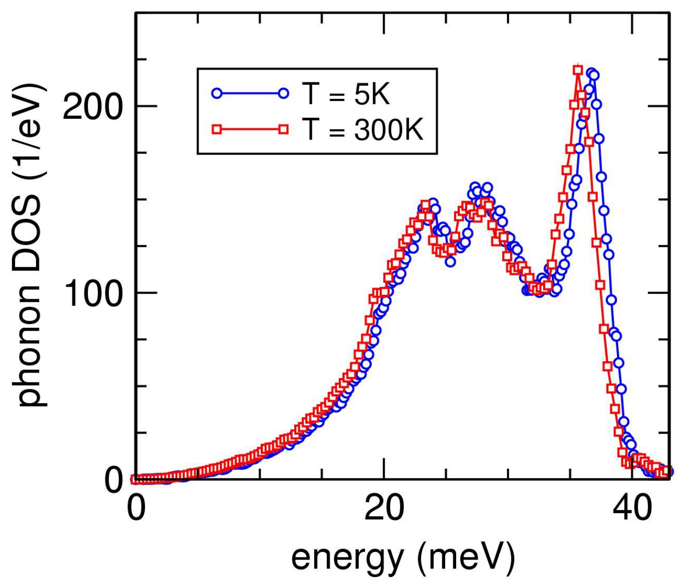


☆ the partial phonon DOS is extracted from the spectrum

V.G.Kohn et al., Phys.Rev. B 58 (1998)

M.Hu et al., Nucl.Instrum.Methods A 428 (1999)

W.Sturhahn, Hyperfine Interact. 125 (2000)



Interpretation of NRIXS spectra:

- NRIXS spectra directly provide the Fourier transform of the self-intermediate scattering function

$$S(\mathbf{k},E) = \frac{1}{2\pi\hbar}\int \left\langle \mathrm{e}^{\mathrm{i}\mathbf{k}\hat{\mathbf{r}}(t)}\mathrm{e}^{-\mathrm{i}\mathbf{k}\hat{\mathbf{r}}(0)} \right\rangle \mathrm{e}^{\mathrm{i}Et/\hbar} dt$$

- In the quasi-harmonic approximation the partial projected phonon density-of-states is obtained by a multi-phonon expansion

$$\begin{aligned}
S(\mathbf{k},E) &= f(\mathbf{k})\delta(E) + \sum_{n=1}^{\infty} S_n(\mathbf{k},E) \\
S_1(\mathbf{k},E) &= f(\mathbf{k})\,\frac{E_R}{E\,(1-\exp[-\beta E])}\,g(\mathbf{k},|E|) \\
S_n(\mathbf{k},E) &= \frac{1}{nf(\mathbf{k})}\int S_{n-1}(\mathbf{k},E')S_1(\mathbf{k},E-E')dE' \\
f(\mathbf{k}) &= \exp\left[-\int \frac{E_R}{E}\,\coth(\frac{\beta E}{2})\,g(\mathbf{k},E)dE\right]
\end{aligned}$$

W.Sturhahn and V.G.Kohn, Hyperfine Interact. 123/124 (1999)

Information from NRIXS spectra:

- directly from the data, S(E)

  - temperature

$$T = -\frac{E}{k_B} \ln\left[\frac{S(-E)}{S(E)}\right]$$

  - mean square displacement

$$\langle u^2 \rangle = -\frac{1}{k^2} \ln\left[1 - \int \{S(E) - S(0)\}\, dE\right]$$

  - kinetic energy

$$E_{kin} = \frac{1}{4E_R} \int (E - E_R)^2 S(E) dE$$

  - average force constant

$$D = \frac{k^2}{2E_R^2} \int (E - E_R)^3 S(E) dE$$

- quasi-harmonic lattice model

  - partial phonon density of states

$$\mathcal{D}(E)$$

  - Debye sound velocity

$$\mathsf{v}_D = \left(\frac{M}{2\rho\pi^2\hbar^3}\,\frac{E^2}{\mathcal{D}(E \to 0)}\right)^{1/3}$$

  - Grüneisen parameter

$$\gamma_D = \frac{1}{3} + \frac{\rho}{\mathsf{v}_D}\left(\frac{\partial \mathsf{v}_D}{\partial \rho}\right)_T$$

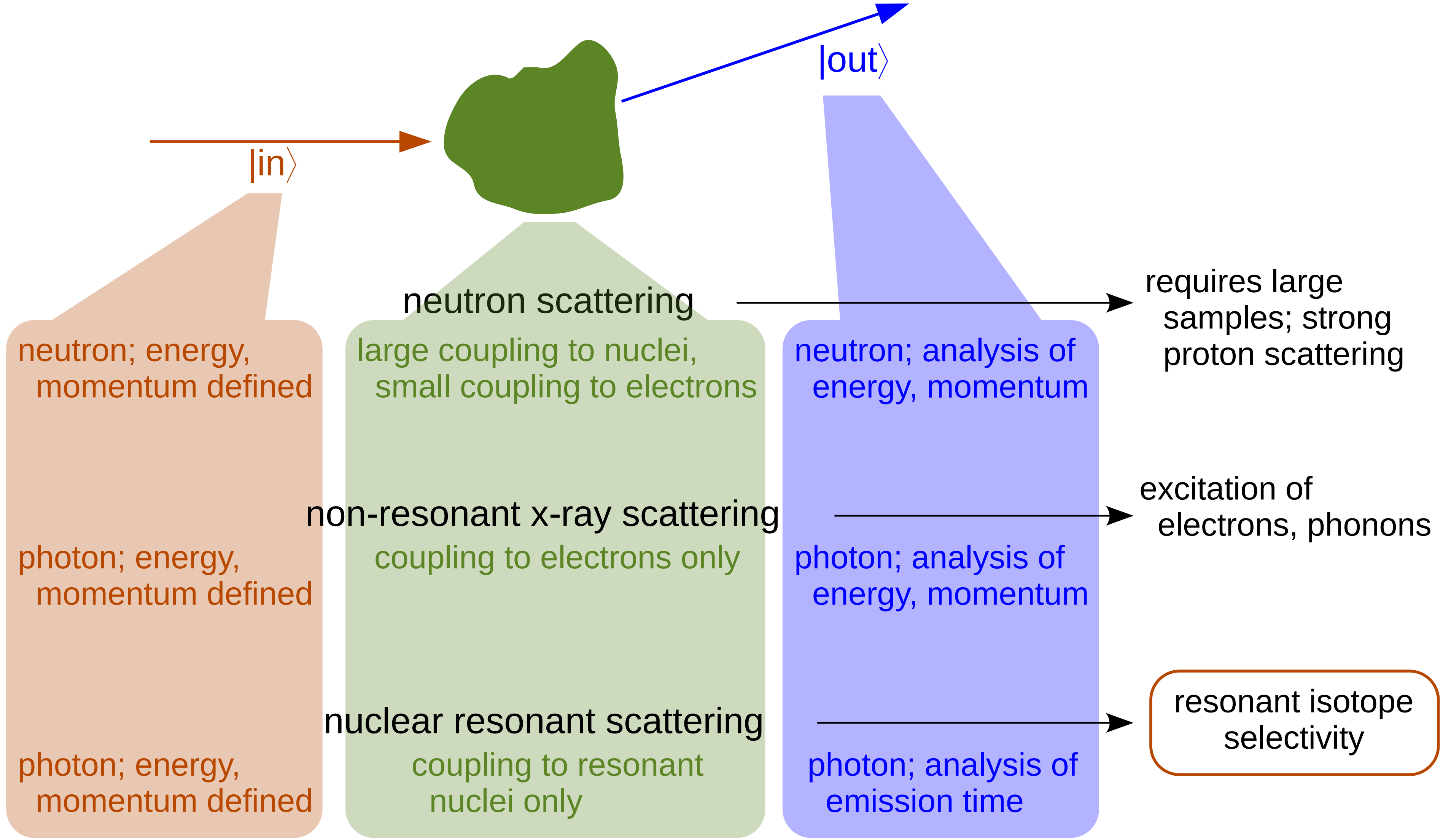
  - isotope fractionation

$$\ln\beta = -\frac{\Delta m}{M}\,\frac{1}{8(k_B T)^2} \int E^2 \mathcal{D}(E)\, dE$$

k ~ wave number of nuclear transition
E_R ~ recoil energy
ρ ~ mass density

M ~ mass of resonant isotope
Δm ~ isotope mass difference
k_B ~ Boltzmann's constant
T ~ temperature

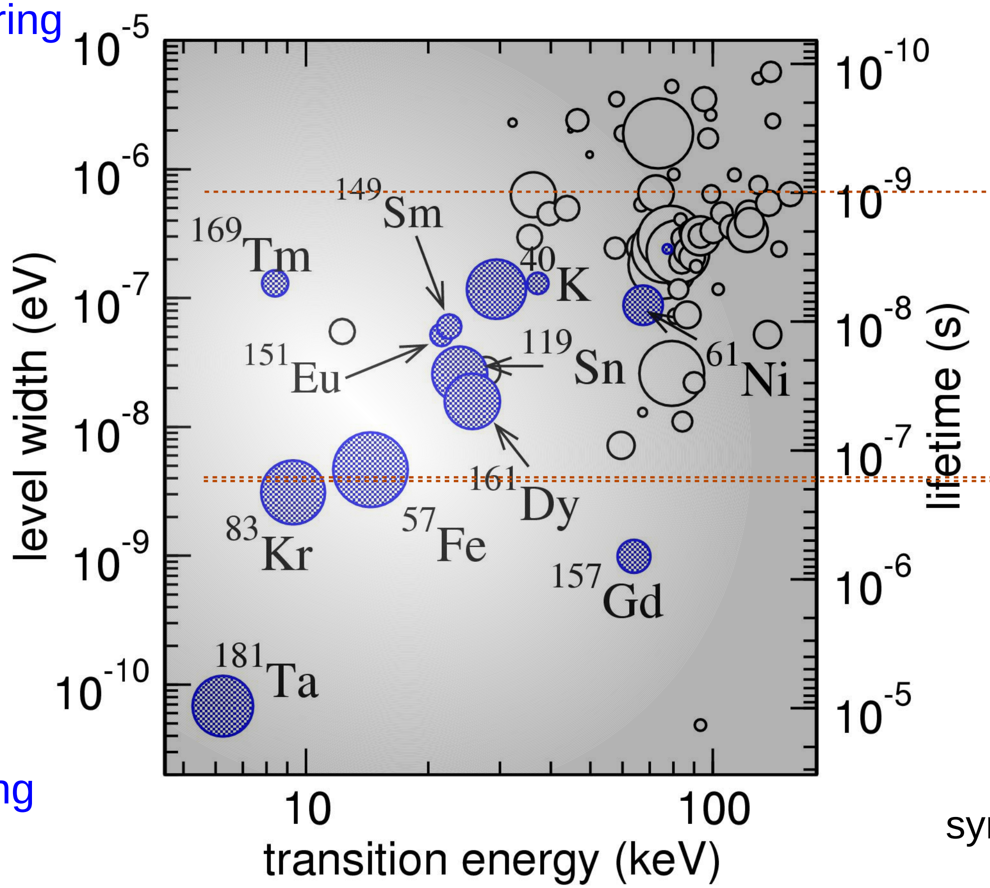
Methods:


|in⟩
|out⟩
neutron scattering
neutron; energy, momentum defined
large coupling to nuclei, small coupling to electrons
neutron; analysis of energy, momentum
requires large samples; strong proton scattering
non-resonant x-ray scattering
photon; energy, momentum defined
coupling to electrons only
photon; analysis of energy, momentum
excitation of electrons, phonons
nuclear resonant scattering
photon; energy, momentum defined
coupling to resonant nuclei only
photon; analysis of emission time
resonant isotope selectivity

Isotopes for nuclear resonant scattering:

larger scattering strength

easier timing



detector resolution

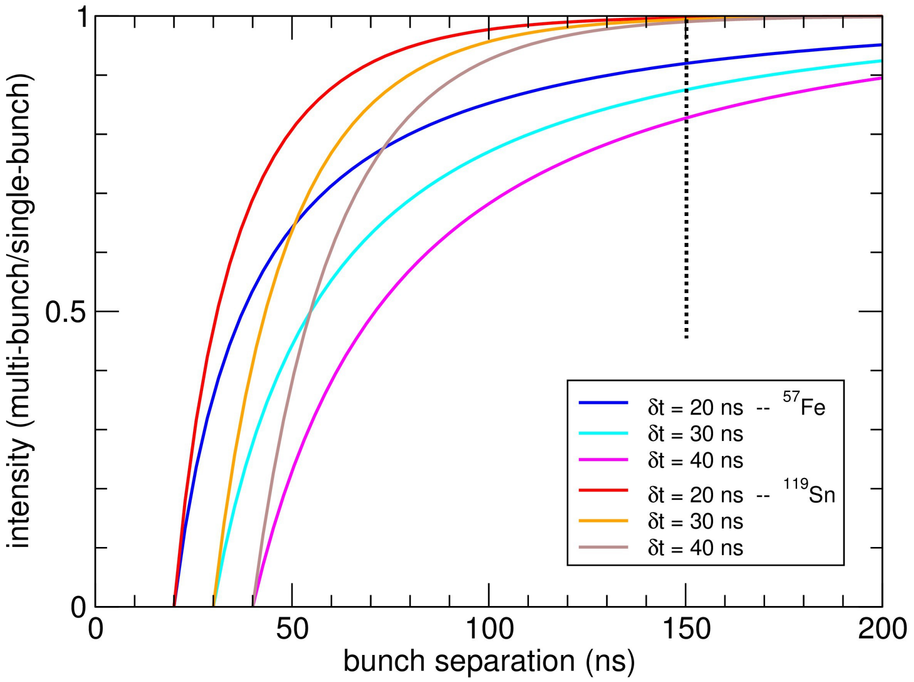
APS, ESRF bunch separation

symbol area is proportional to the nuclear resonant cross section

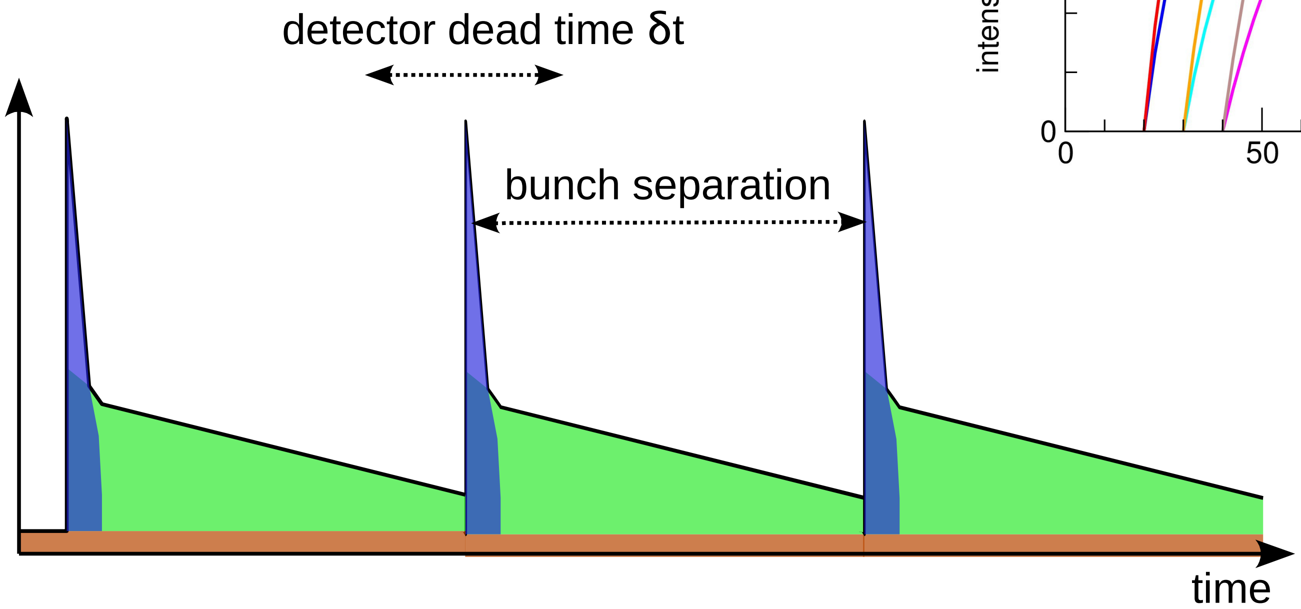
more absorption

less intensity

Time structure of synchrotron radiation:

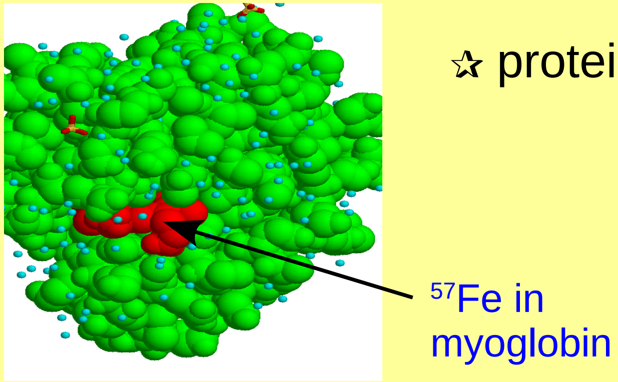


detector dead time and bunch separation determine the detectable counts in NRIXS.

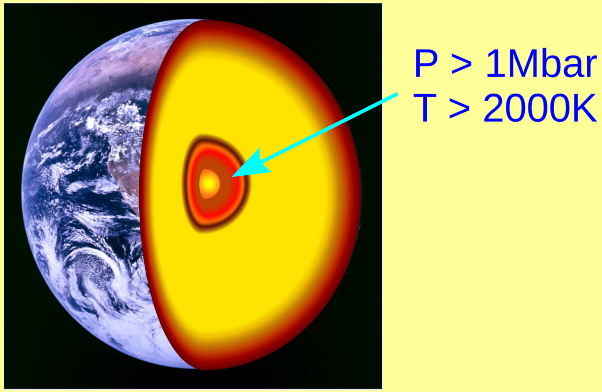


Target applications:

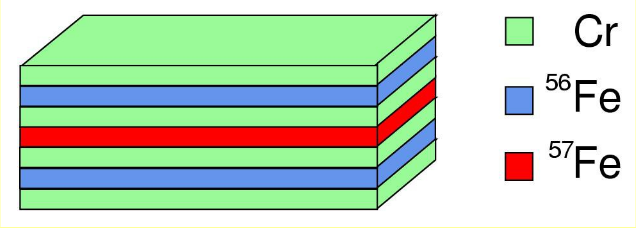
- perfect isotope selectivity & complete suppression of nonresonant signals
- excellent sensitivity (10^{12} nuclei in the focused beam)



☆ proteins and other large molecules

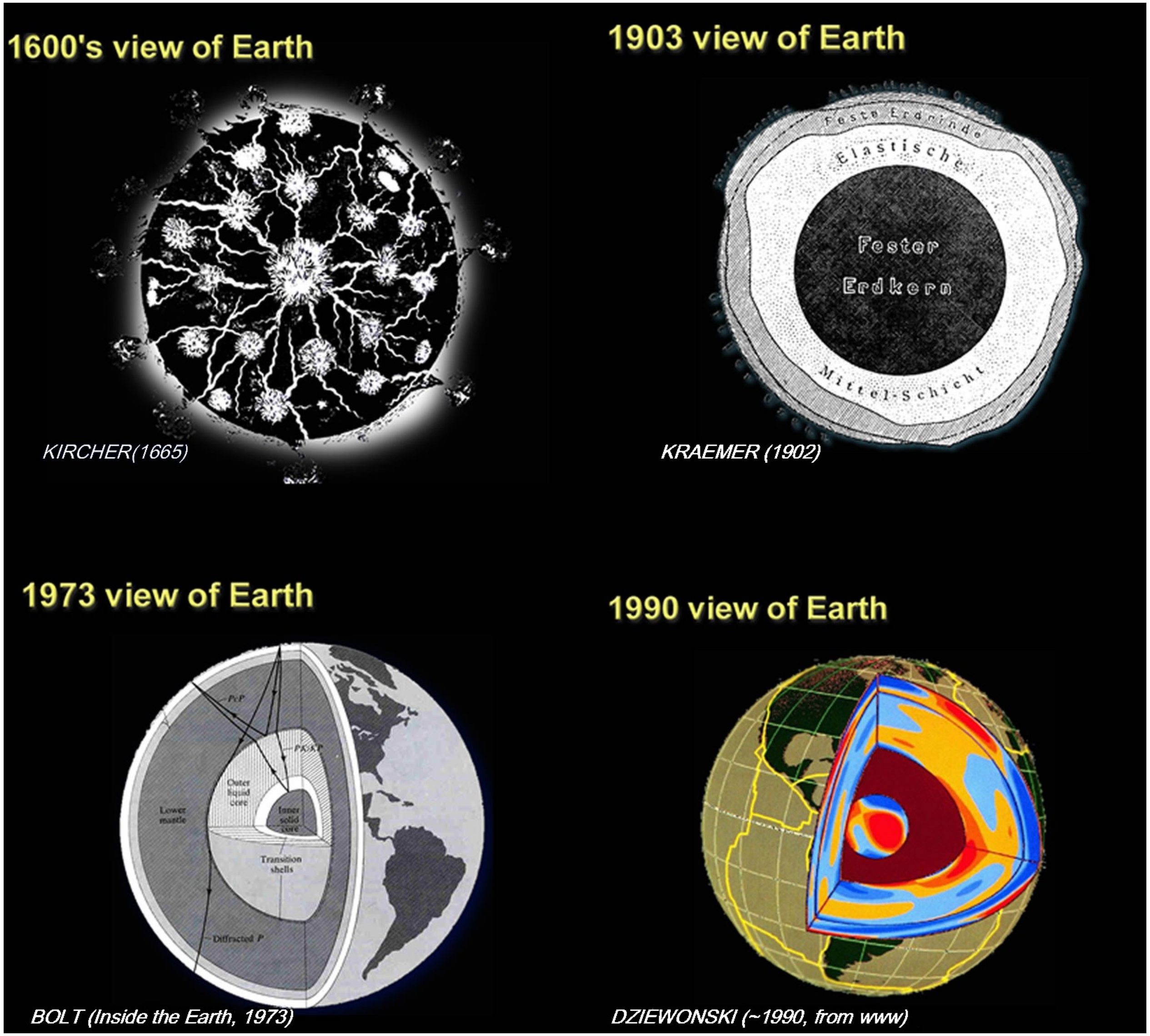


☆ materials under high pressure



☆ nanostructures

Probes have improved models of Earth's interior:



- ☆ seismic studies
- ☆ gravity and magnetic fields
- ☆ cosmo-chemical models
- ☆ geodynamical modeling

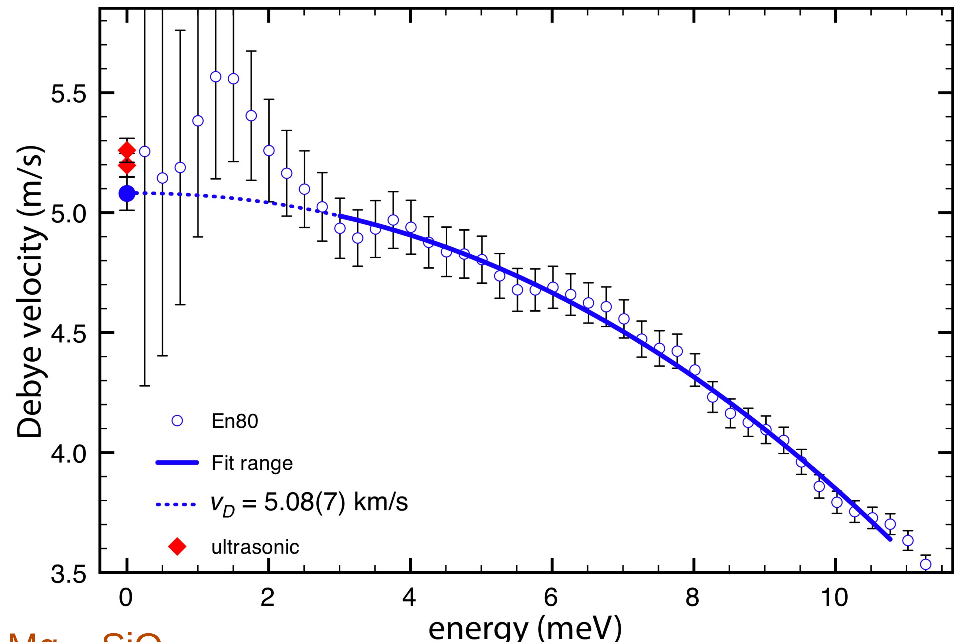
- ☆ material properties

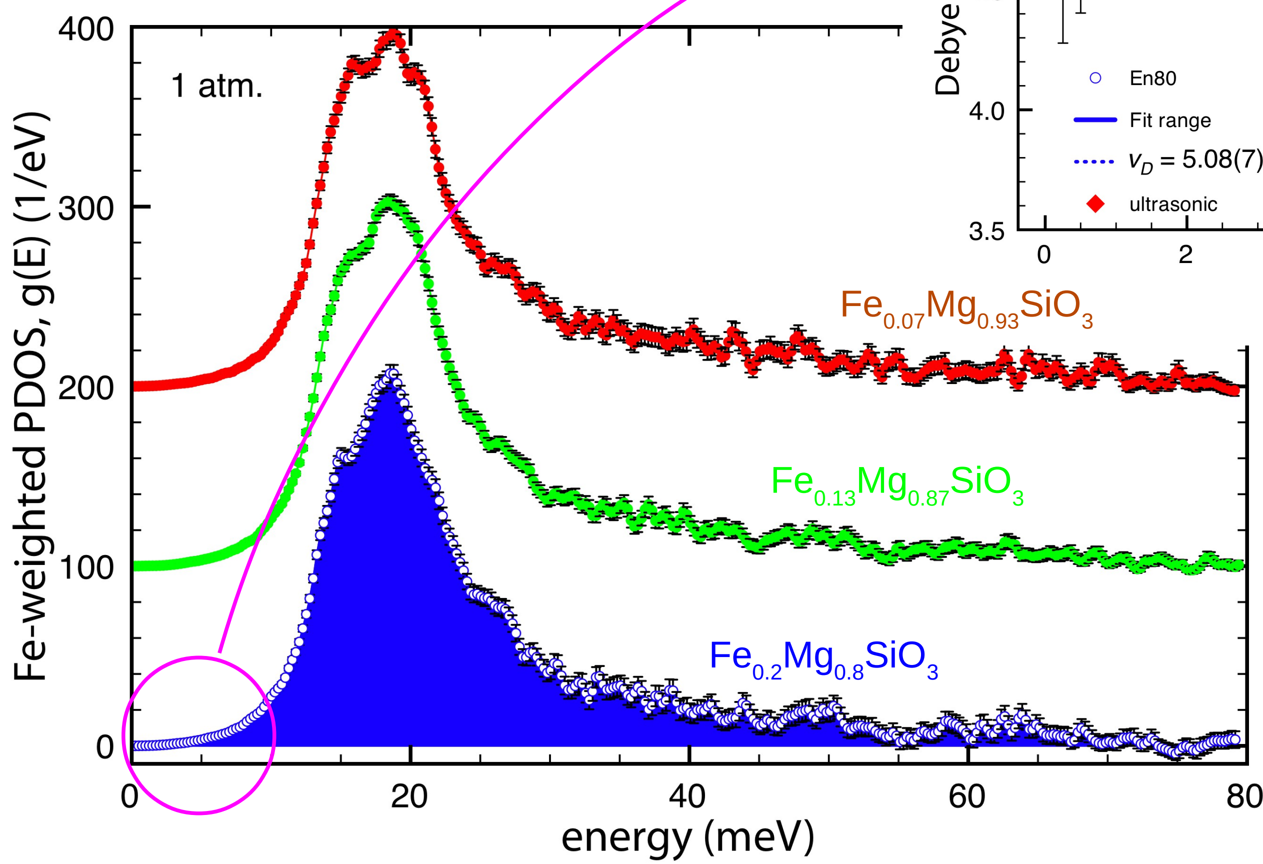
Sound velocities in (Fe,Mg)SiO_3 orthoenstatites:

☆ the Debye sound velocity average is obtained from the partial phonon DOS

M. Hu et al., Phys. Rev. B 67 (2003)

W. Sturhahn and J.M. Jackson, GSA special paper 421 (2007)





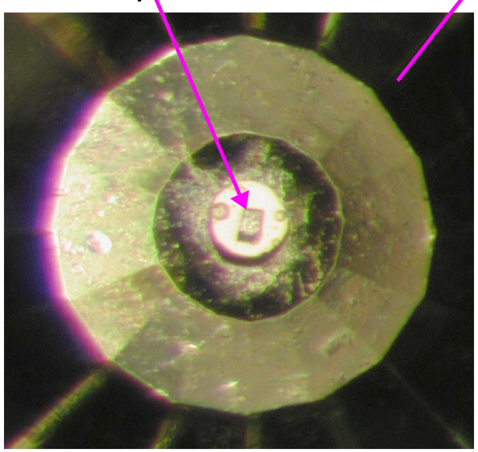
☆ excellent agreement with traditional methods

J.M. Jackson, E.A. Hamecher, W. Sturhahn, Eur. J. Mineral. 21 (2009)

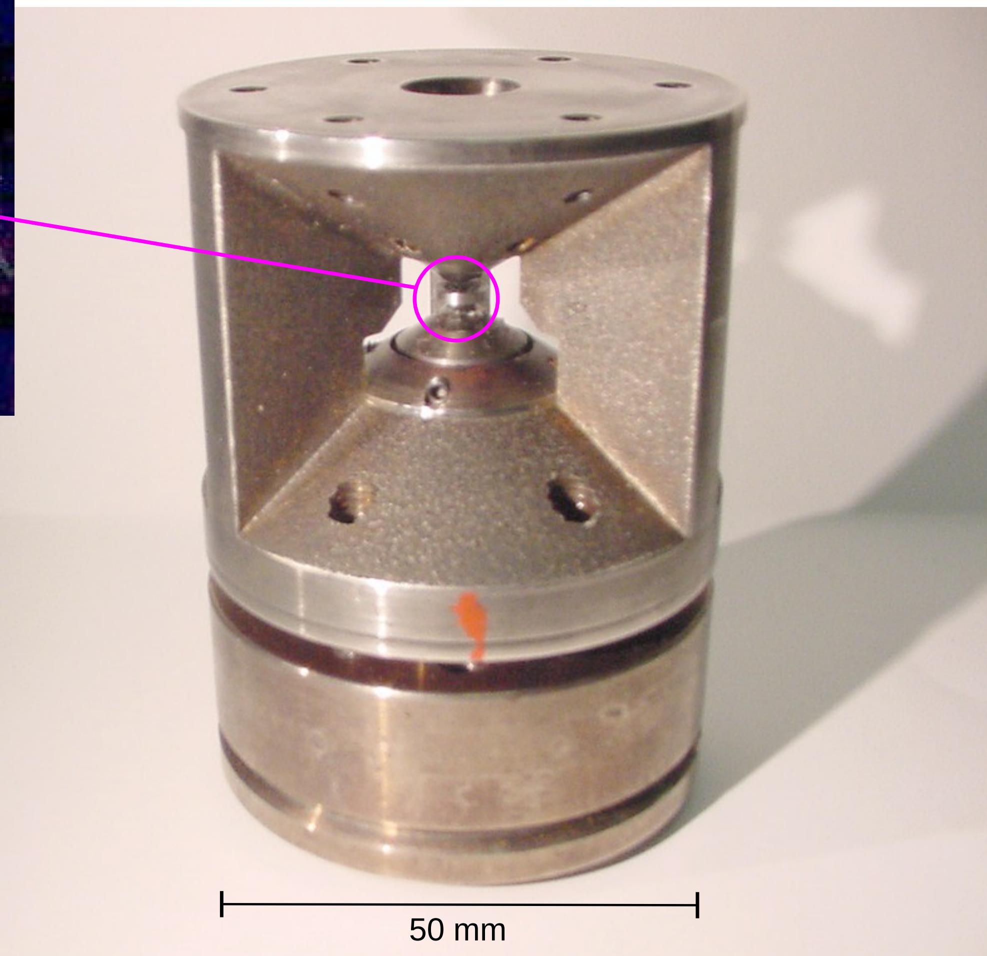
Diamond anvil cells for Mbar pressures:

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

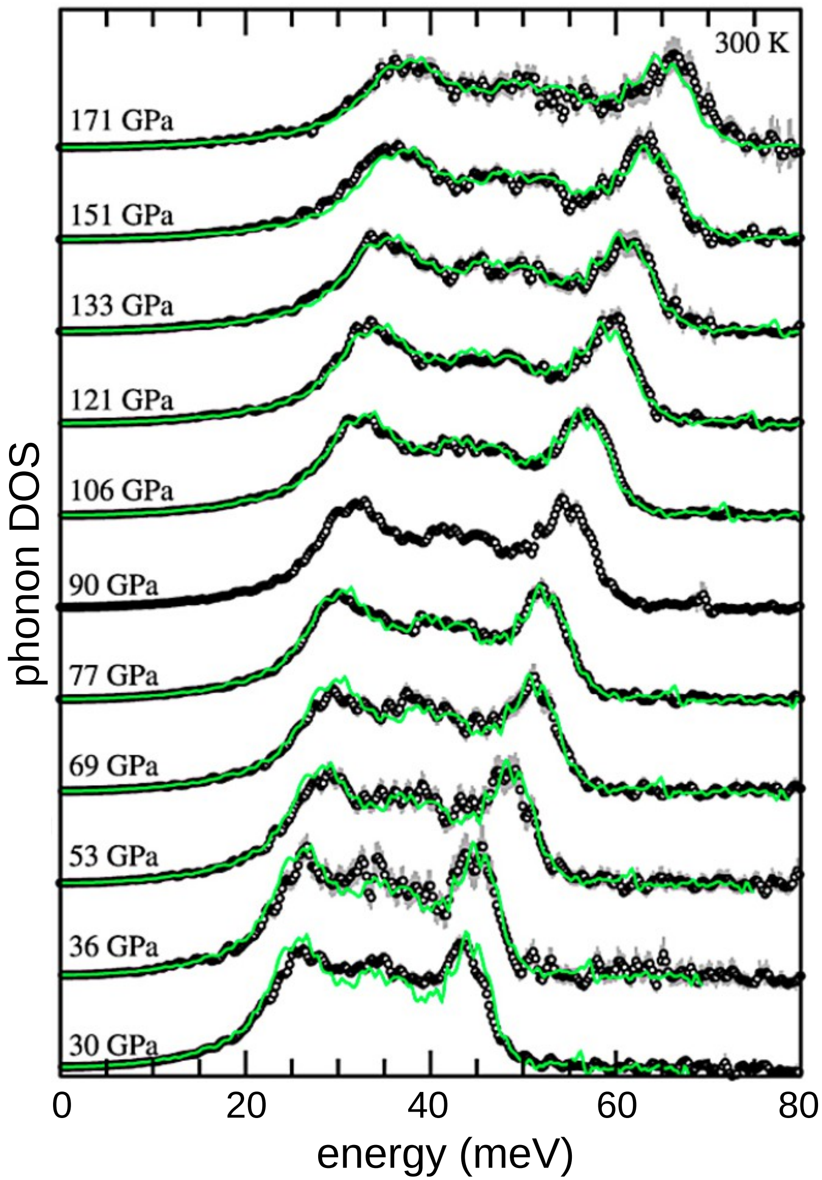
sample



100 μm



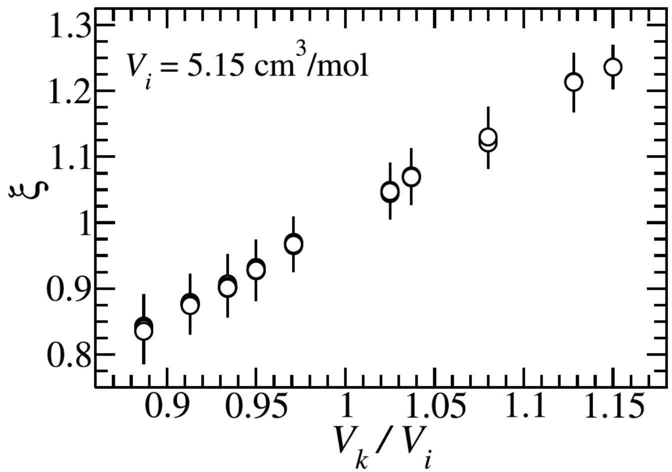
NRIXS on hcp-Fe:



☆ hcp–Fe is the major component of Earth's core

☆ the phonon DOS of hcp–Fe shows a fairly well defined scaling behavior

$$\mathcal{D}(E,V) = \xi(V/V_i)\,\mathcal{D}(\xi(V/V_i)\cdot E, V_i)$$



☆ the scaling gives the Grüneisen parameter

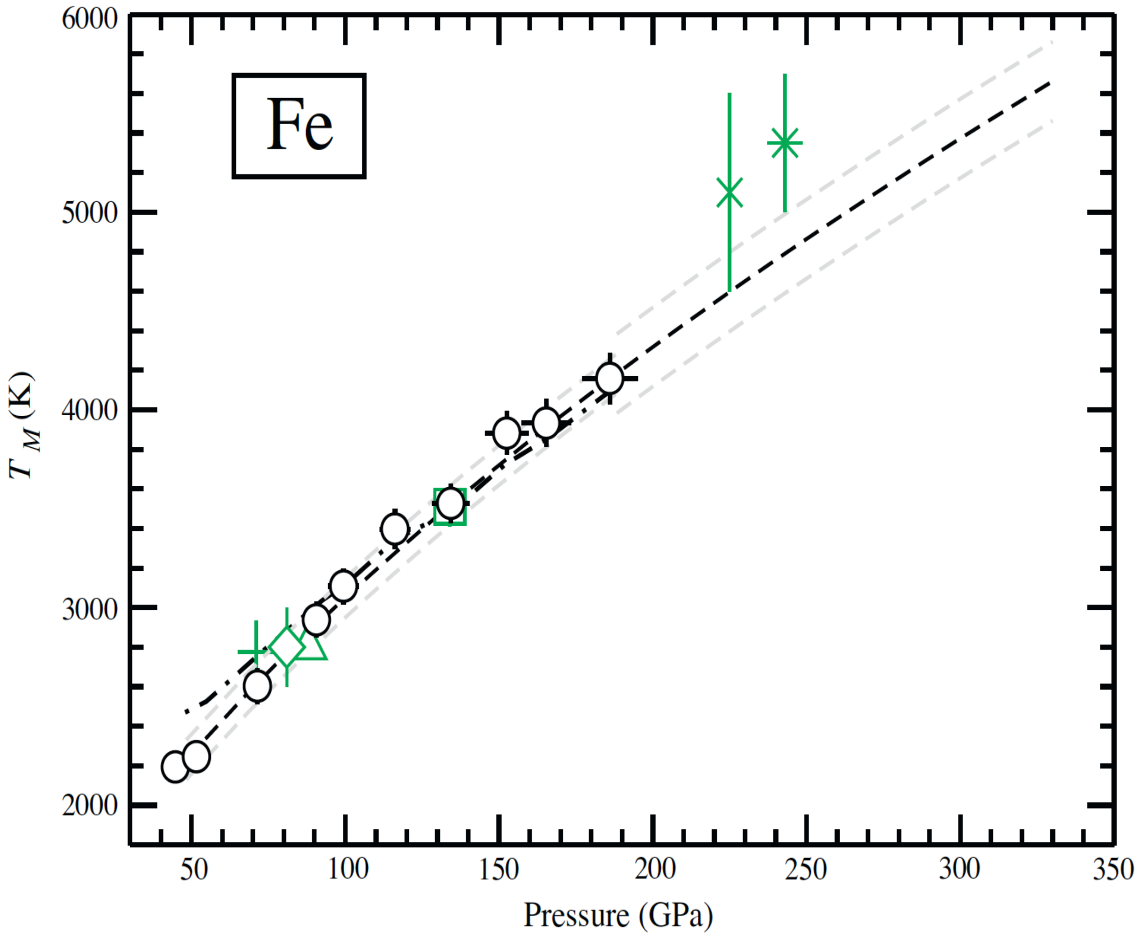
$$\gamma(V) = \gamma_0\,(V/V_0)^q$$

with γ_0= 1.98(2) and q = 1

C.A.Murphy, J.M.Jackson., W.Sturhahn, B.Chen: Geophys. Res. Lett. 38 (2011)
C.A.Murphy, J.M.Jackson., W.Sturhahn: J. Geophys. Res. 118 (2013)

NRIXS and melting:

☆ The Lindemann criterium: $\langle u^2 \rangle_{T_m} = C\, R^2(T_m)$



☆ from the phonon DOS of hcp-Fe we get at high temperatures

$$\begin{aligned} \langle u^2 \rangle_T &= k_B T \, \frac{2E_R}{3k_0^2} \int \frac{1}{E^2}\, \mathcal{D}(E)\, dE \\ &\equiv \frac{1}{k_0^2}\, \frac{T}{T_{LM}} \end{aligned}$$

☆ melting temperatures

$$T_m = T_{m0} \left(\frac{V}{V_{m0}} \right)^{2/3} \frac{T_{LM}(V)}{T_{LM}(V_{m0})}$$

C.A. Murphy, J.M. Jackson., W. Sturhahn, B. Chen, Phys. Earth Planet. Inter. 188 (2011)

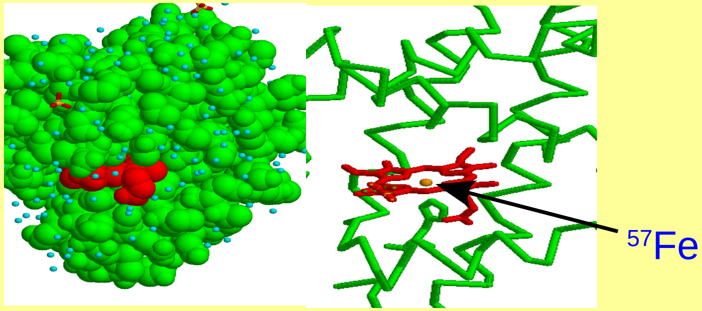
Biophysics applications:

☆ iron has several functions in biology

- oxygen metabolism

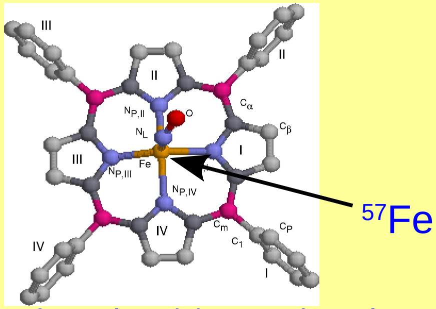
  ATP production
  oxygen transport (myoglobin, hemoglobin)

- electron transfer (cytochrome-f)
- cellular signaling (with NO, O_2, CO)
- active centers in enzymes, e.g., N_2-genase, H_2-genase



Myoglobin

J.T. Sage et al., Phys.Rev.Lett. 86 (2001)



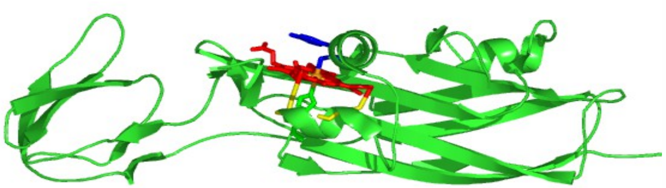
Nitrosyl-Fe(II)-tetraphenyl-porphyrin

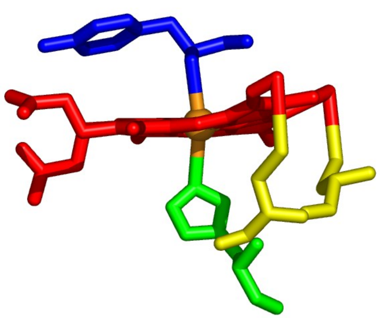
B.K. Rai et al., Biophys.J. 82 (2002)

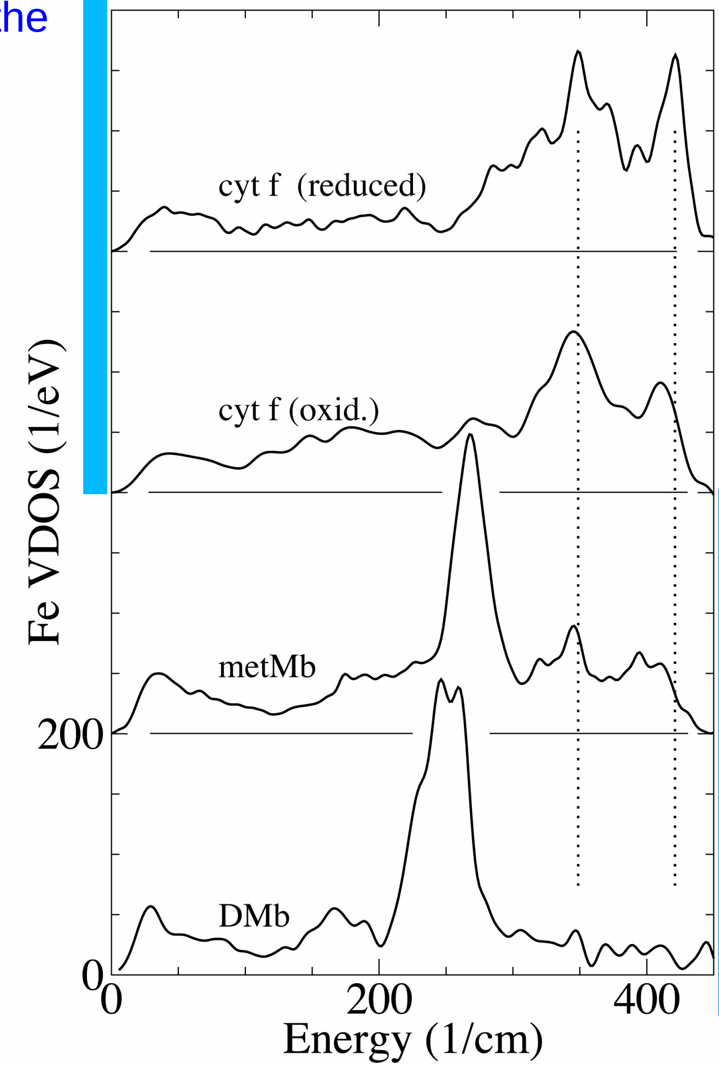
☆ NRIXS determines the complete frequency spectrum and vibration amplitudes of the probe ^{57}Fe located at the active site of the protein.

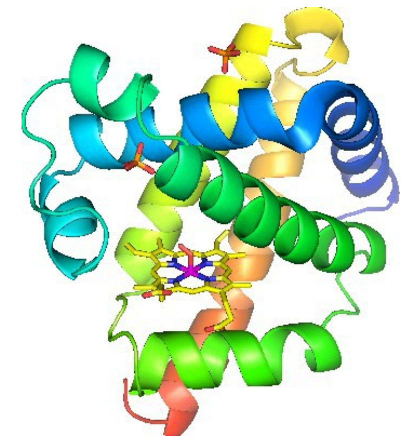
Phonon modes in proteins:

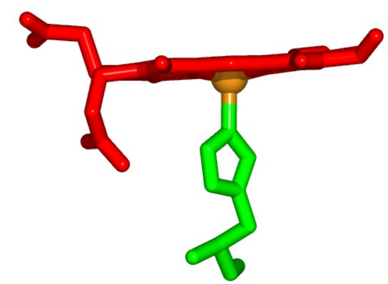
Cytochrome f is an electron-transfer membrane protein and part of the cytochrome b-f complex of oxygenic photosynthesis









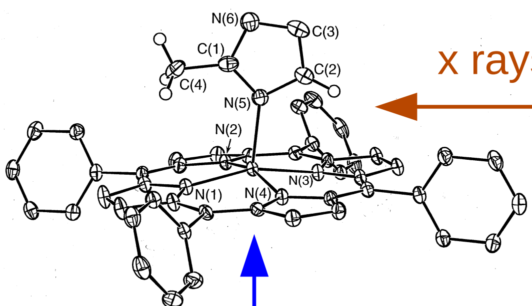


Myoglobin is an oxygen ligand-binding protein, e.g., found in muscle tissues

K.L. Adams et al.,
J. Phys. Chem. B 110 (2006)
B. Leu et al.,
J. Phys. Chem. B 113 (2009)

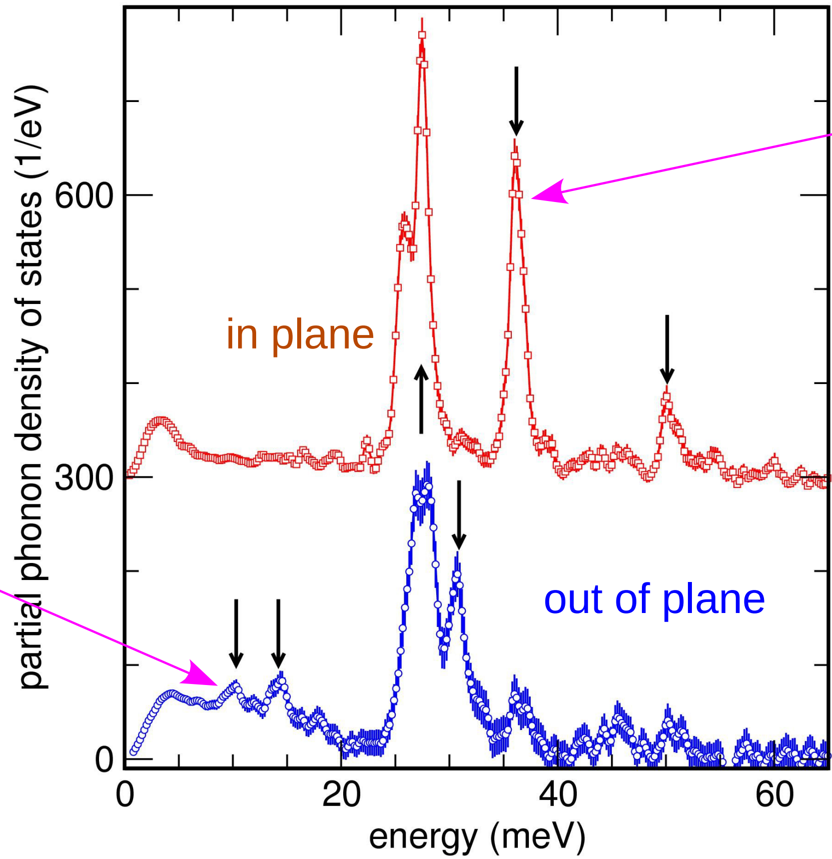
Polarization of phonon modes from NRIXS:

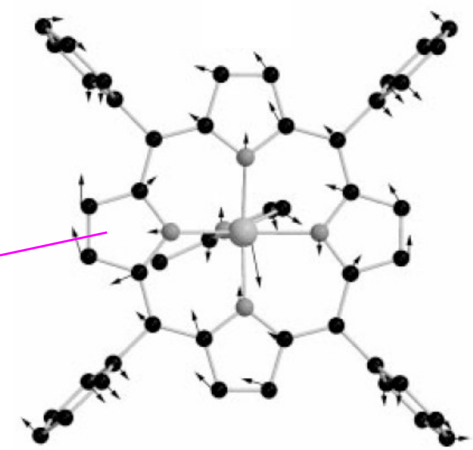
✰ [Fe(TPP)(2-MeIm)] is a model system for heme proteins

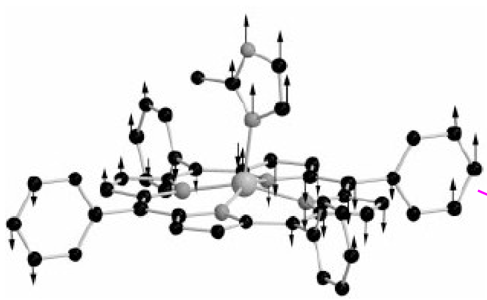


x rays “in plane”

x rays
“out of plane”







B.K. Rai et al.,
Phys.Rev. E 66 (2002)

Selection rules:

- NRIXS spectra are described by

$$S(\mathbf{k},E) = \frac{1}{2\pi\hbar}\int \left\langle \mathrm{e}^{\mathrm{i}\mathbf{k}\hat{\mathbf{r}}(t)}\mathrm{e}^{-\mathrm{i}\mathbf{k}\hat{\mathbf{r}}(0)} \right\rangle \mathrm{e}^{\mathrm{i}Et/\hbar} dt$$

- The polarization of a particular phonon gives the direction of its contribution to atomic displacement.

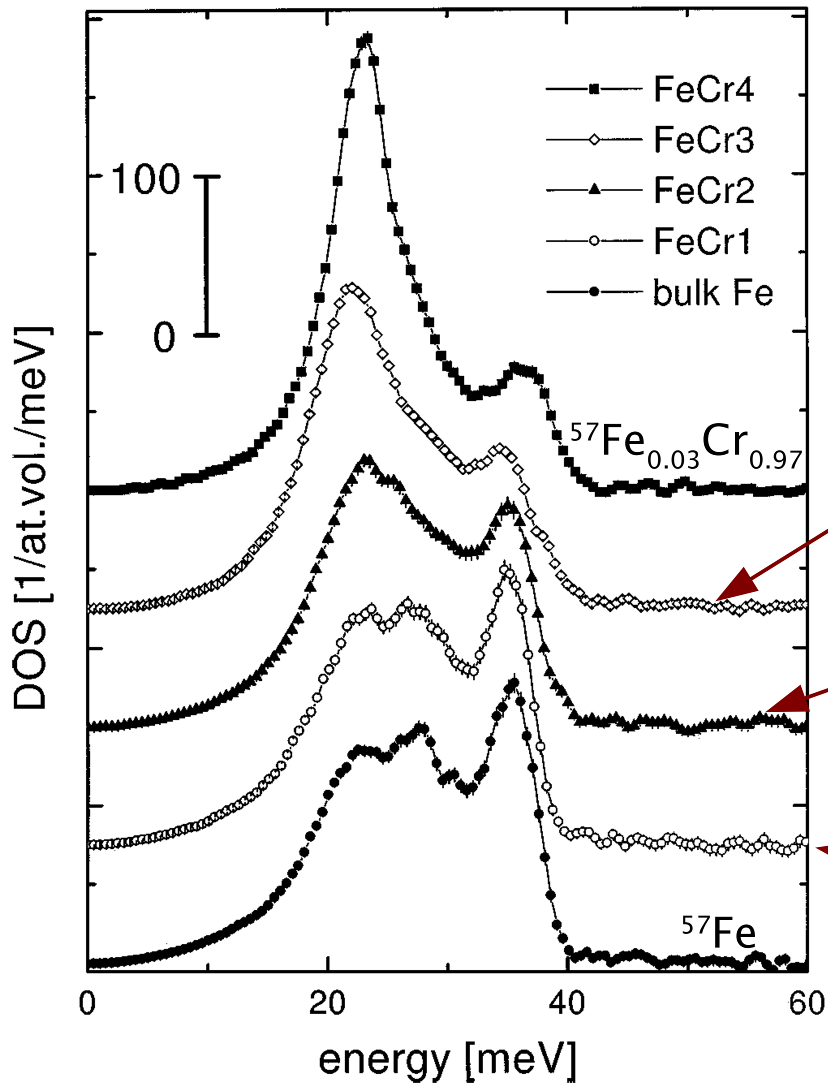
- Phonon polarizations perpendicular to the x-rays have $\mathbf{k}\cdot\mathbf{e} = 0$ and are excluded.

- Excluded are

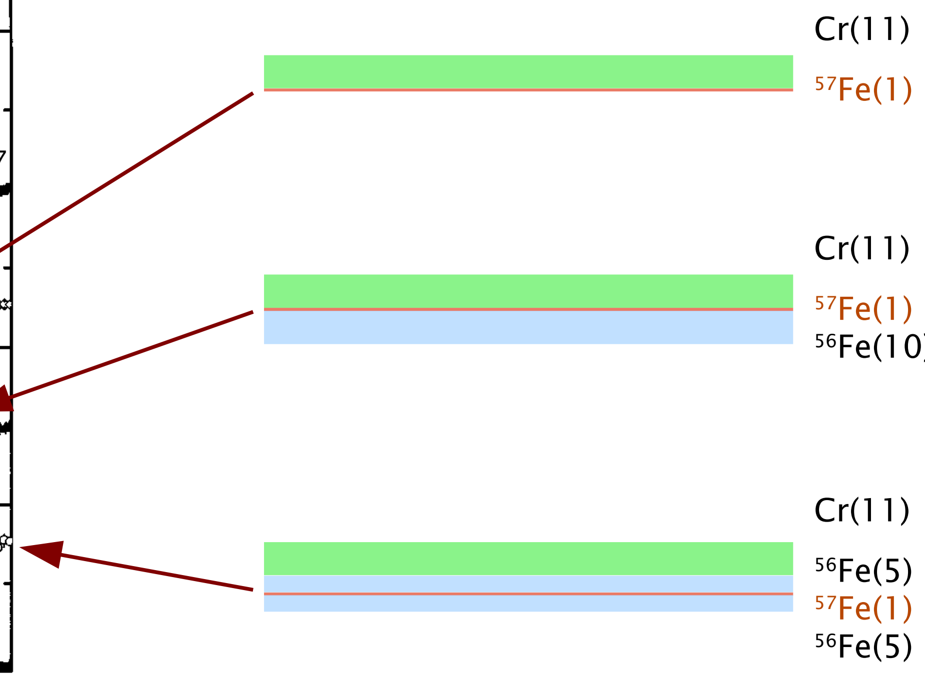
  longitudinal phonons (p-waves) moving perpendicular to the x-rays;

  transverse phonons (s-waves) moving in the direction of the x-rays.

Phonons in tracer layers:

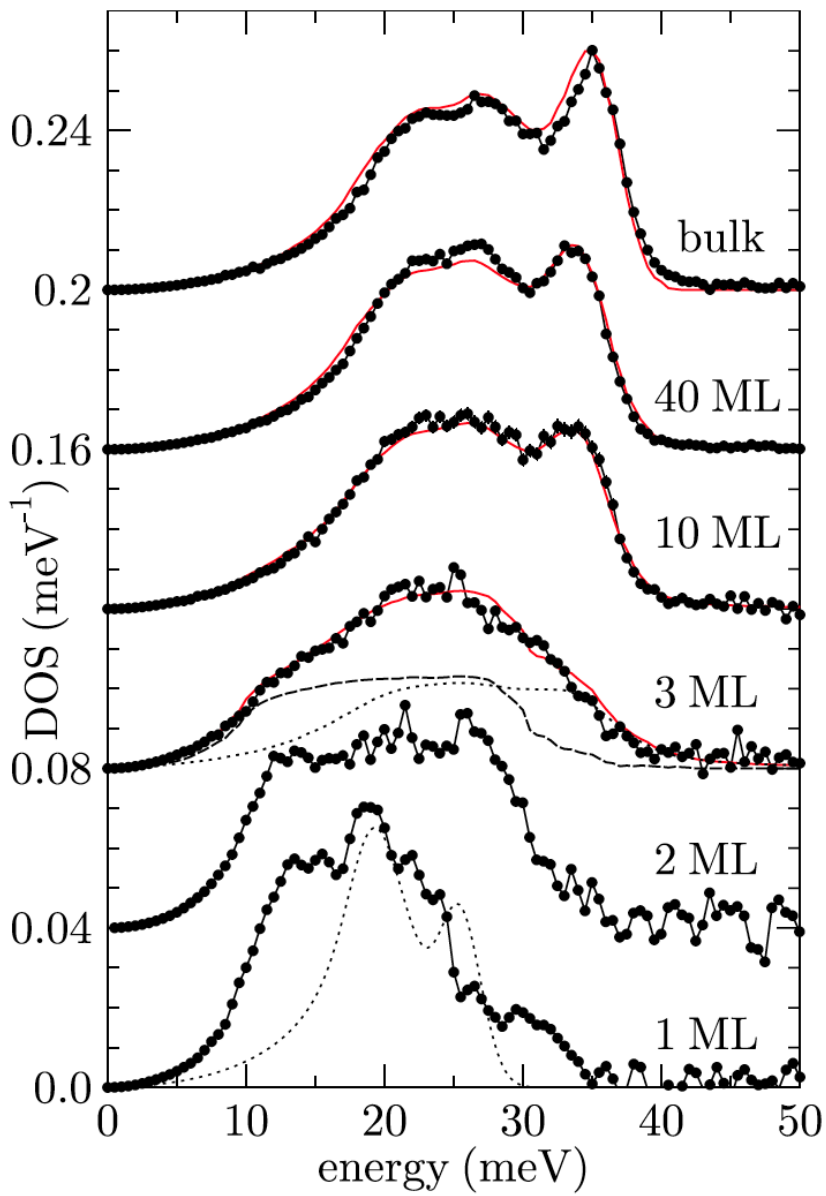


- ✰ Fe films embedded in Cr show significant reduction of longitudinal modes
- ✰ resonant modes around 23 meV are strongly expressed



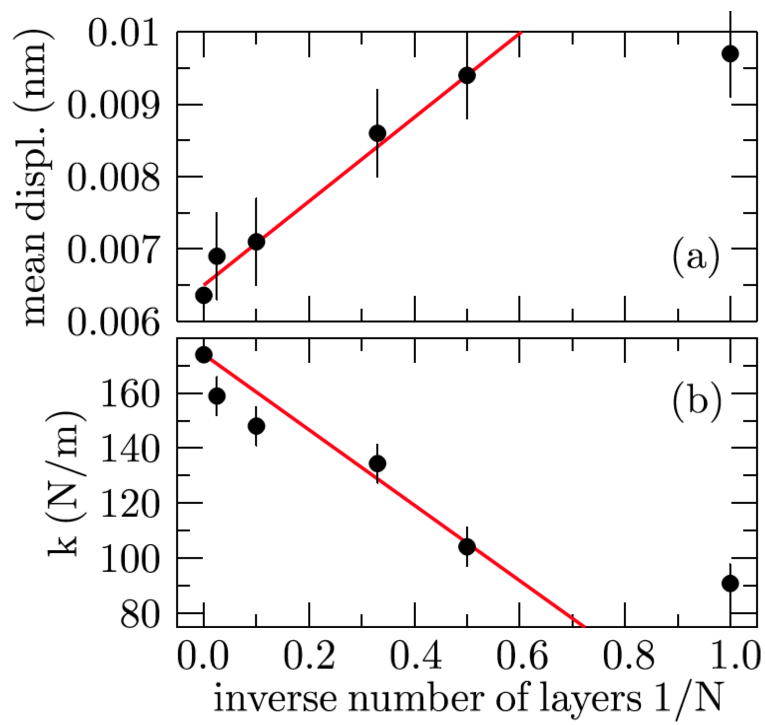
T.Ruckert, W.Keune, W.Sturhahn, M.Y.Hu, J.P.Sutter, E.E.Alp: Hyperfine Interact. 126 (2000)
W.Keune, S.Hong, M.Y.Hu, J.Zhao, T.S.Toellner, E.E.Alp, W.Sturhahn, T.S.Rahman, B.Roldan Cuenya: Phys. Rev. B 96 (2018)

Fe layers on W:



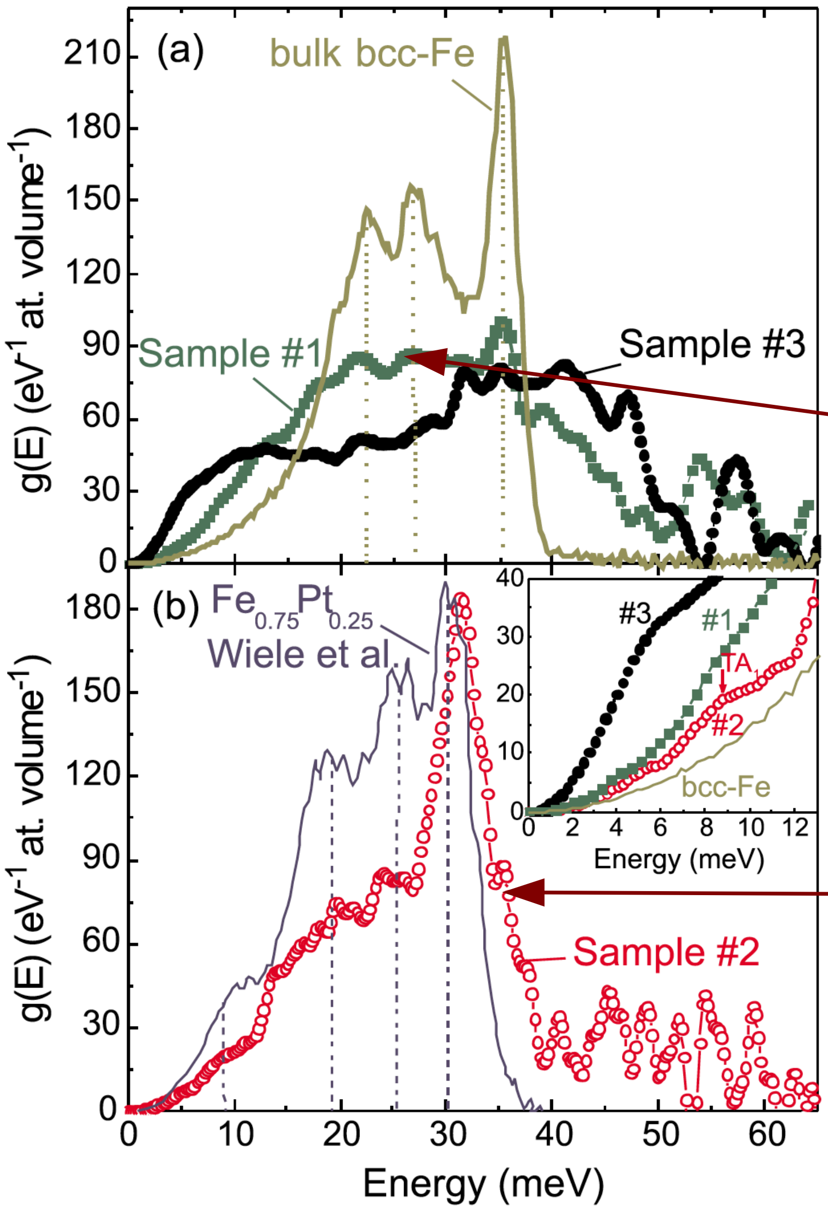
☆ Fe films on W also show a significant reduction of longitudinal modes

☆ but resonant modes around 20 meV are weakly expressed

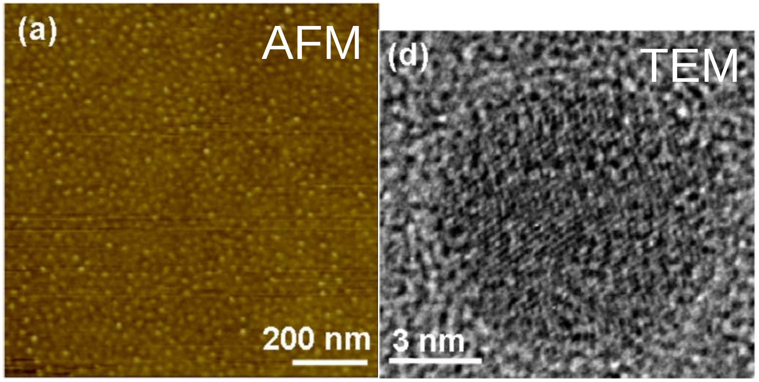


S. Stankov et al., Phys. Rev. Lett. 99 (2007)

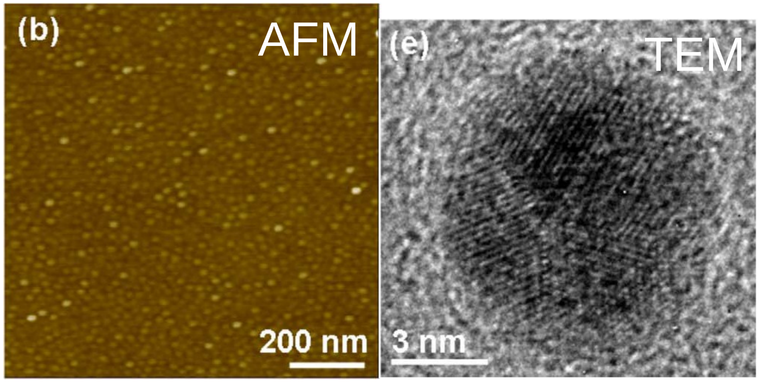
Nano-clusters:



☆ self-assembled ^{57}FePt nano-clusters show very different phonon DOS for bcc and fcc structure



bcc structure

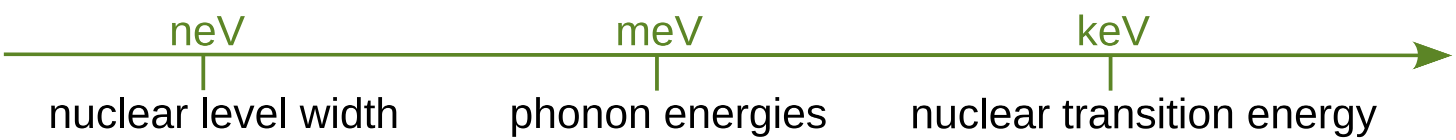


fcc structure

B. Roldan Cuenya et al., Phys. Rev. B 80 (2009)

In conclusion:

- the “three energy scales” make NRIXS work



- NRIXS provides a wealth of vibrational information
  - ☆ under extreme conditions (pressure, temperature)
  - ☆ at active centers of proteins and enzymes
  - ☆ about nano-structures

- in particular we obtain
  - ☆ the partial phonon density of states

Ende