Inelastic x-ray scattering, IXS

Esen Ercan Alp

Advanced Photon Source,
Argonne National Laboratory

alp@anl.gov

Neutron and X-Ray Summer School
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Argonne and Oak Ridge National Laboratory

Inelastic X-Ray Scattering & Spectroscopy @ APS

IXS

MCS

NRIXS

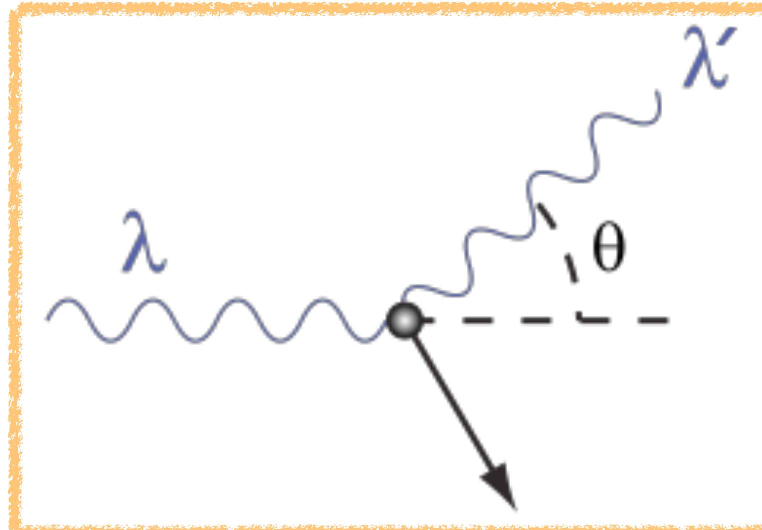
RIXS

XRS

XES

NRIS

Compton



- Nuclear Resonant Inelastic X-Ray scattering, NFS, NRIXS: Sectors 3, 16, (30)
- Momentum Resolved High Energy Resolution IXS (HERIX) Sectors 3, 30
- Resonant Inelastic X-Ray Scattering, RIXS (MERIX): Sectors 9, 30 --> 27
- X-Ray Raman Scattering, XRS (LERIX): Sectors 13, 16, 20
- X-Ray Emission Spectroscopy, XES (MINIX): Sectors 13, 16, 17

IXS: Inelastic X-Ray Scattering

A set of **vastly different** techniques based on measuring exact:

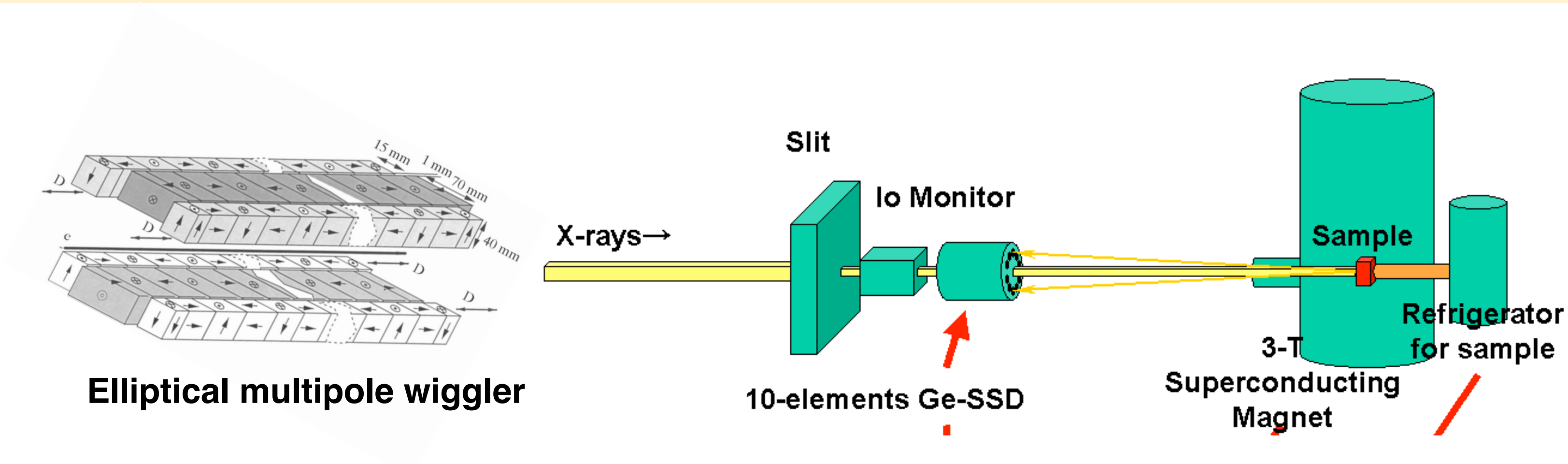
i) **energy**, and
ii) **momentum** transfer in a scattering experiment.

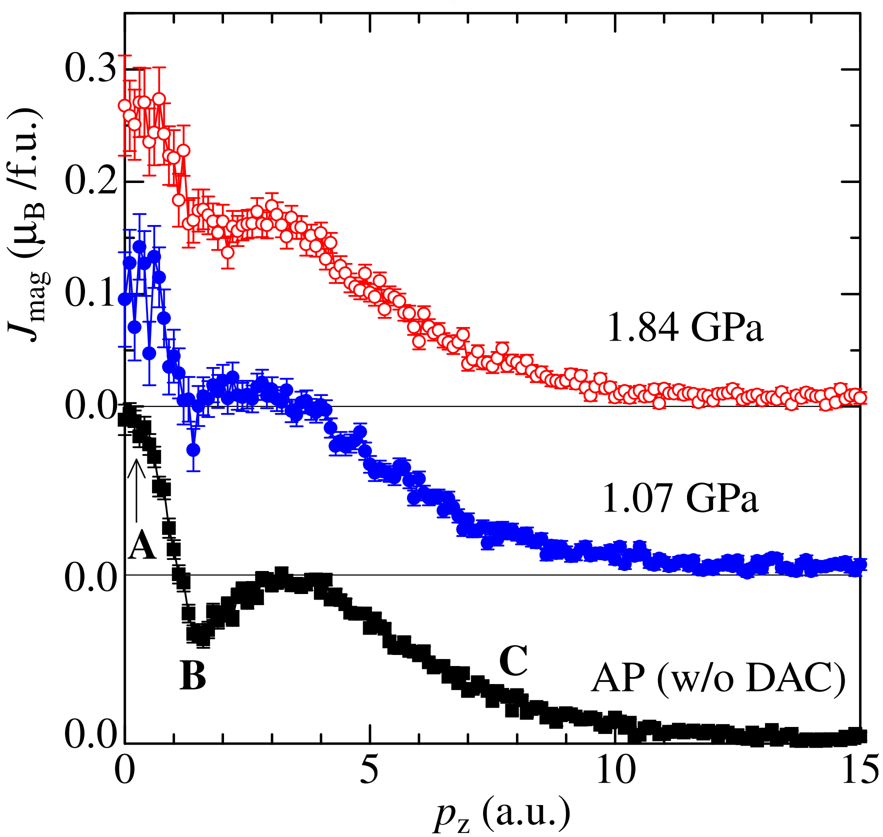
It provides **thermodynamic, elastic, electronic and chemical** information about the scattering system.

Since X-ray energies extend from a few eV to a few hundred keV, we need to measure energy loss or gain with a resolution changing from

nano-eV
meV,
eV, and
keV.

Magnetic Compton Scattering under high-pressure: e.g. $ErCo_2$



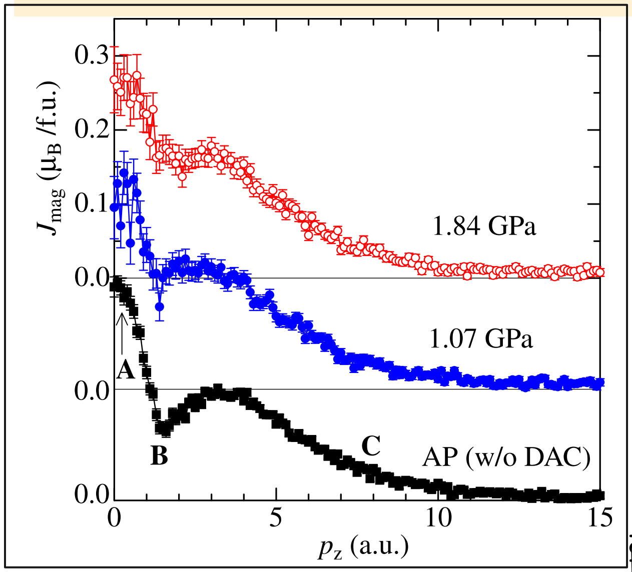


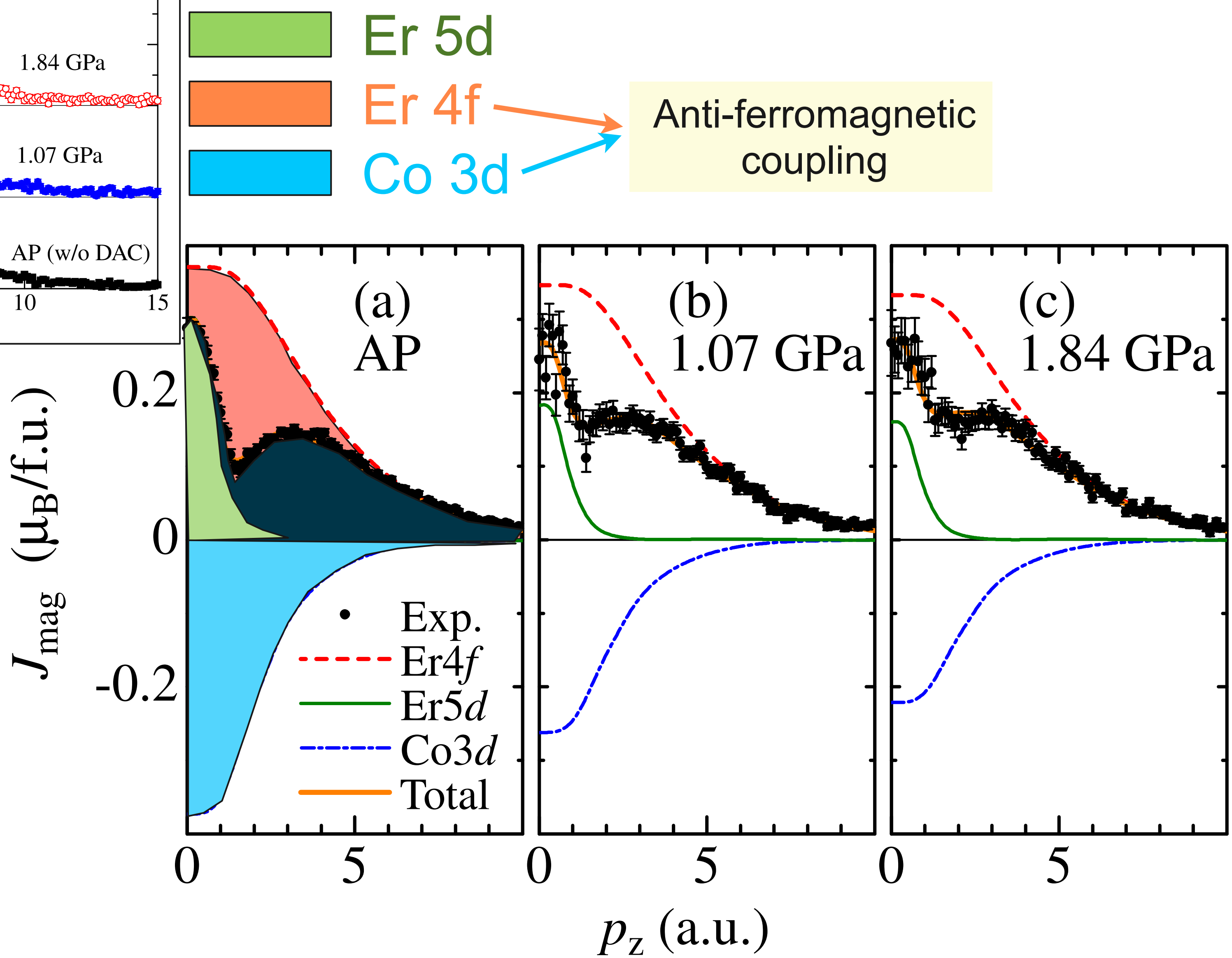
One dimensional projection of electron spin density

$$J_{mag}(\mathbf{p}_z) = \frac{1}{\mu} \iint_{\infty}^{\infty} (n_{\uparrow}(\mathbf{p}) - n_{\downarrow}(\mathbf{p})) d\mathbf{p}_x d\mathbf{p}_y$$

Shinji Watanabe,....Y. Sakurai, J. Phys. Soc. of Japan 80 (2011) 093705

Magnetic Compton Scattering under high-pressure





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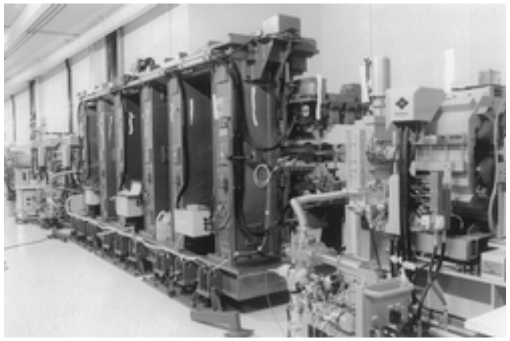
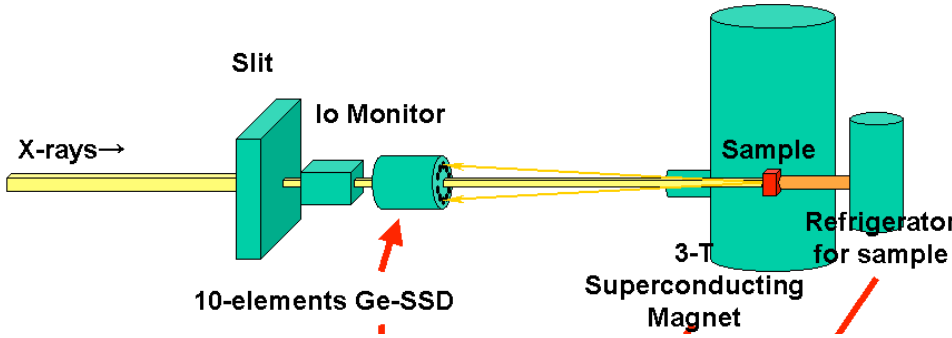
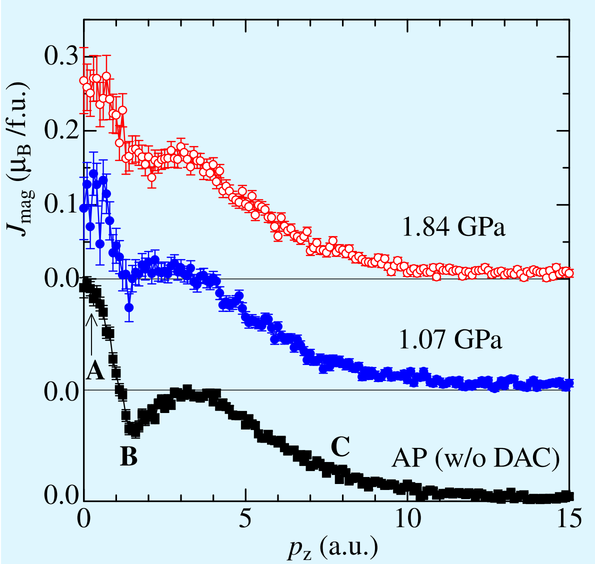
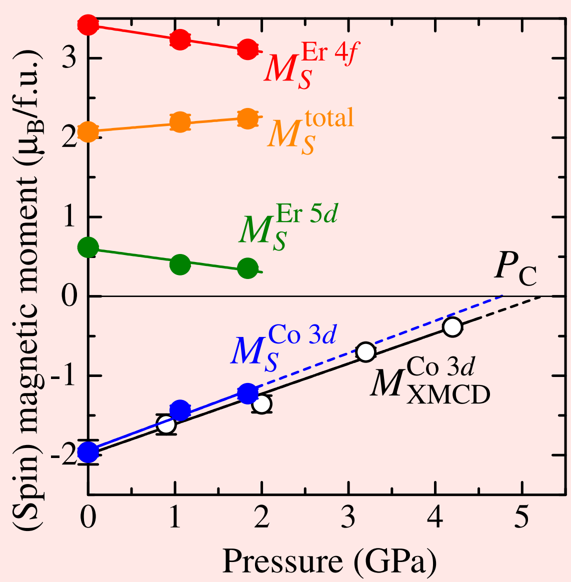
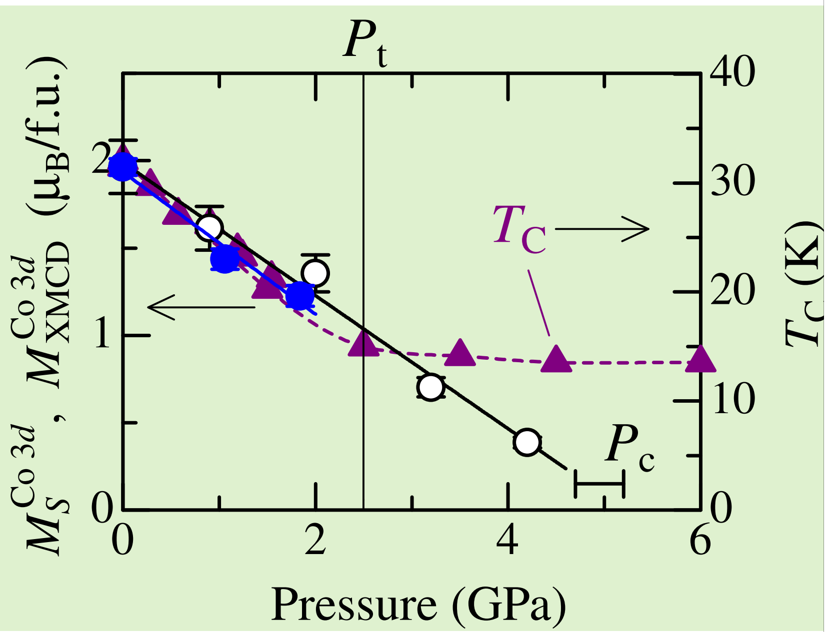
Magnetic Compton Scattering under high-pressure: $ErCo_2$











MCS can determine element specific band broadening, and magnetic moment reduction.
MCS is a quantitative probe of for spin magnetic moments under high pressure.

Shinji Watanabe,....Y. Sakurai, J. Phys. Soc. of Japan 80 (2011) 093705

IXS: Inelastic X-Ray Scattering

IXS can measure

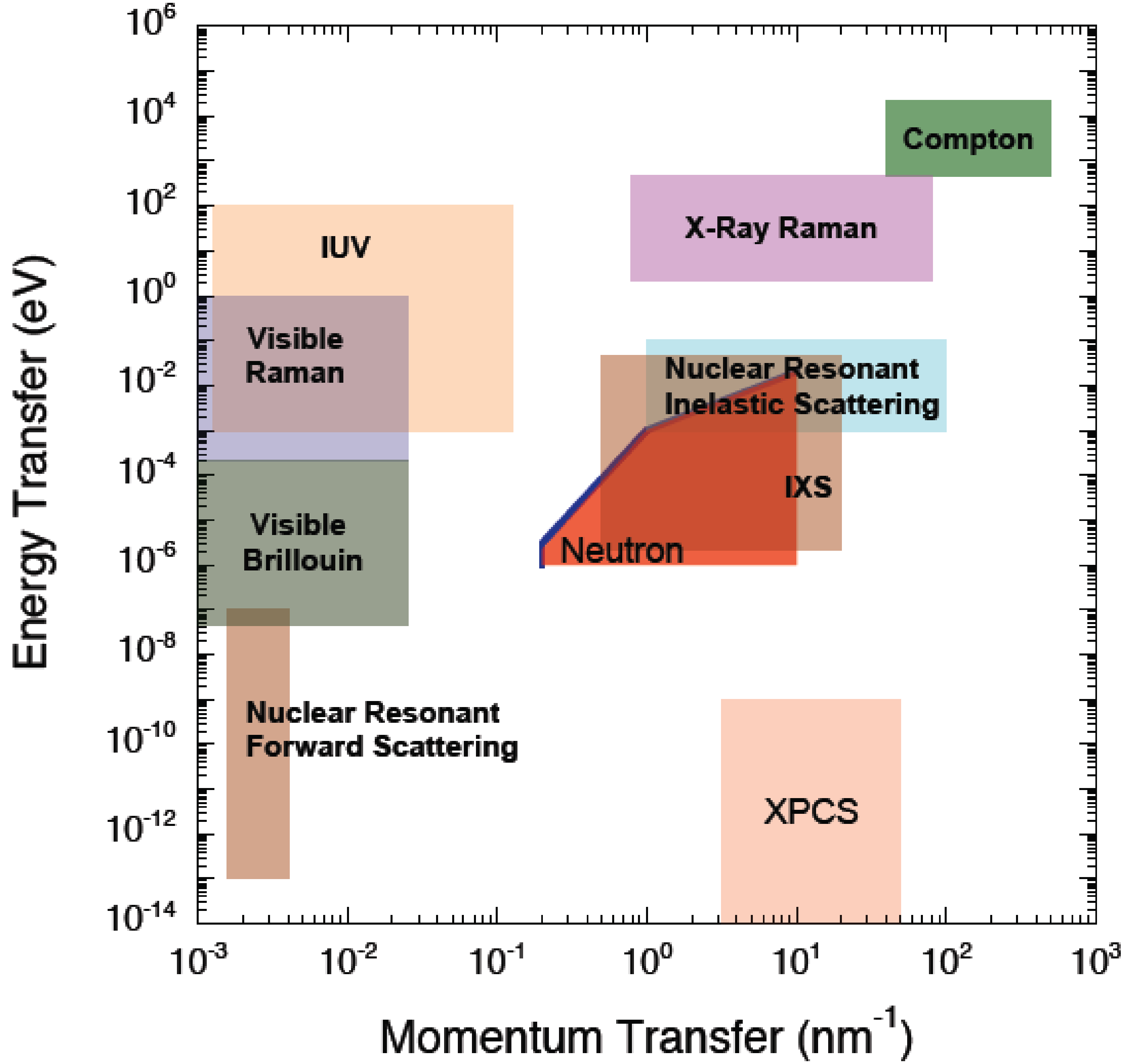
- nuclear hyperfine interactions (neV),
- collective excitations of atoms such as phonons (meV),
- electronic excitations like d-d excitations, charge-transfer energy, plasmons or magnons (eV),
- core-valence electron boundary to reconstruct Fermi surface (keV)
- determine orbital occupancies (keV)

1920-1930 : P. Debye, A. Compton and J. DuMond :

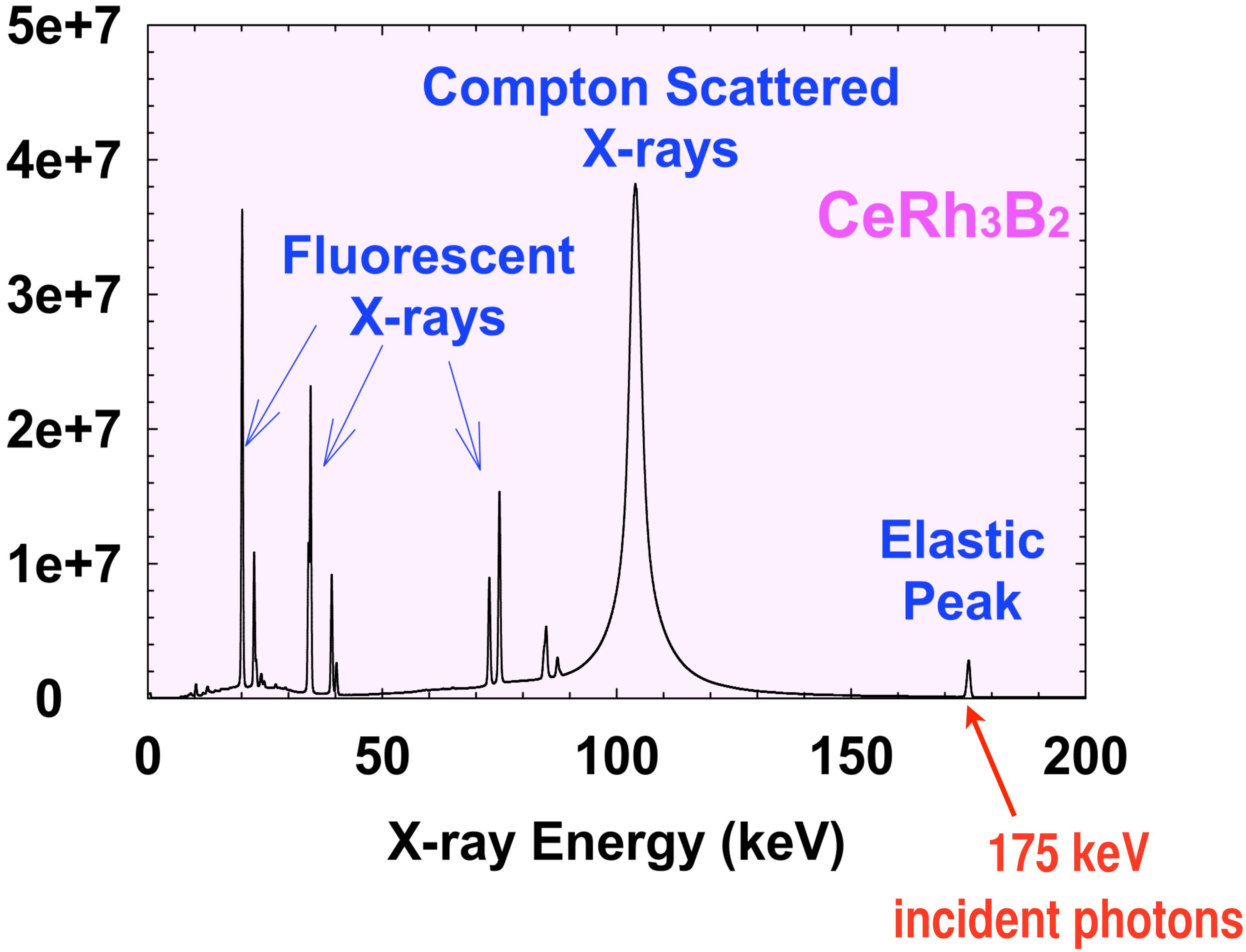
1960-1990: Development of

i) pure silicon and germanium with $\Delta d/d \sim 10^{-9}$,
ii) sophisticated high resolution monochromators,
iii) low-noise detectors
iv) crystal analyzers, and
v) the third generation synchrotrons

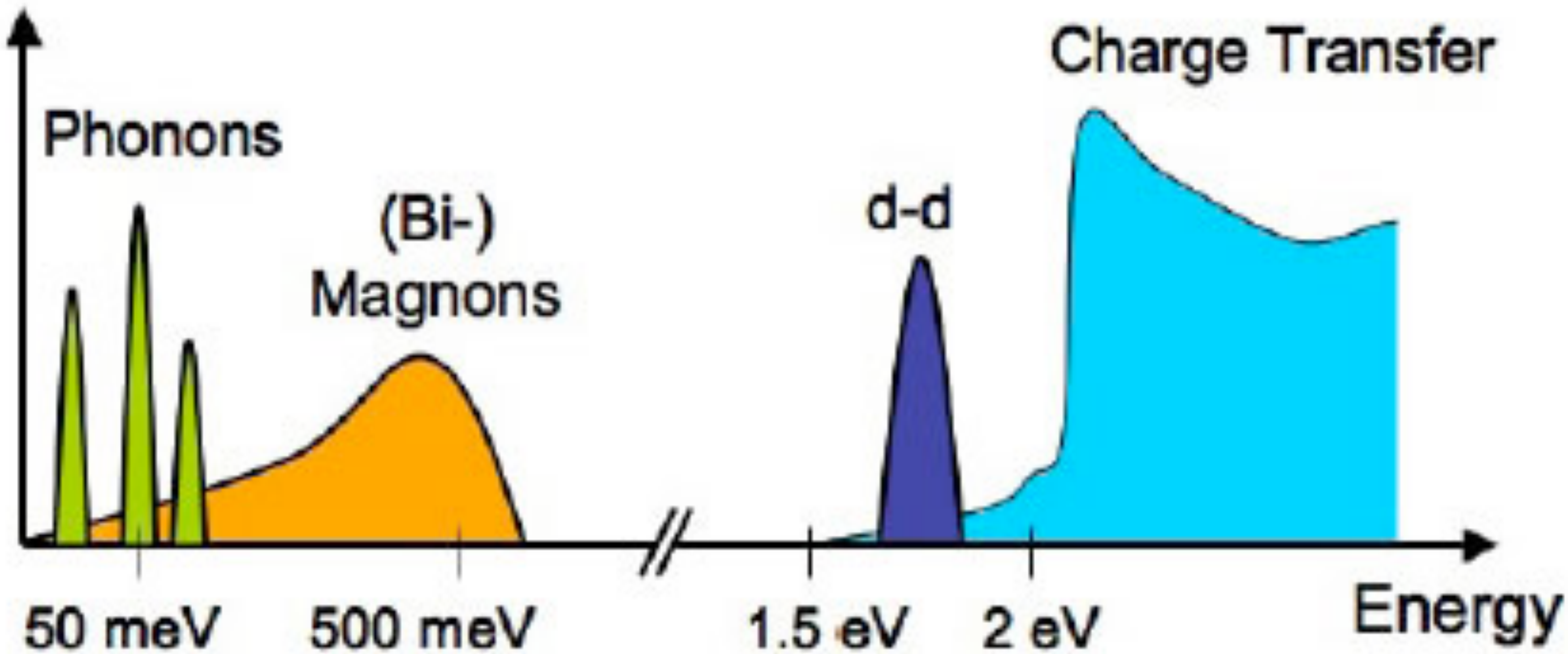
1990-present: More than a dozen new instruments around the world



Compton
X-Ray Raman
IUV
Visible Raman
Nuclear Resonant Inelastic Scattering
IXS
Neutron
Visible Brillouin
Nuclear Resonant Forward Scattering
XPCS
Energy Transfer (eV)
Momentum Transfer (nm-1)
10^6
10^4
10^2
10^0
10^-2
10^-4
10^-6
10^-8
10^-10
10^-12
10^-14
10^-3
10^-2
10^-1
10^0
10^1
10^2
10^3



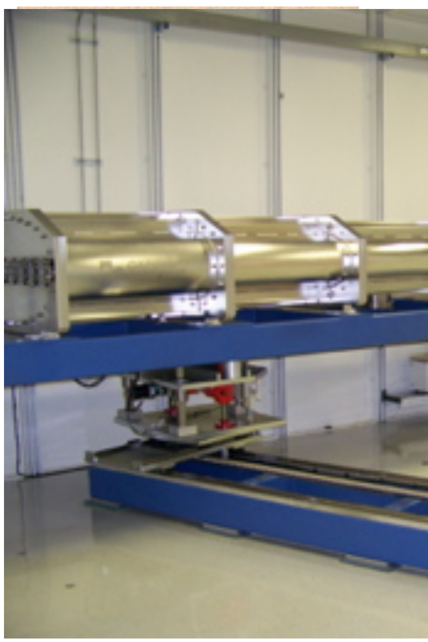
Courtesy: Y. Sakurai, Spring-8

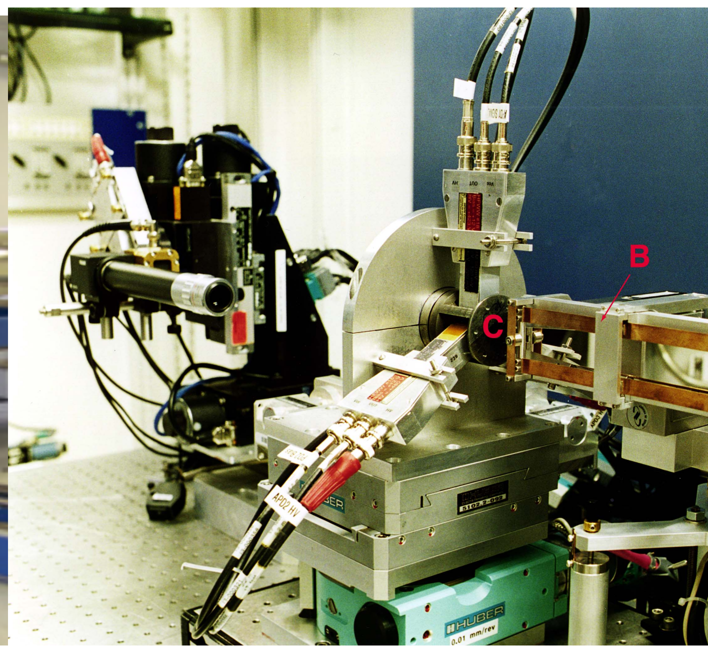

Charge Transfer
Phonons
(Bi-)
Magnons
d-d
50 meV
500 meV
1.5 eV
2 eV
Energy

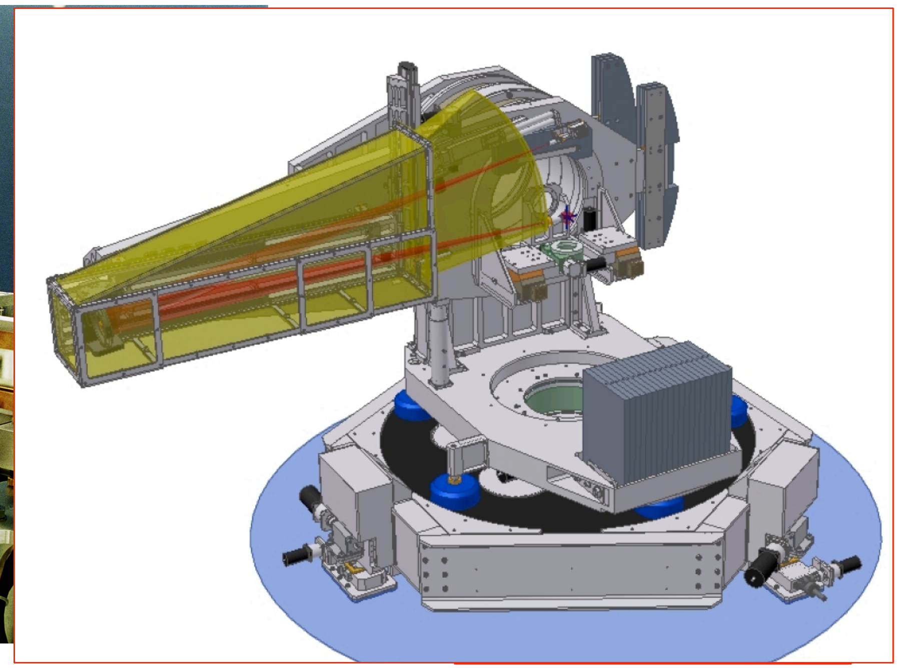
Inelastic X-Ray Scattering: A plethora of different techniques

IXS

- **Non-Resonant**
  - **ΔE ~ keV** Compton
  - **ΔE ~ meV** IXS
- **Resonant** — X-Ray Raman, X-Ray Emission
  - **ΔE ~ neV-meV** NRS
  - **ΔE ~ 100 meV** RIXS



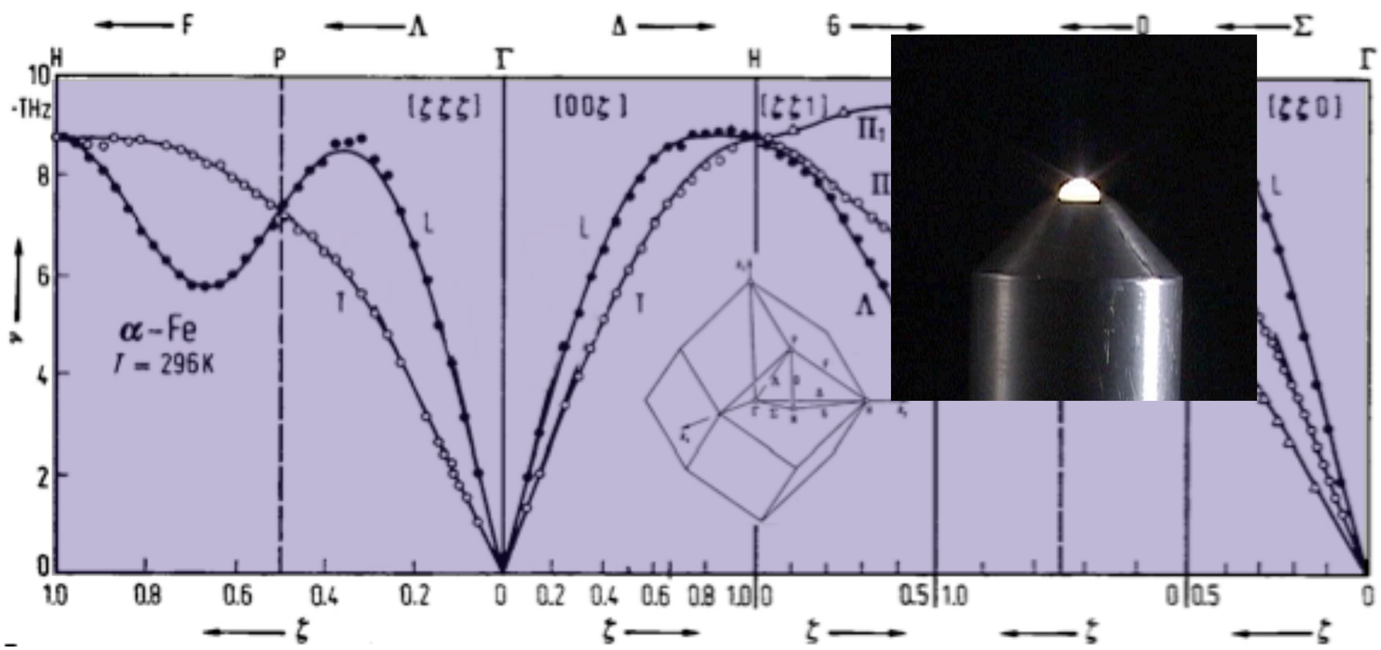


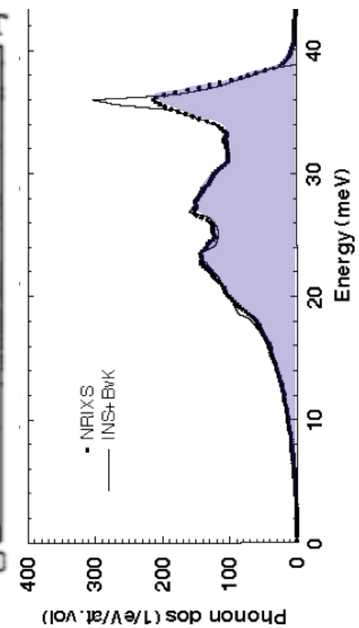


Inelastic X-Ray Scattering: A plethora of different techniques

IXS

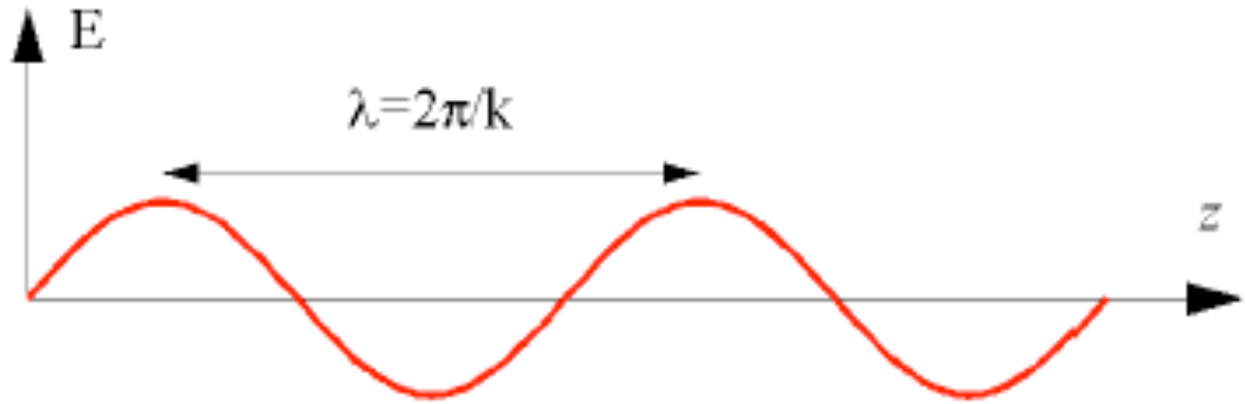
- **Non-Resonant**
  - **ΔE ~ meV**
    IXS
- **Resonant**
  - **ΔE ~ 1 meV**
    Nuclear resonant



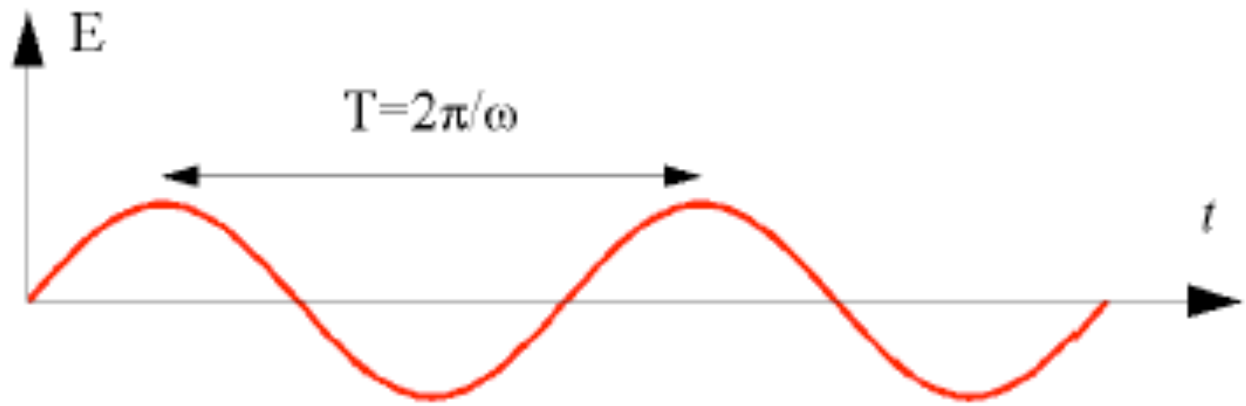


Electromagnetic waves

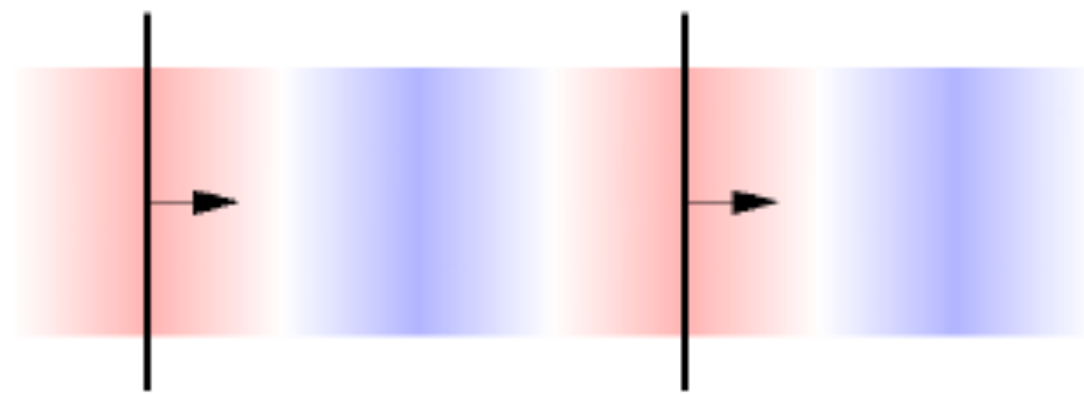
Spatial variation
k= wave number
λ=wavelength



Temporal variation
ω = angular frequency



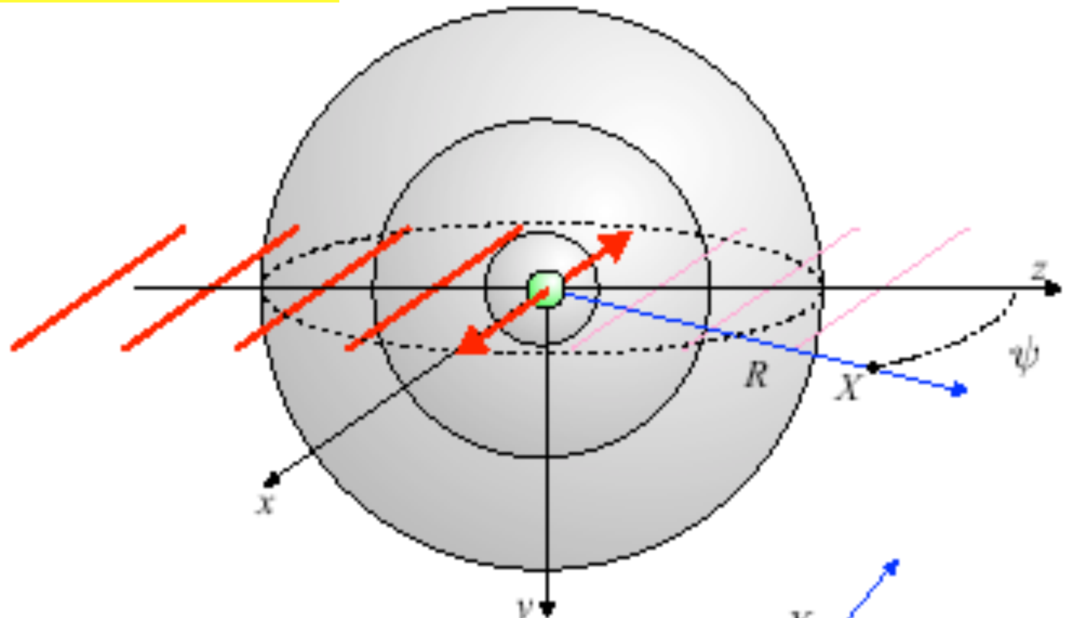
Top view showing high and low field amplitudes



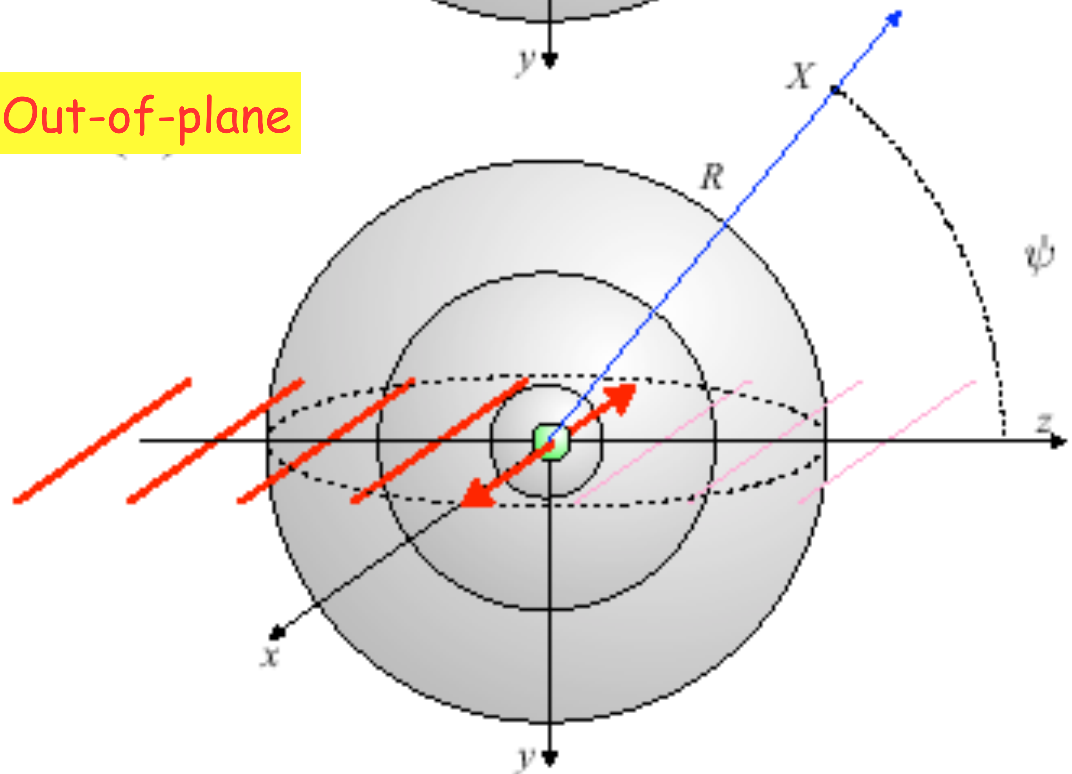
Classical description of scattering of radiation by a charged particle

The incident plane wave incident upon an electron sets the electron in oscillation. The oscillating electron then radiates, experiencing a phase shift of π.

In-plane



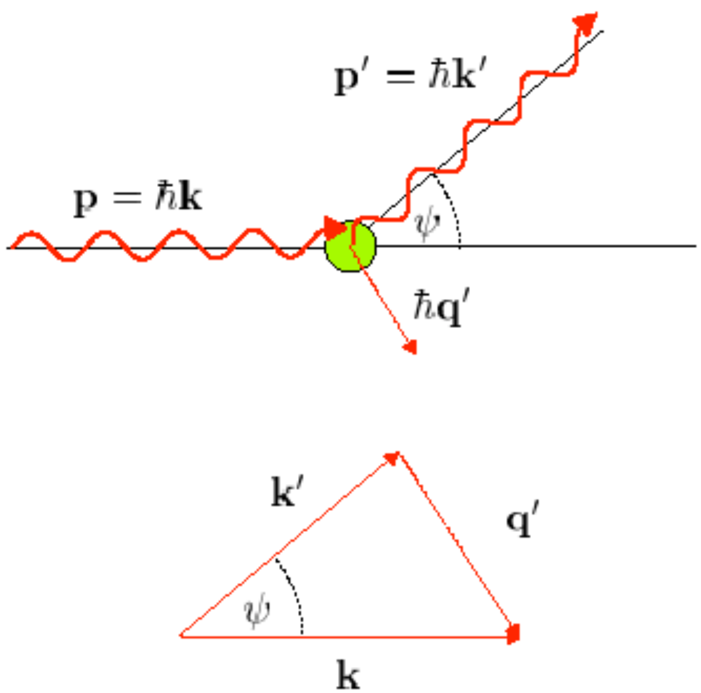
Out-of-plane



First order Born approximation

For weakly scattering media, it is possible to obtain solution to the integral equation by a perturbation approach, provided that the scattering medium is weakly interaction with the probe of x-rays.

The first order Born approximation states that amplitude of the scattered wave far away from the scatterer depends entirely on one and only one Fourier component of the scattering potential, namely the one that corresponds to the transferred momentum $K=k(s-s_0)$.



Conservation of momentum has a correspondence between classical and quantum mechanical treatment:

$$p = \hbar k$$

$$\Delta p = p - p' = \hbar k'$$

If a plane wave is incident on the scatterer in the direction of s, the Fourier component of the scattering potential can be determined.

And if one has the ability to vary the amount of momentum transfer at will, then, the scattering potential can be reconstructed.

This is the essence of x-ray scattering experiments.

What is being measured ?

$$\frac{d^2\sigma}{d\Omega\, d\omega} = r_0^2 \frac{\omega_f}{\omega_i} \left| \mathbf{e}_i \cdot \mathbf{e}_f \right| N \sum_{i,f} \left| \langle i | \sum e^{i\mathbf{Q}\mathbf{r}_j} | f \rangle \right|^2 \delta(E_f - E_i - \hbar\omega)$$

Thomson cross section

Dynamical structure factor S(Q,w)

$$S(\mathbf{Q},\omega) = \frac{1}{2\pi} \int dt\, e^{-i\omega t} \langle \phi_i | \sum_{ll'} f_l(\mathbf{Q}) e^{-i\mathbf{Q}\cdot\mathbf{r}_l(t)} f_{l'}(\mathbf{Q}) e^{i\mathbf{Q}\cdot\mathbf{r}_{l'}(0)} | \phi_i \rangle$$

Density-density correlations

$$f(Q) = f_{ion}(Q) + f_{valence}(Q)$$

Atomic form factor

$$S(Q,\omega) = \sum_{q,j} \left| \sum_{s} f_s(Q) \frac{\hbar}{\sqrt{2m_s}} e^{-W_s} e^{i\vec{Q}\cdot\vec{R}_s} \left[\vec{Q}\cdot\vec{e}(q,s,j) \right] \right|^2 \frac{\left(\frac{1}{e^{\hbar\omega/kT}-1} + \frac{1}{2} \pm \frac{1}{2} \right)}{\omega_{q,j}} \delta\left(\omega \pm \omega_{q,j}\right)$$

Dynamic structure factor

Sum over phonon branch j at reduced momentum transfer, q

Sum over different atoms in the unit cell

Atomic form factor for each atom

scaling with square root of mass

Debye-Waller factor to account for bond strength

phonon occupation probability

Phase of the scattering amplitude

phonon frequency

Polarization factor between momentum transfer and photon's electric field

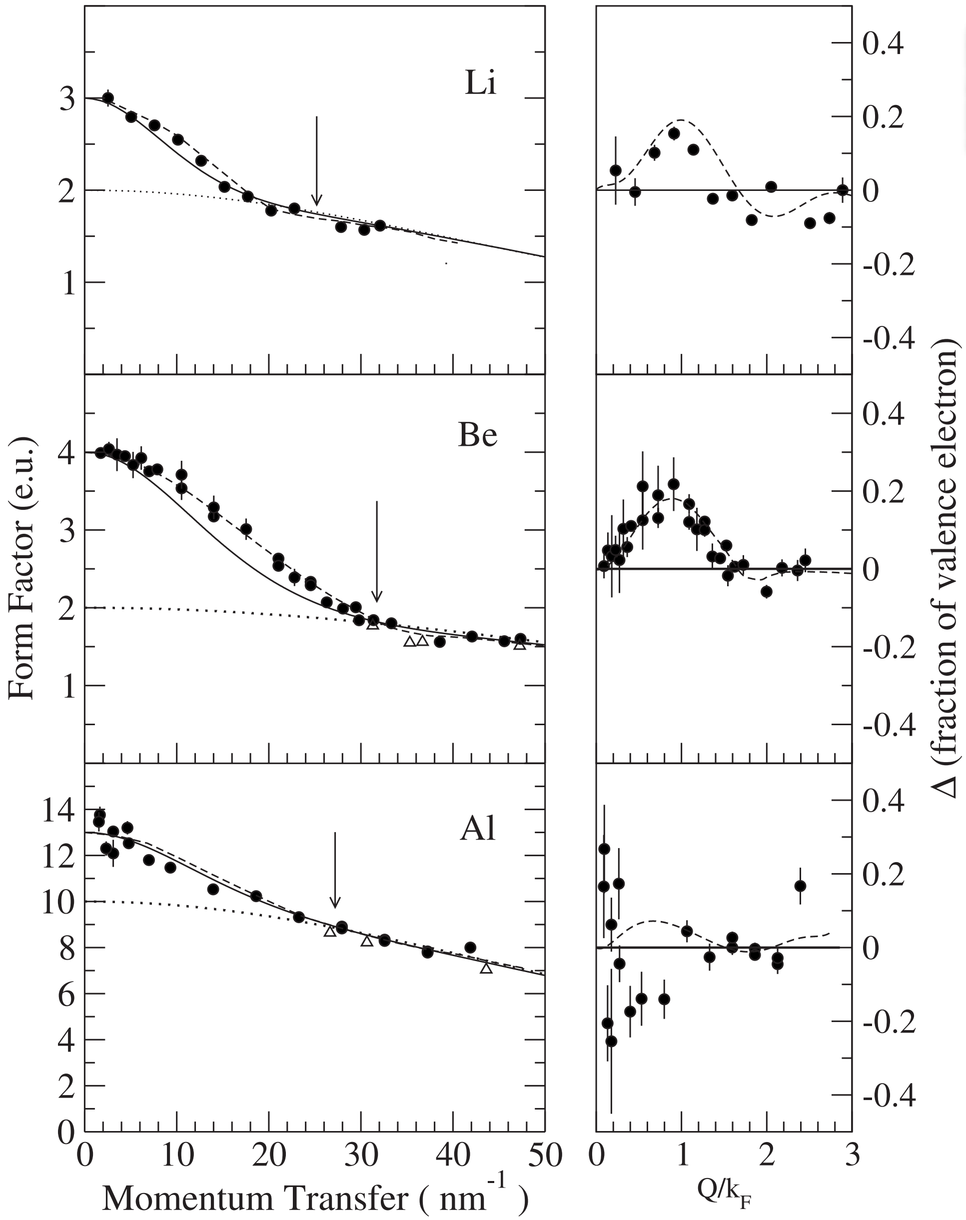
delta-function in ω

PHYSICAL REVIEW B **77**, 064301 (2008)

Atomic form-factor measurements in the low-momentum transfer region for Li, Be, and Al by inelastic x-ray scattering

A. Alatas,[1,*] A. H. Said,[1,2] H. Sinn,[1] G. Bortel,[1,†] M. Y. Hu,[1,‡] J. Zhao,[1] C. A. Burns,[2] E. Burkel,[3] and E. E. Alp[1]

$$f(Q) = f_{ion}(Q) + f_{valence}(Q)$$



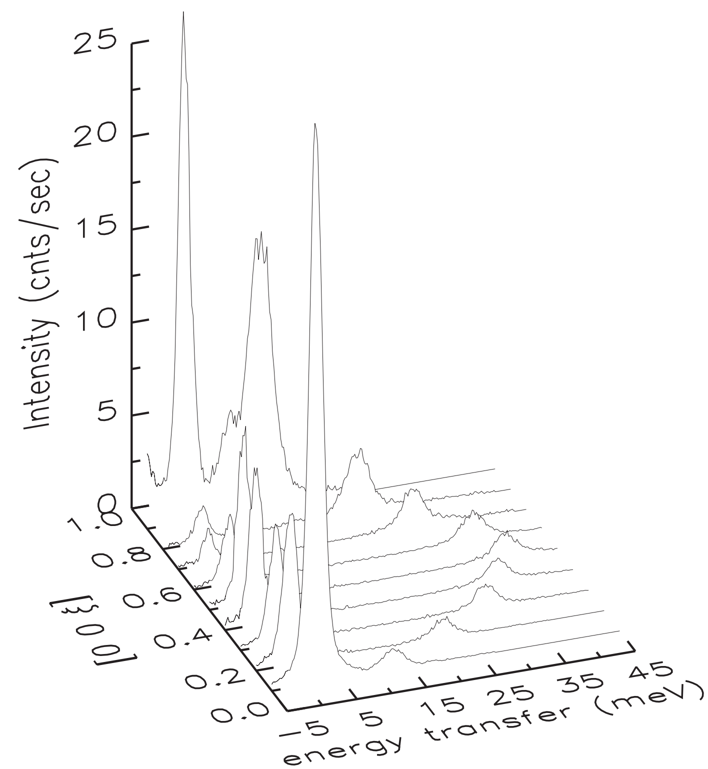


FIG. 2. Energy scans for lithium along the [0 ζ ζ] direction for longitudinal modes.

Scattering geometry and physics

The physical origin of the correlations depend on how 1/**q** compares with the characteristic length, l_c , of the system, which is related to spatial inhomogeneity (due to thermal or concentrations fluctuations)

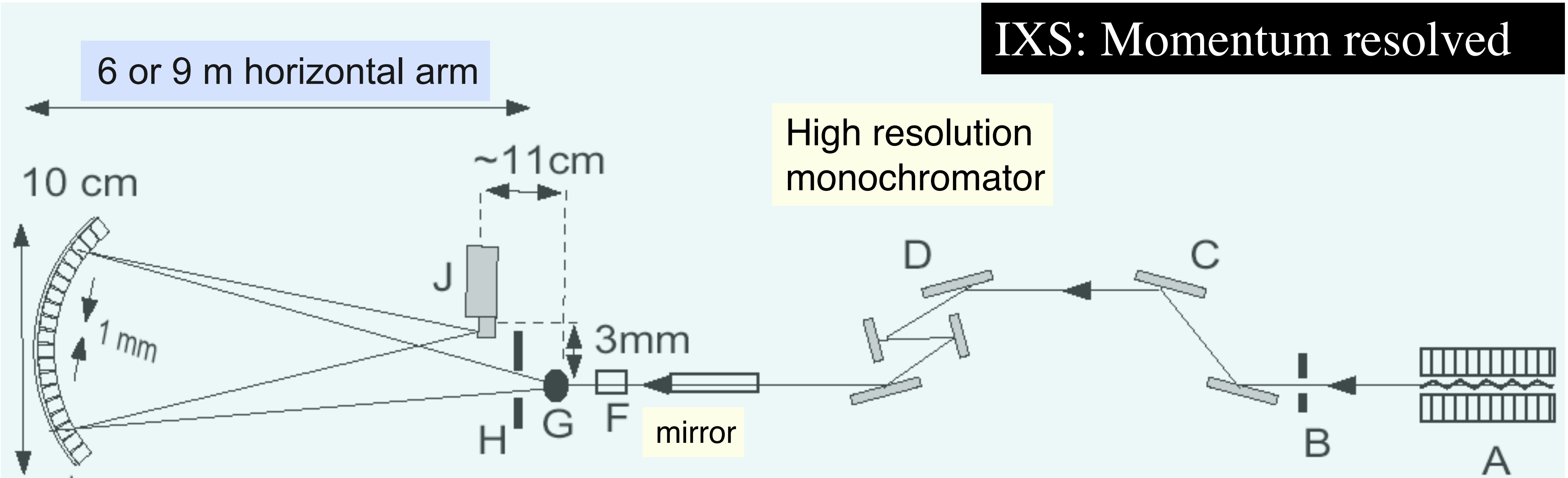
$$\text{when } \mathbf{q}\cdot l_c << 1 \Rightarrow \text{ Collective excitations}$$

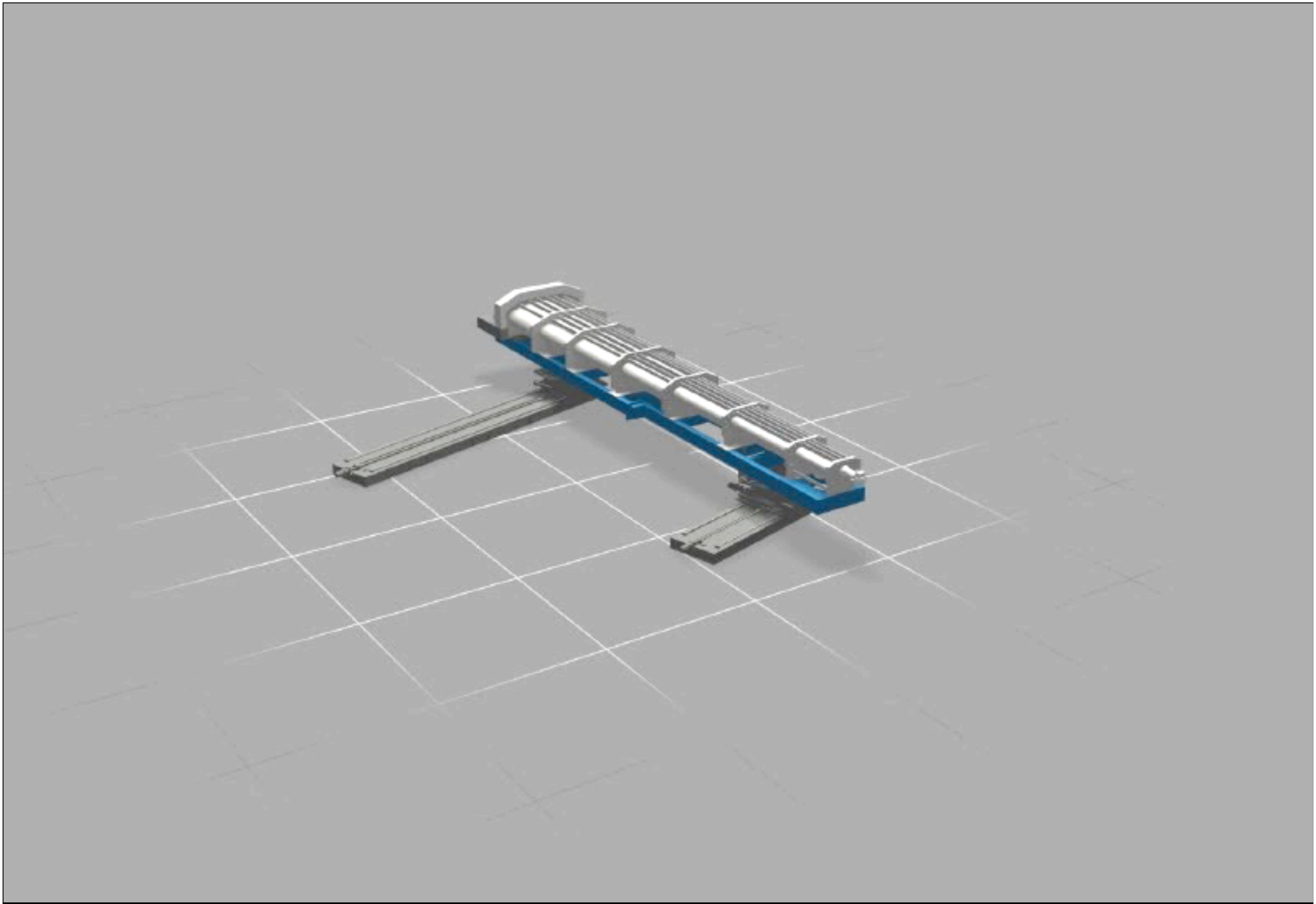
$$\text{when } \mathbf{q}\cdot l_c >> 1 \Rightarrow \text{ Single particle excitations}$$

$$\text{when } \frac{1}{\mathbf{q}} \approx d \;\; and \;\; \omega \approx \text{phonon frequency} \Rightarrow \text{ Collective ion excitations (PHONON)}$$

$$\text{when } \frac{1}{\mathbf{q}} \approx r_c \;\; and \;\; \omega \approx \text{plasma frequency} \Rightarrow \text{ Valence electron excitations}$$

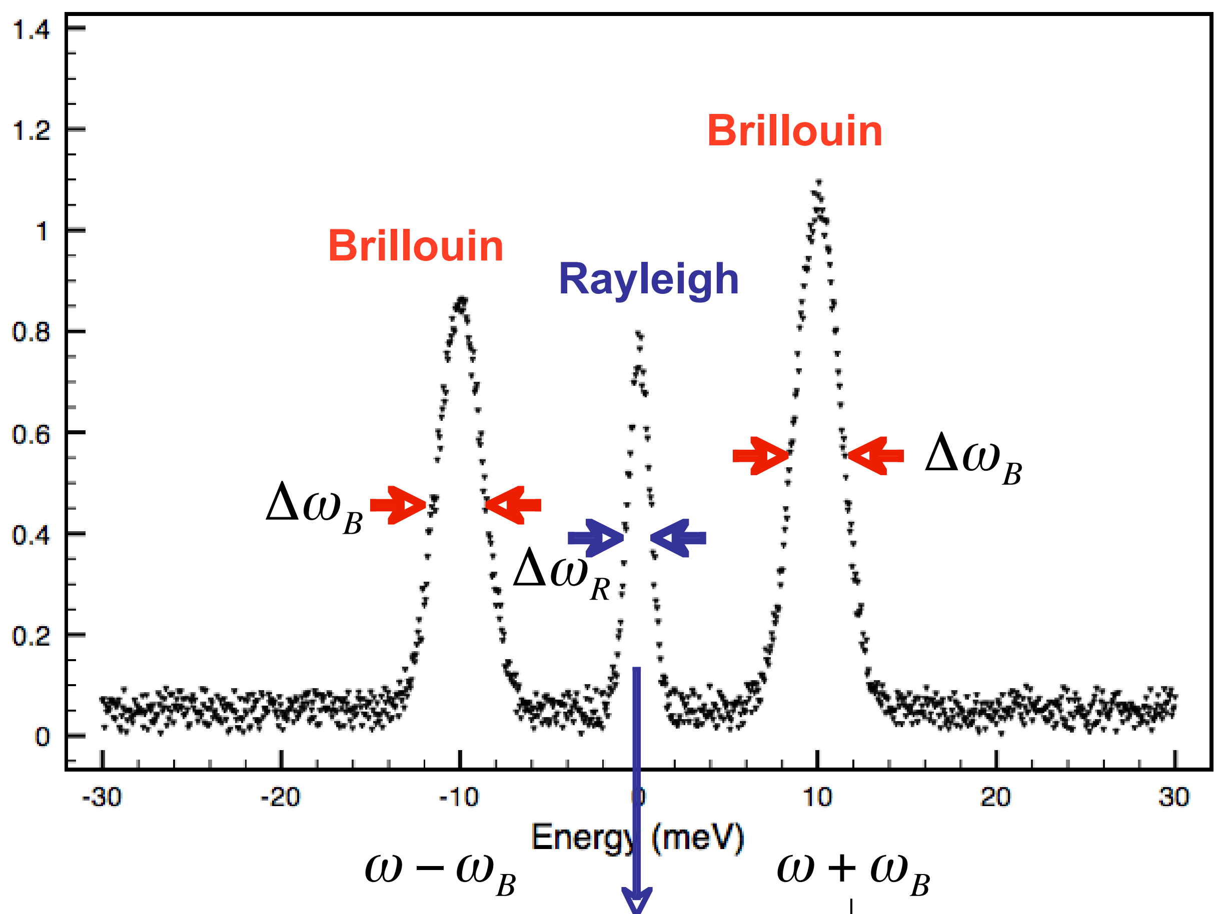
High-resolution inelastic x-ray scattering (IXS) at Sector 3 and Sector 30





30-ID-C: HERIX Spectrometer

30-ID-C: HERIX Spectrometer



Entropy fluctuations, $\Delta\omega_R \sim \alpha q^2$

Concentration fluctuations $\Delta\omega_R \sim Dq^2$

Pressure fluctuations

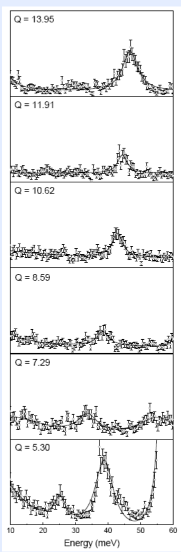
$$\omega_B(q) = V \cdot q$$

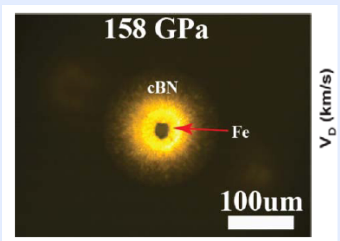
$$\Delta\omega_B \sim Vq^2$$

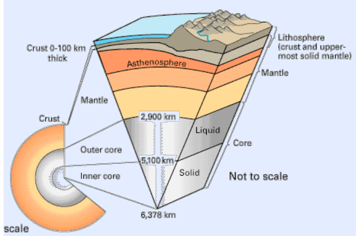
High Energy Resolution Inelastic X-ray Scattering

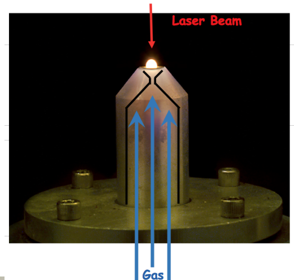
APS-U will provide two enhanced HERIX spectrometers optimized for high-pressure and high-resolution work at HERIX-3-ID and HERIX-30-ID, respectively.

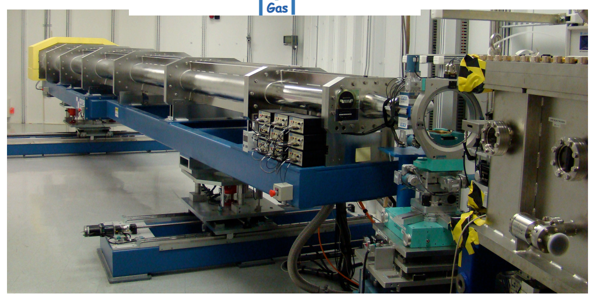
High-pressure/high-temperature setup
The goal: 2 Mbar, 2000 K

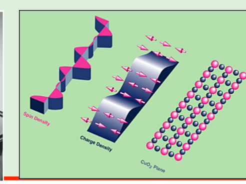


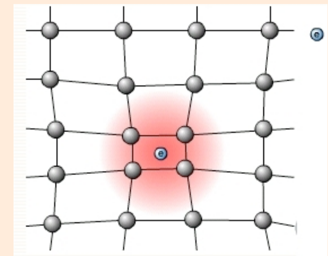


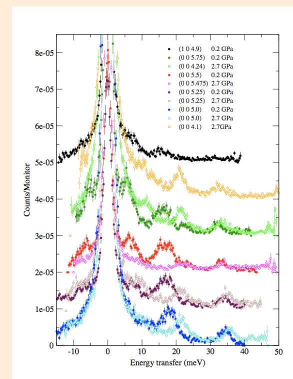












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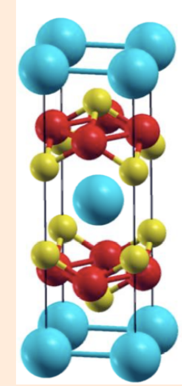


Mineral physics and earth sciences
Sound velocity, elastic constants

Dynamics of liquids and liquid crystals stripe or nematic phases

Role of phonons in pnictide superconductors

$\phi\omega\nu\acute{\eta}$ (phonē), *sound*

- Phonons are periodic oscillations in condensed systems.

- They are inherently involved in thermal and electrical conductivity.

- They can show anomalous (non-linear) behavior near a phase transition.

- They can carry sound (acoustic modes) or couple to electromagnetic radiation or neutrons (acoustical and optical).

- Have energy of $\hbar\omega$ as quanta of excitation of the lattice vibration mode of angular frequency ω. Since momentum, $\hbar k$, is exact, they are delocalized, collective excitations.

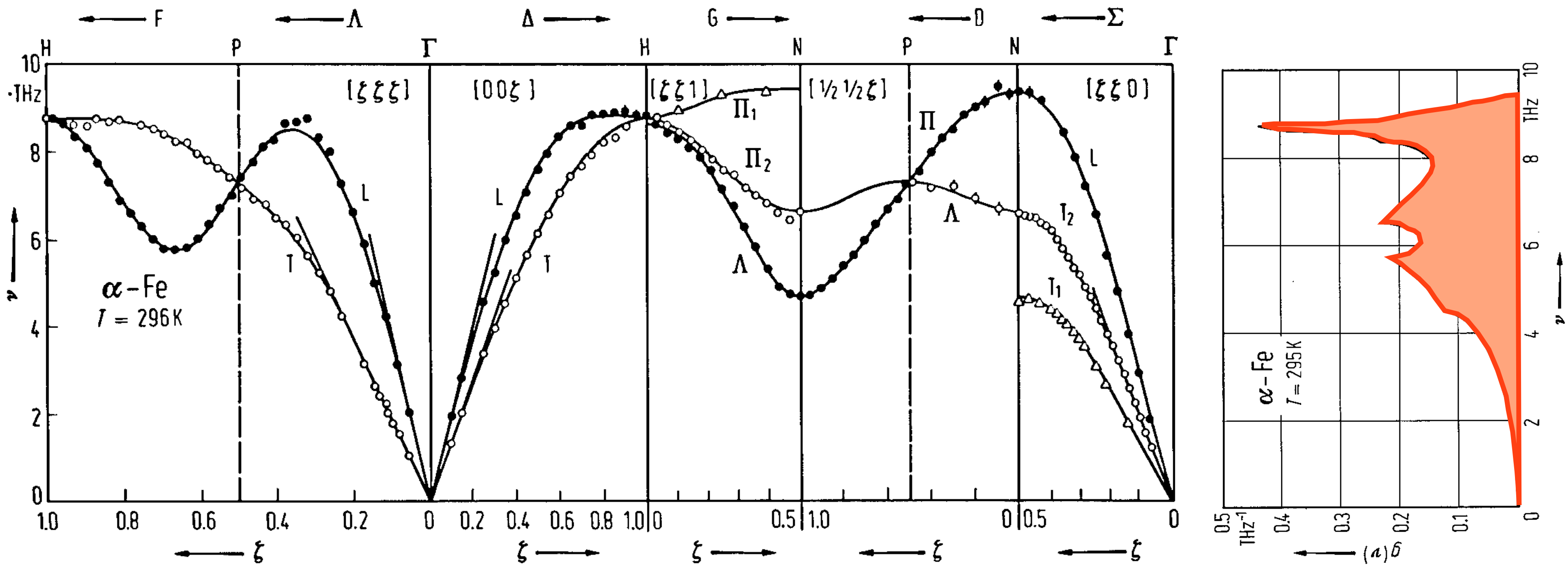
- Phonons are bosons, and they are not conserved. They can be created or annihilated during interactions with neutrons or photons.

- They can be detected by Brillouin scattering (acoustic), Raman scattering, FTIR (optical).

- Their dispersion throughout the BZ can ONLY be monitored with x-rays (IXS), or neutrons (INS).

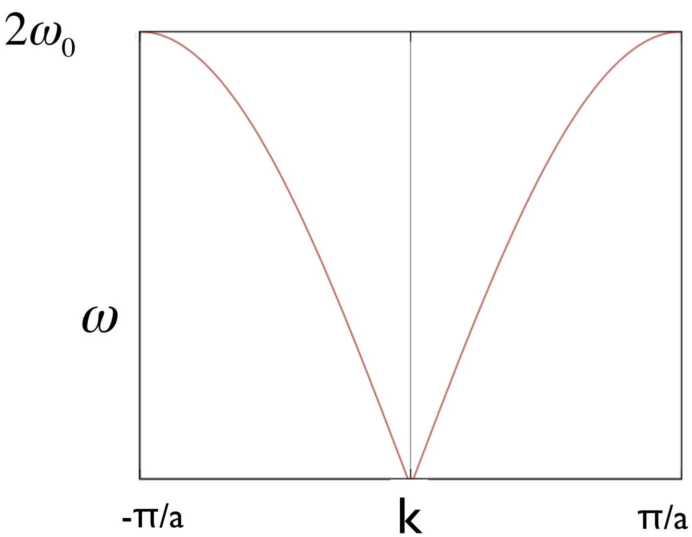
- Accurate prediction of phonon dispersion require correct knowledge about the force constants: COMPUTATIONAL TECHNIQUES ARE ESSENTIAL.

Dispersion relations and phonon density of states
α -iron (bcc)



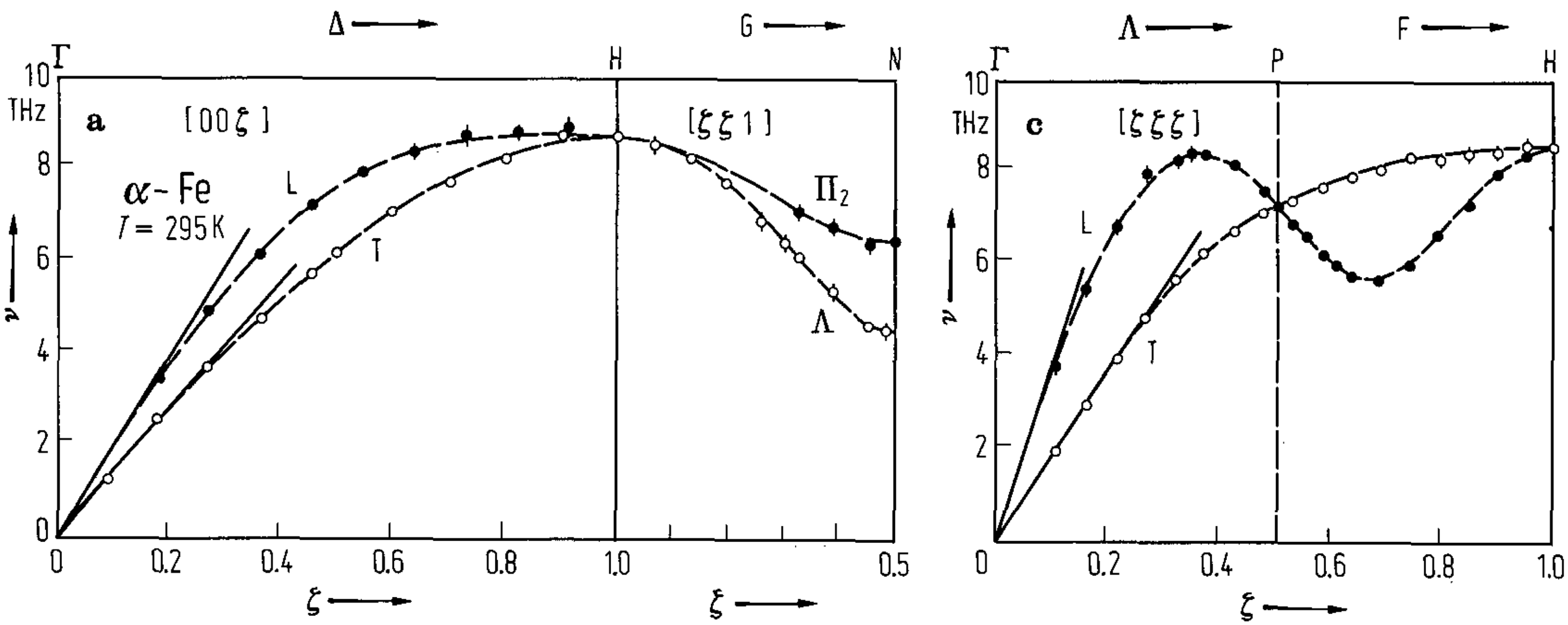
V. J. Minkiewicz, G. Shirane, and R. Nathans, Phys. Rev. 162 (1967) 528, and
Landolt-Börnstein, New Series, Group III, Vol 13, Eds. K.-H Hellwege, and J. L. Olsen, Springer Verlag, Berlin (1981) p. 53-56.

Dispersion relations



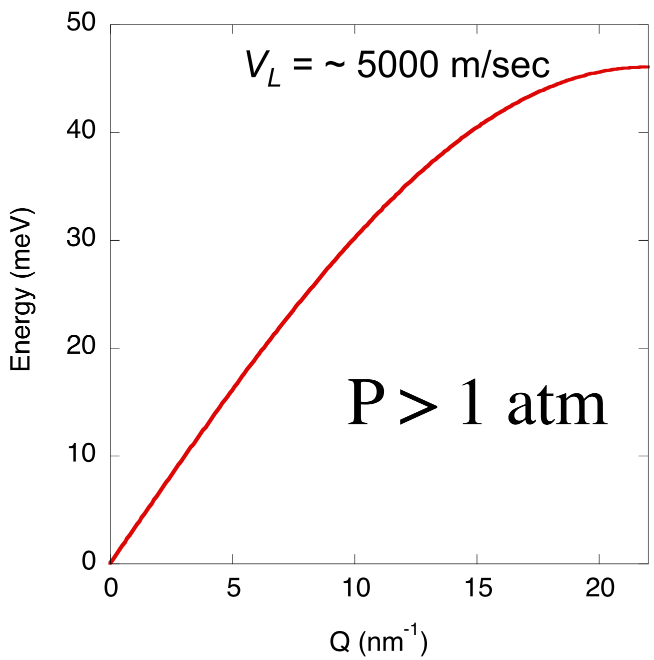
$$\omega(k) = 2\omega\left(\sin\left|ka/2\right|\right)$$

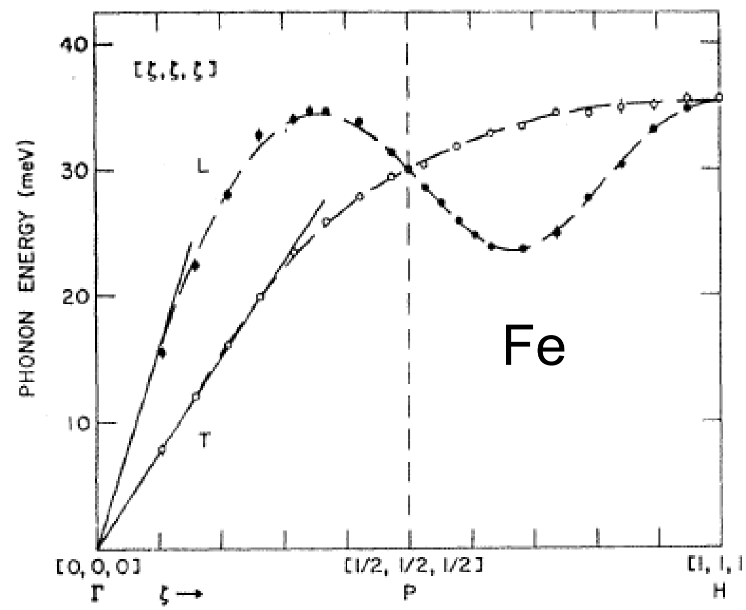
$$\frac{\partial \omega_k}{\partial k}$$: sound velocity



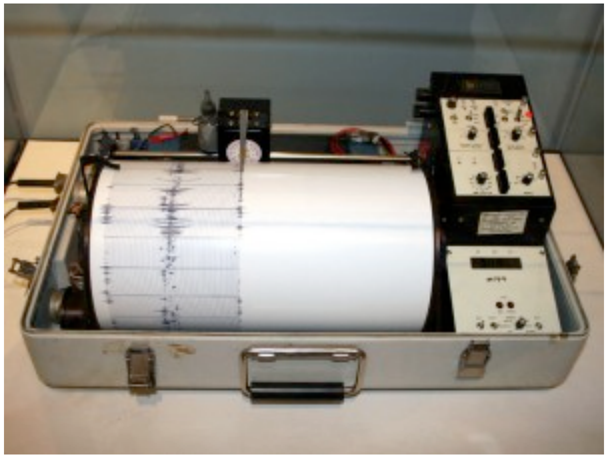
$$E = \frac{2\hbar}{\pi} V_L Q_{\max} \sin\left(\frac{\pi}{2}\frac{Q}{Q_{\max}}\right)$$

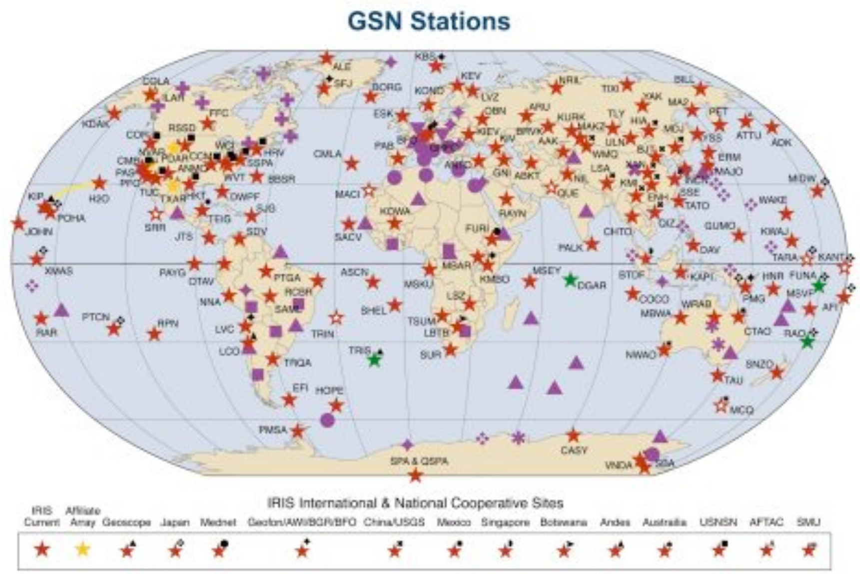
$$E(meV) = 4.192 \cdot 10^{-4} \cdot V_L(\text{m/sec}) Q_{\max}(\text{nm}^{-1}) \cdot \sin\left(\frac{\pi}{2}\frac{Q}{Q_{\max}}\right)$$

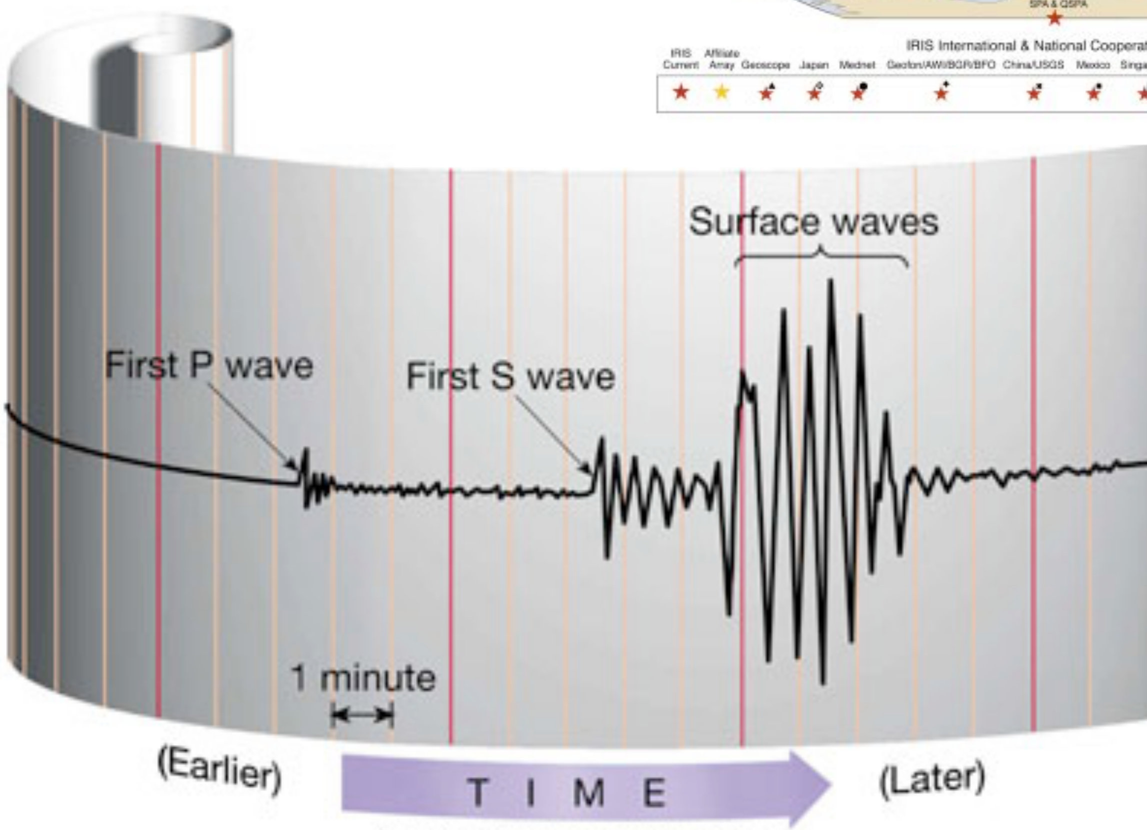




Seismic waves







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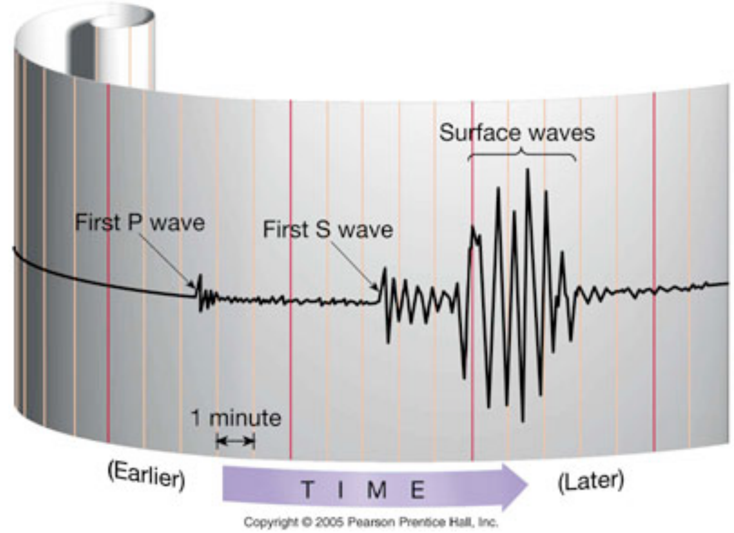
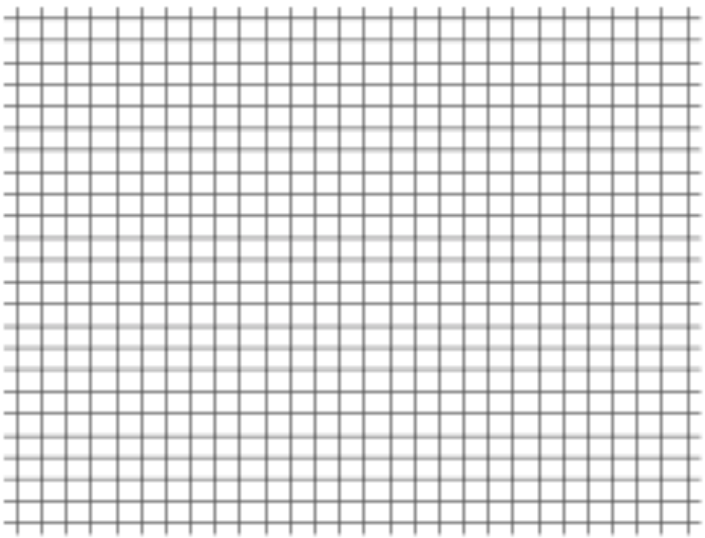
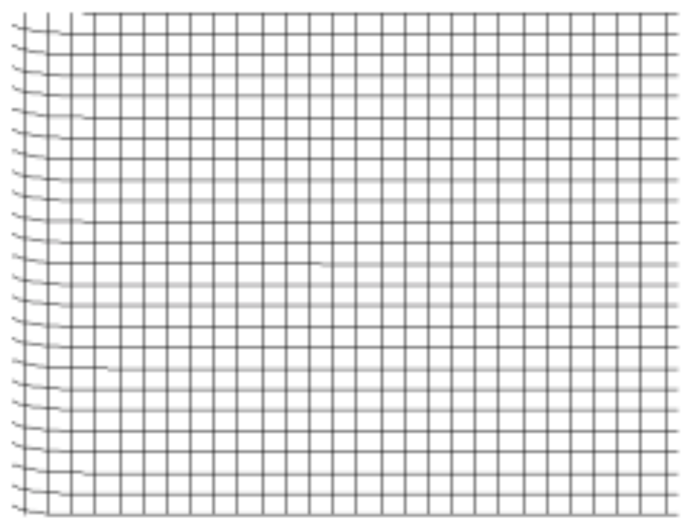
Seismic waves

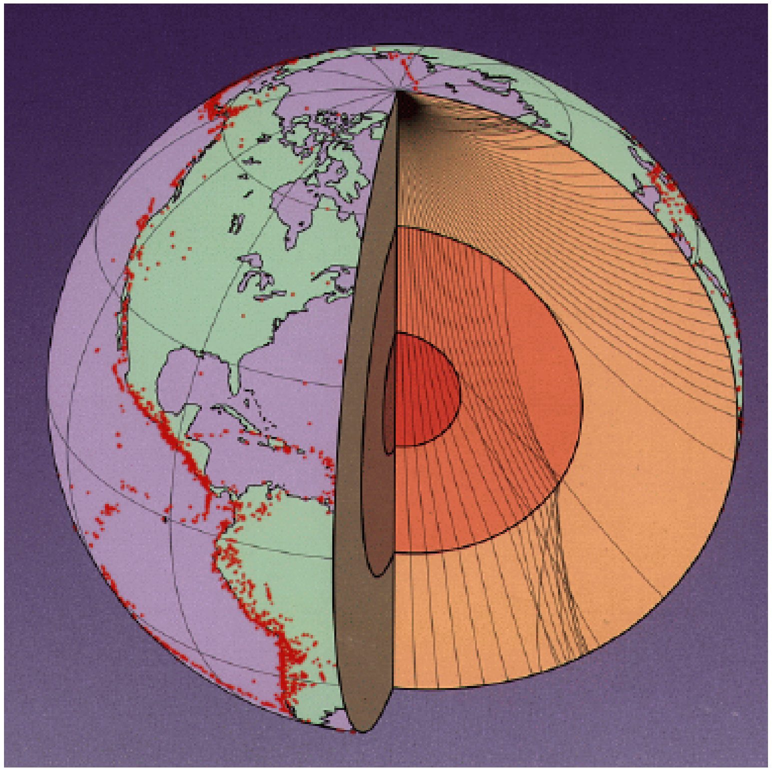


Longitudinal --> Compression --> Primary: V_P

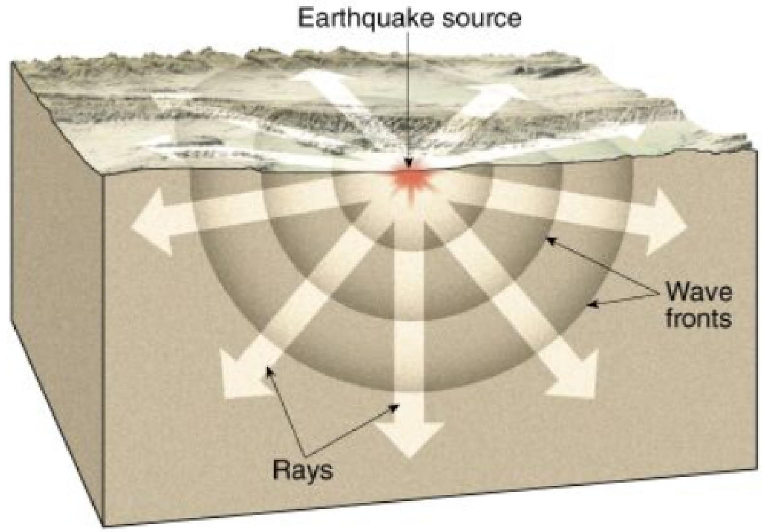


Transverse --> Shear --> Secondary: V_S





SEISMOLOGY

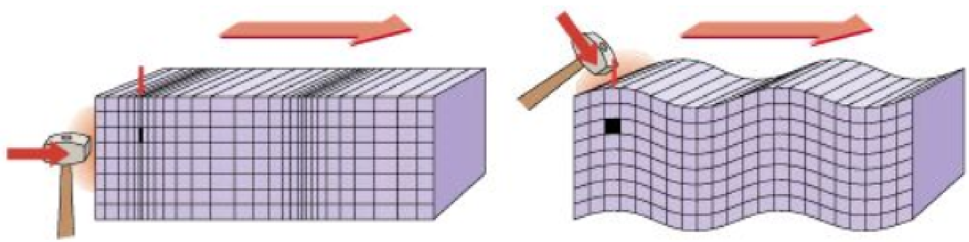


- Later, an S wave shadow zone was recognized, meaning no S waves were received at seismographs stations from 104° to 180° from an earthquake; the S wave shadow zone is caused by the outer core, which is liquid iron/nickel.

P Waves

S-Waves

Pressure or Primary Waves

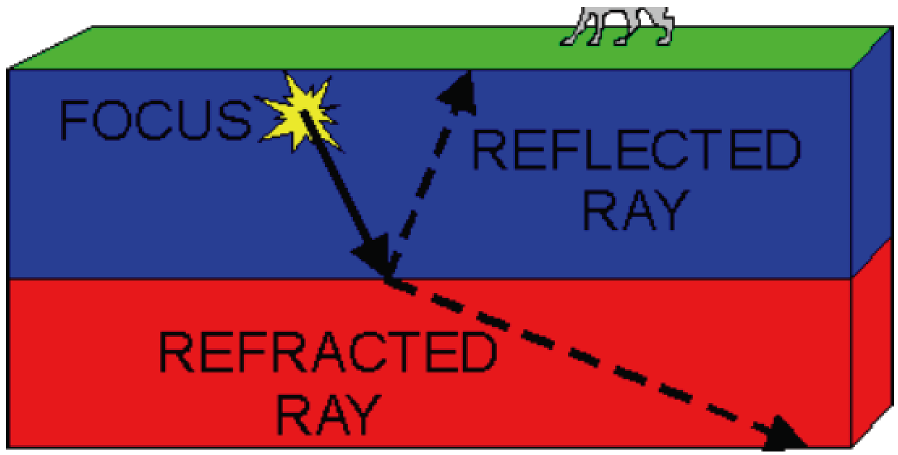


Shear or Secondary Waves

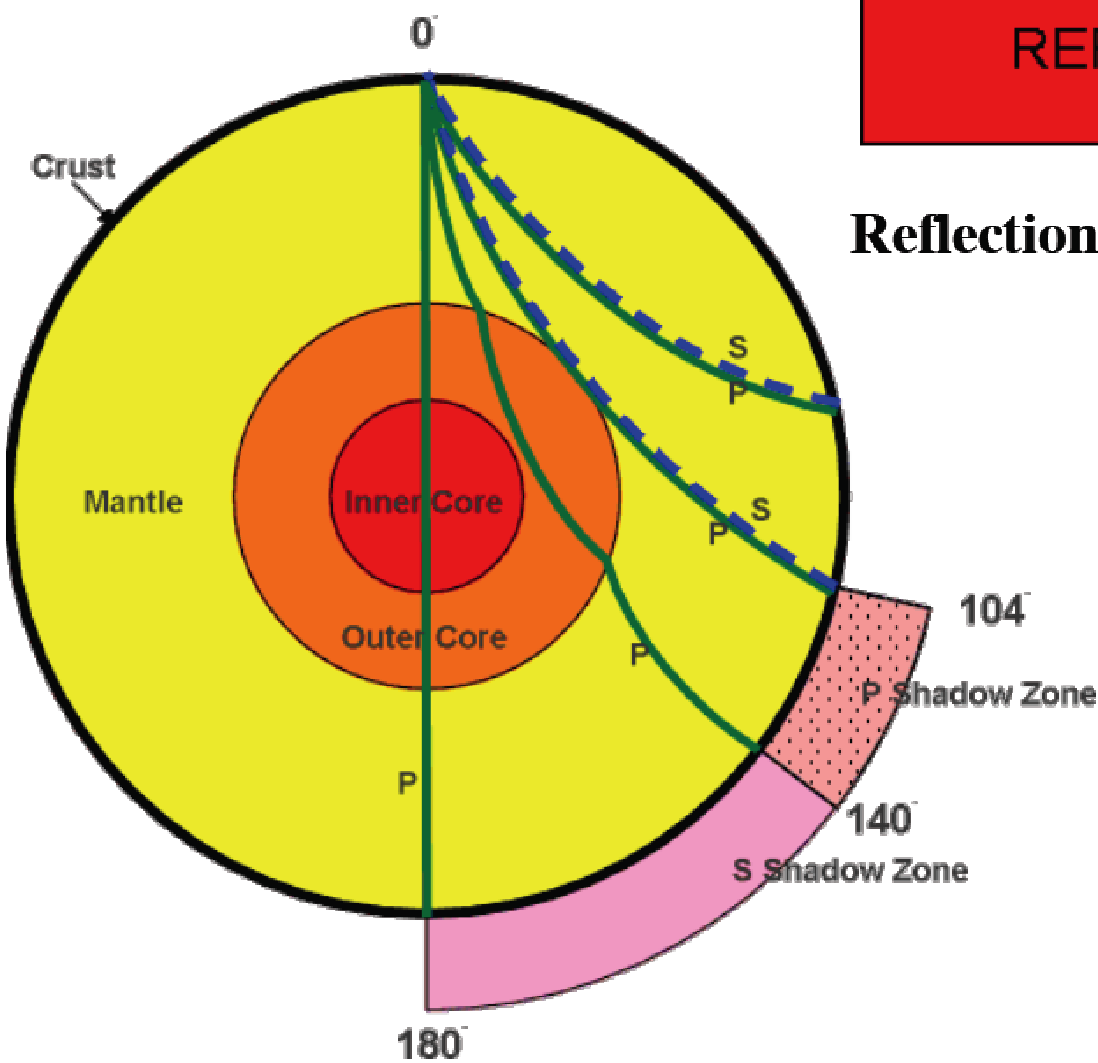
$$V_P = \alpha = \sqrt{\frac{\lambda + 2\mu}{\rho}} = \sqrt{\frac{\frac{4}{3}K + \mu}{\rho}}$$

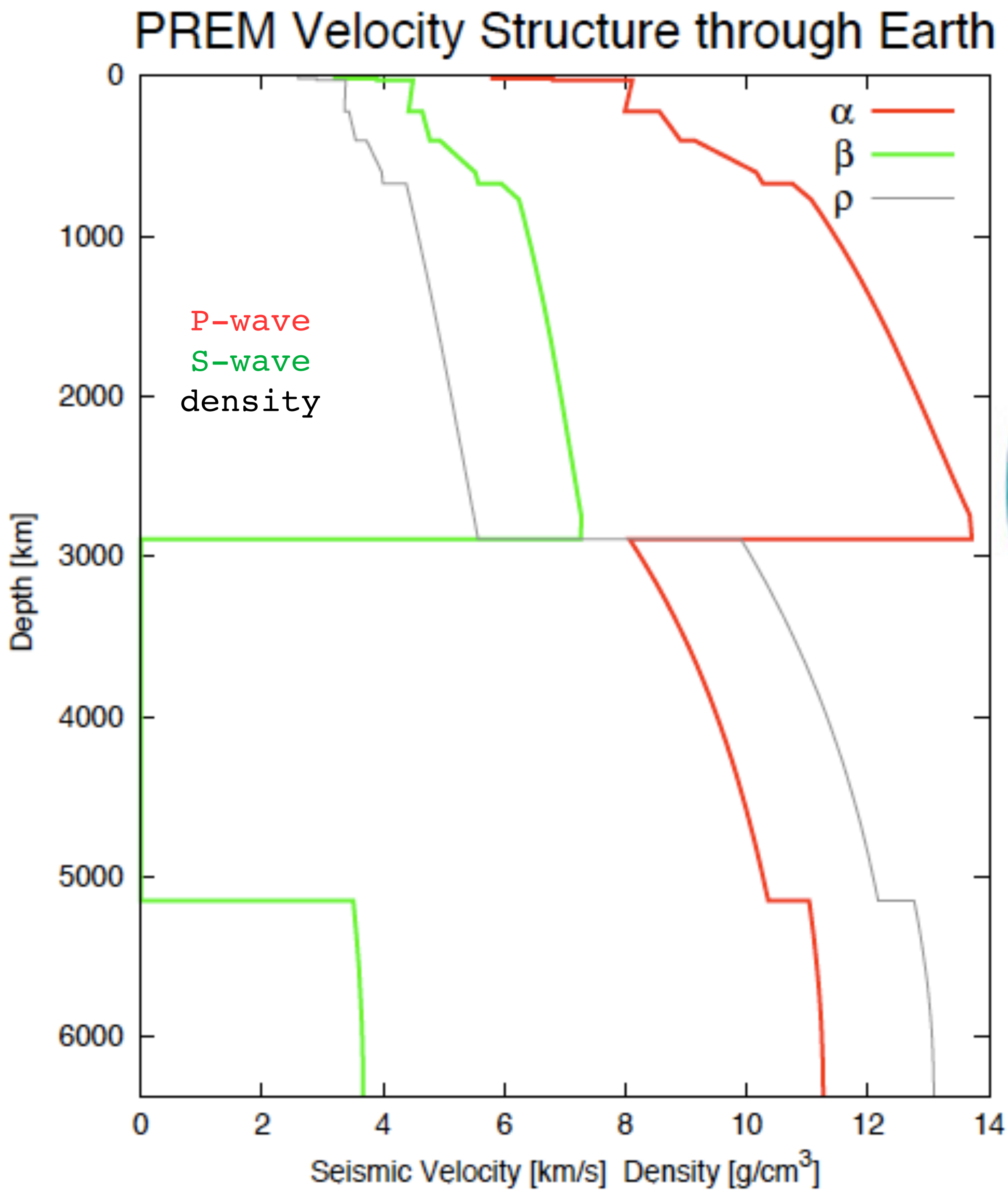
$$V_S = \beta = \sqrt{\frac{\mu}{\rho}}$$

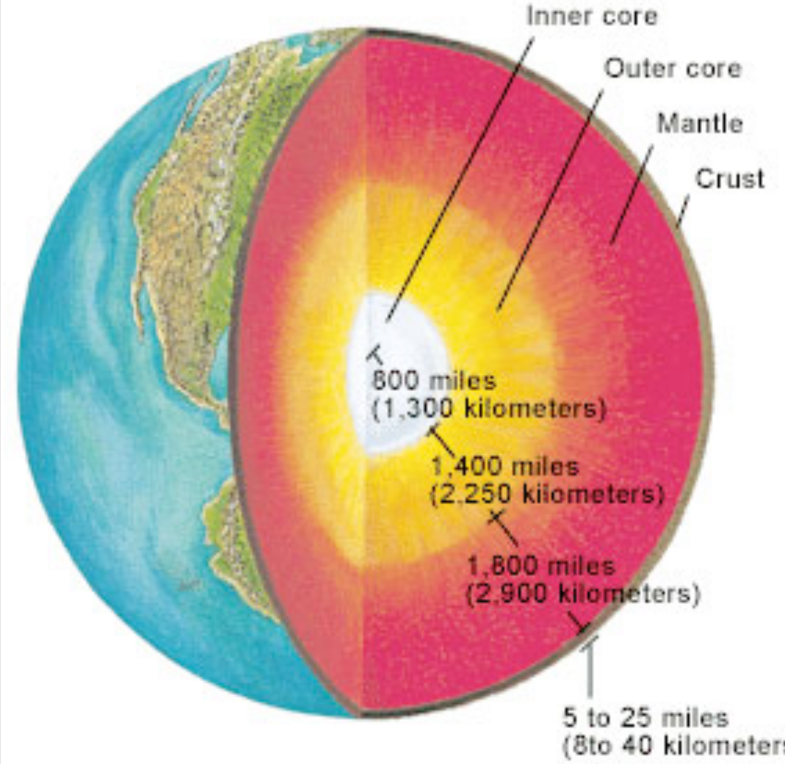
Lamé's constants

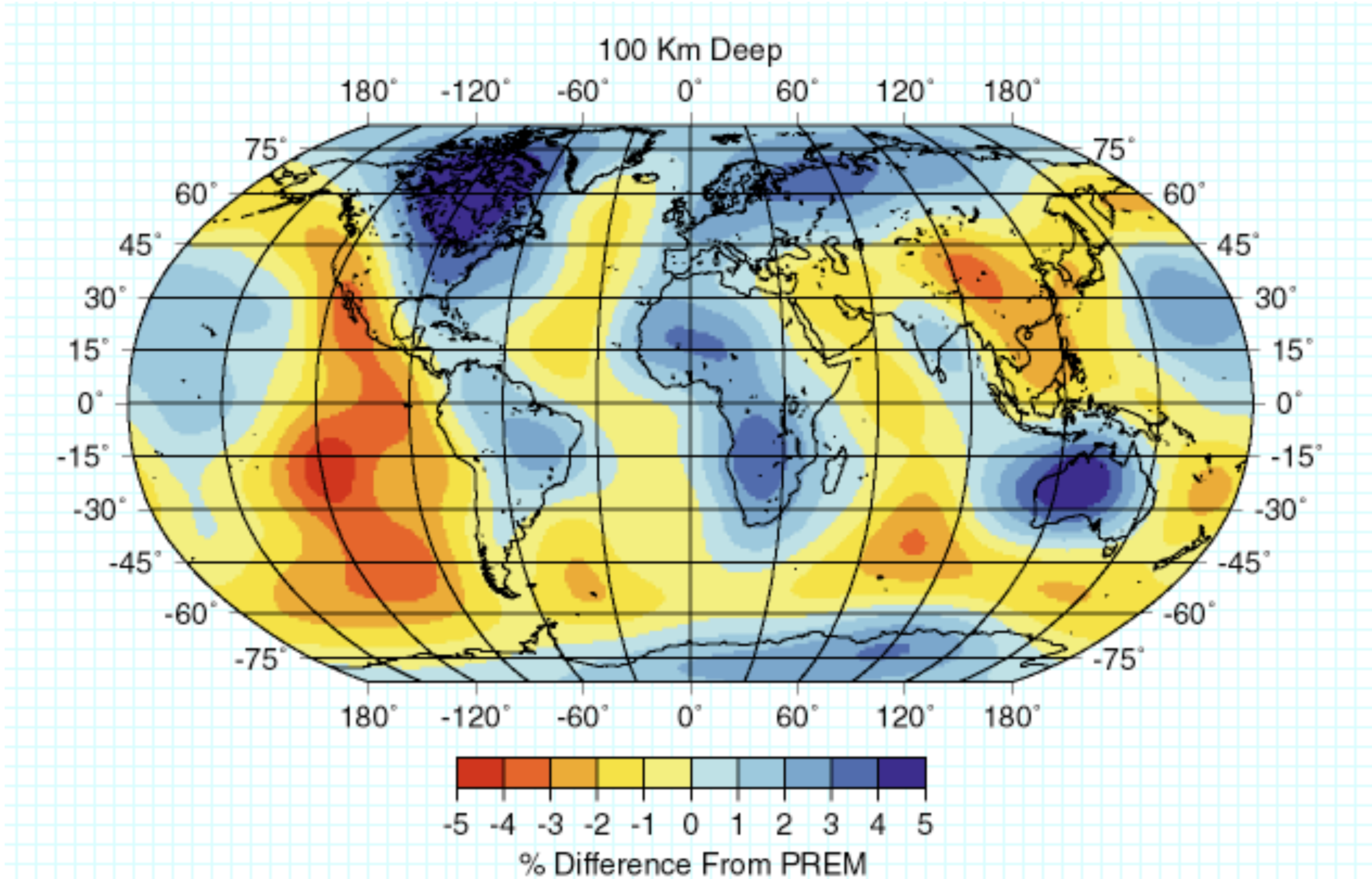


Reflections, Refractions, Snell's Law



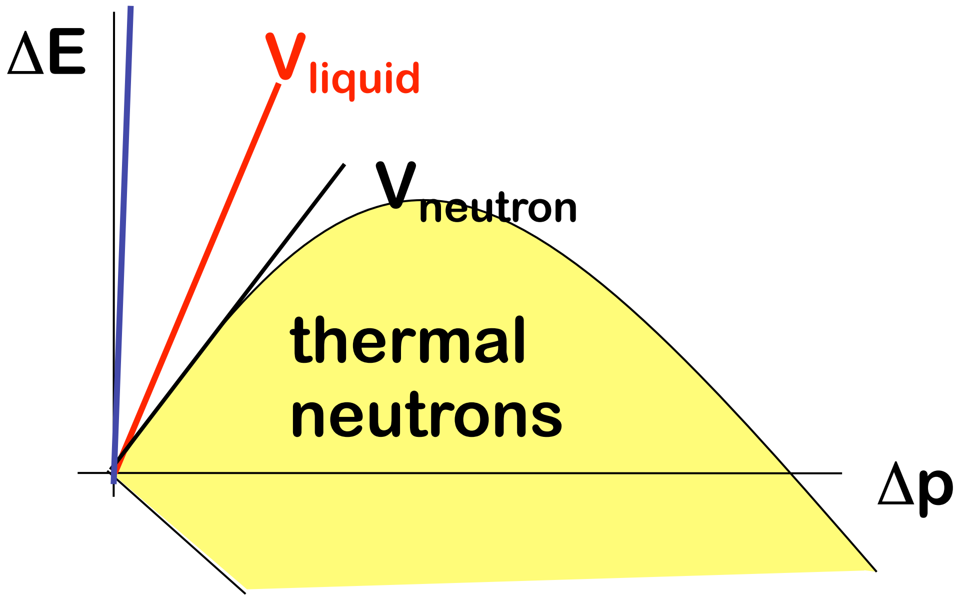

PREM Velocity Structure through Earth
α
β
ρ
P-wave
S-wave
density
Depth [km]
0
1000
2000
3000
4000
5000
6000
0
2
4
6
8
10
12
14
Seismic Velocity [km/s] Density [g/cm3]


Inner core
Outer core
Mantle
Crust
800 miles
(1,300 kilometers)
1,400 miles
(2,250 kilometers)
1,800 miles
(2,900 kilometers)
5 to 25 miles
(8to 40 kilometers



Map of the variations in seismic shear-wave speed with respect to the value in PREM at 100 km depth. The warm colors (red, orange, and yellow) show regions with slower than normal speeds, the darker regions are faster than normal.
(Model S12 WM13, from W.-J. Su, Journal of Geophysical Research, vol. 99(4) 4945-4980, 1994).

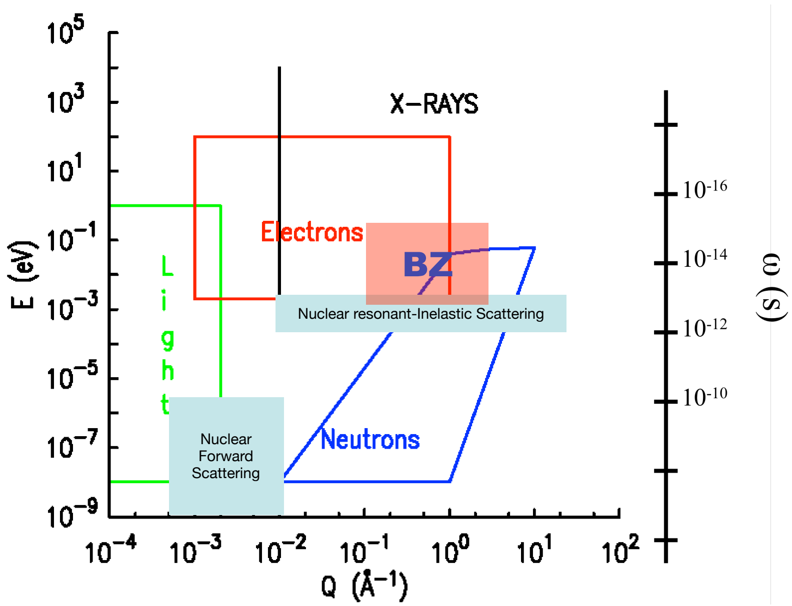
Why x-rays instead of neutrons or visible light ?

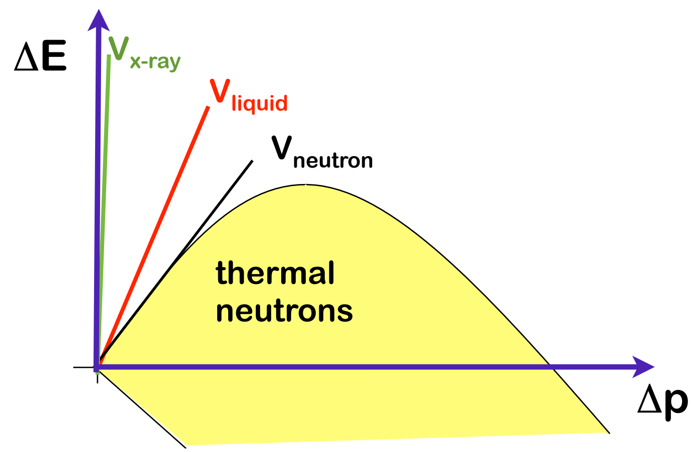


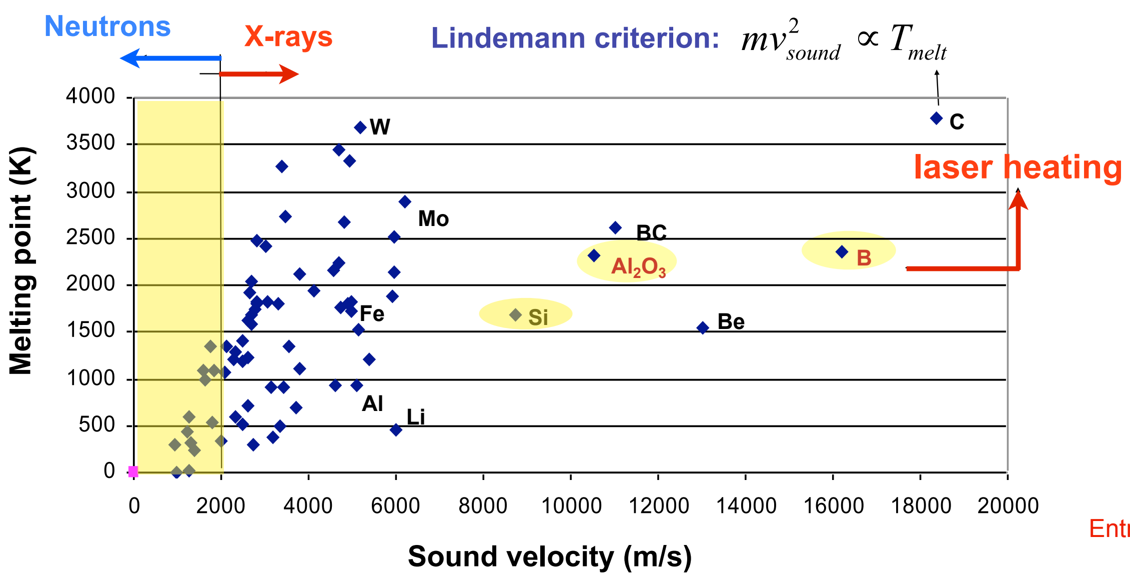
Limited momentum transfer capability of neutrons at low energies favor x-rays to study collective excitations with large dispersion, like sound modes.

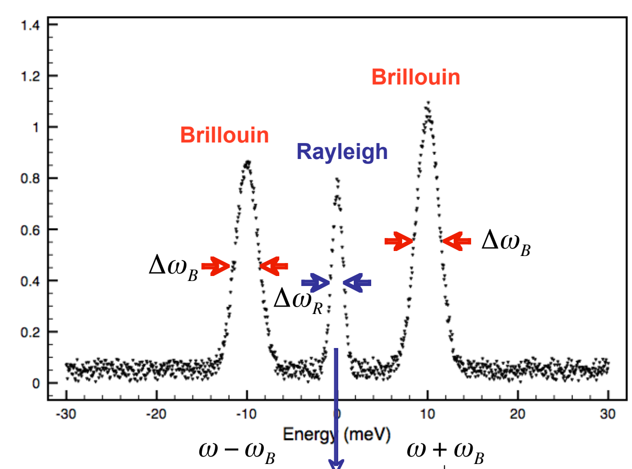
When the sound velocity exceeds that of neutrons in the liquid, x-rays become unique. The low-momentum/high-energy transfer region is only accessible by x-rays.

Why X-Rays ?









Pressure fluctuations

$$\omega_B(q) = V \cdot q$$

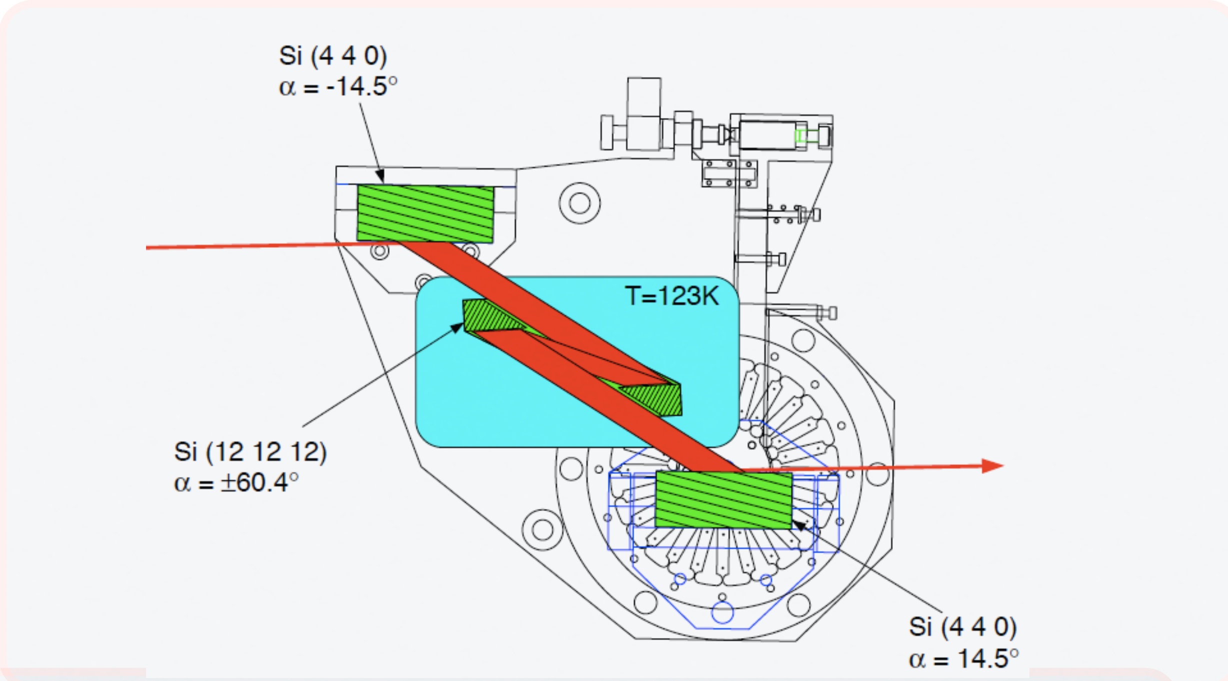
$$\Delta\omega_B \sim Vq^2$$

Entropy fluctuations, $\Delta\omega_R \sim \alpha q^2$

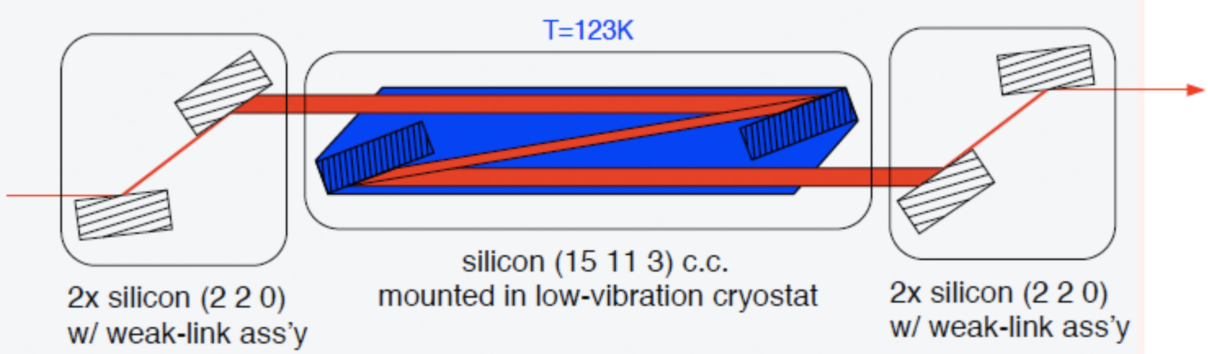
Concentration fluctuations $\Delta\omega_R \sim Dq^2$

Methodology developments

Cryo-cooled monochromators



^{119}Sn @ 14.4 keV
∂E = 1.3 meV

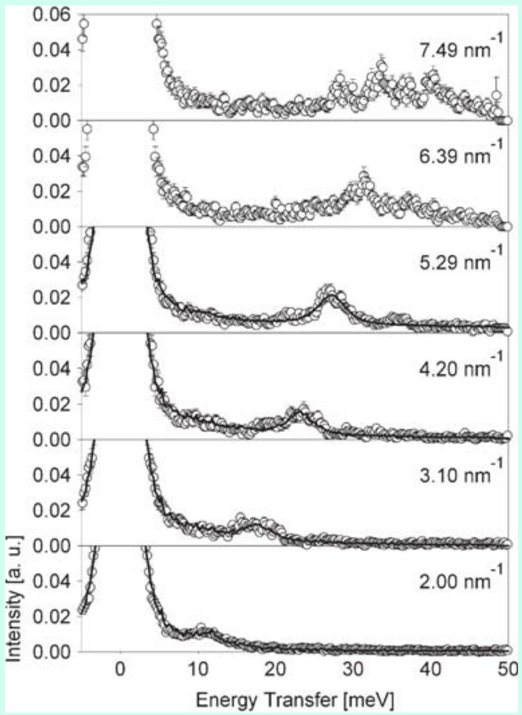


^{151}Eu @ 21.5 keV
∂E = 1.4 meV

Thomas Toellner, Deming Shu, APS

Acoustic phonons in chrysotile asbestos, $Mg_3Si_2O_5(OH)_4$

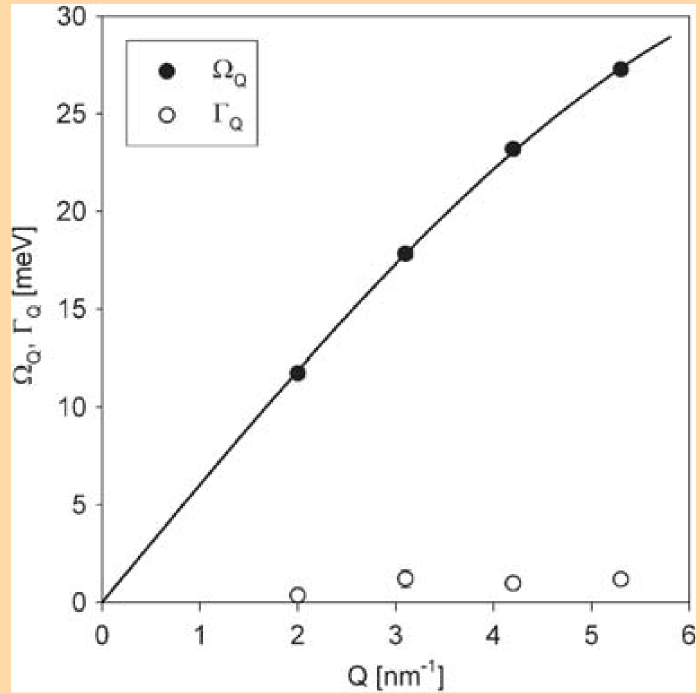
Damped harmonic oscillator model



$$S(\hbar\omega)=\frac{1}{1-e^{-\hbar\omega/kT}}\left[I_c\frac{1}{\pi}\frac{\Gamma_c}{(\hbar\omega)^2+\Gamma_c^{\ 2}}+I_Q\frac{1}{\pi}\frac{4\Gamma_Q\left(\hbar\omega_Q\right)(\hbar\omega)}{\left((\hbar\omega)^2-\Omega_Q^2\right)^2+4\Gamma_Q^{\ 2}(\hbar\omega)}\right]$$

$$\Omega_Q=\left[\left(\hbar\omega_Q\right)^2+\Gamma_Q^{\ 2}\right]^{1/2}$$

Longitudinal sound velocity

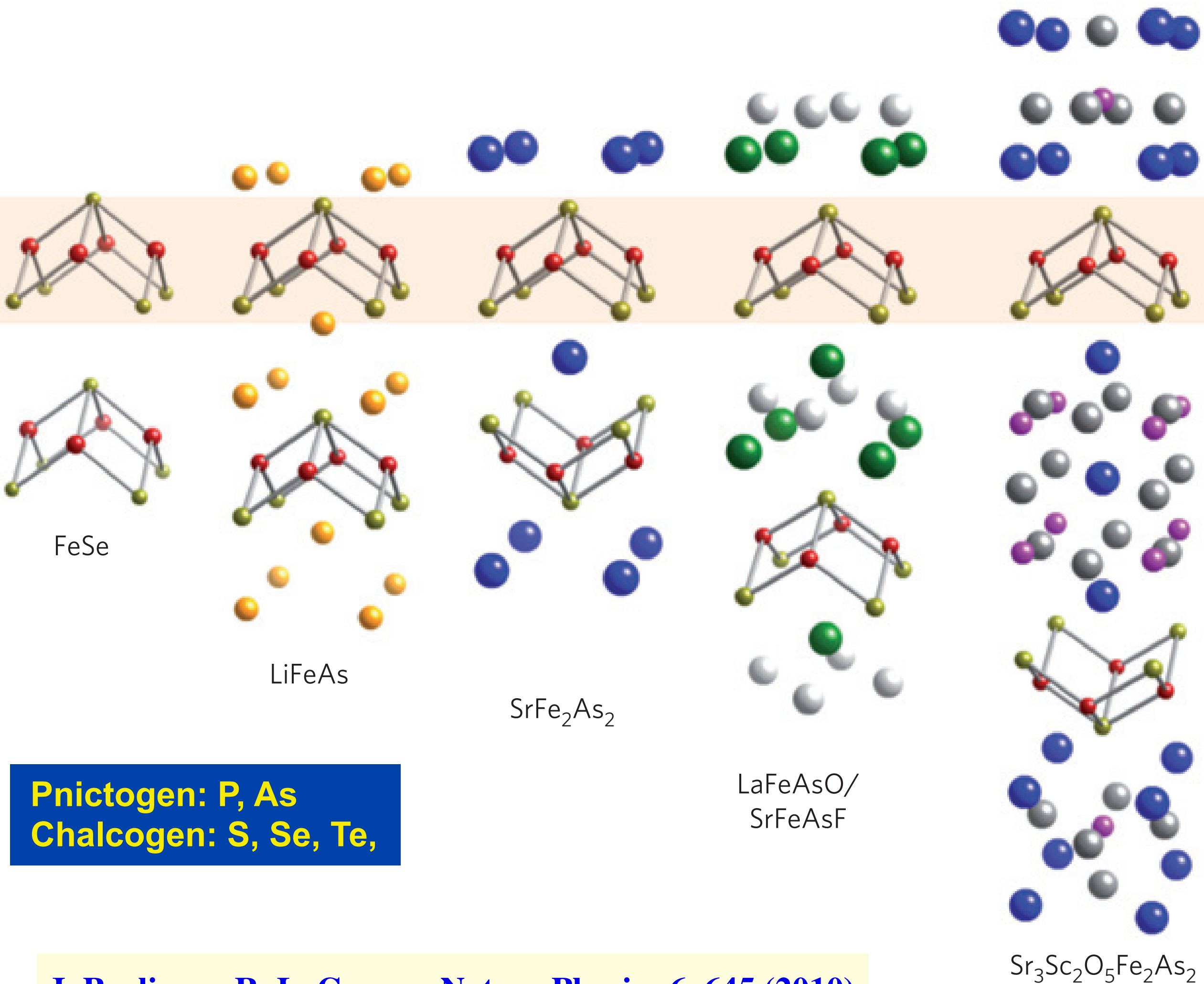


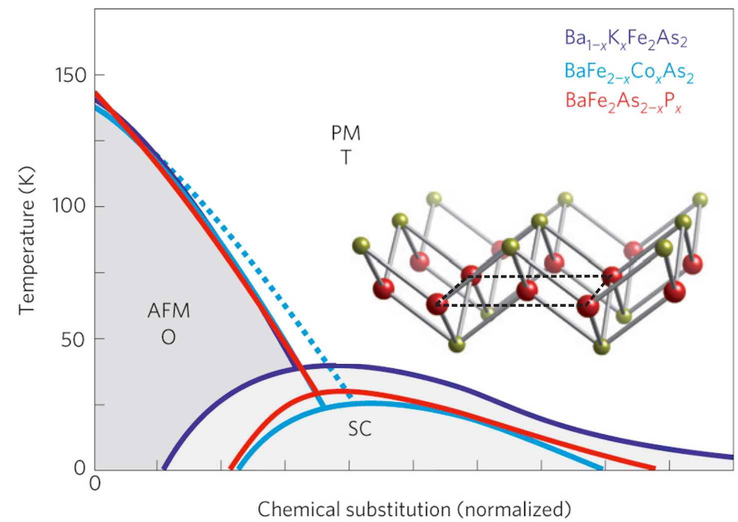
$$E=\frac{2V_L\hbar Q_{\max}}{\pi}\sin\left(\frac{\pi}{2}\frac{Q}{Q_{\max}}\right)$$

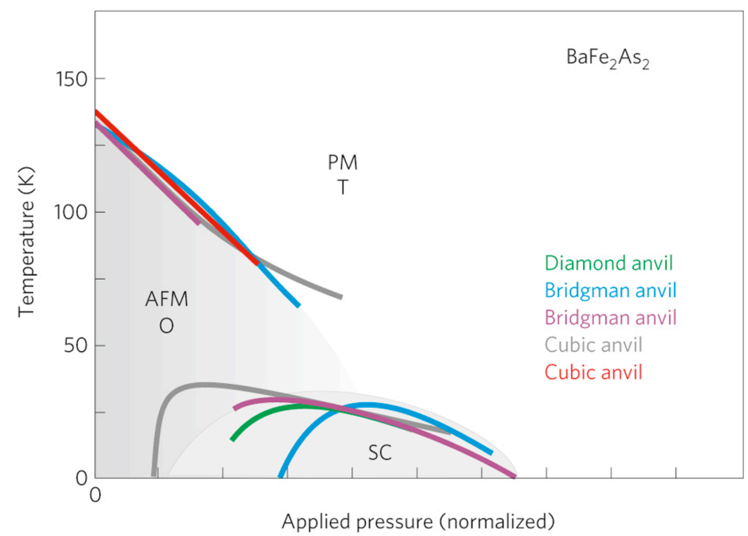
$$E\,(\mathrm{meV})=4.192\cdot 10^4\,V_L Q_{\max}\sin\left(\frac{\pi}{2}\frac{Q}{Q_{\max}}\right)$$

E. Mamontov, S.B. Vakhrushev, Yu. A. Kumzerov, A. Alatas, H. Sinn, Solid State Commun. **149** (15-16), 589-592 (2009).

Pnictides: A scientific opportunity for IXS:







Pnictogen: P, As
Chalcogen: S, Se, Te,

J. Paglione , R. L. Greene, Nature Physics 6, 645 (2010)

Are pnictides BCS type electron-phonon superconductors? Is Migdal-Eliashberg theory obeyed ?

$$T_c = \frac{\omega_{\ln}}{1.2} \exp\left[-\frac{1.04(1+\lambda)}{\lambda - \mu^*(1+0.62\lambda)}\right],$$

~ 26 K, SC transition temperature

$$\alpha_C = \frac{1}{2}\left[1 - \frac{1.04(1+\lambda)(1+0.62\lambda)\mu^{*2}}{[\lambda - \mu^*(1+0.62\lambda)]^2}\right],$$

Isotope effect coefficient

$$\frac{2\Delta}{T_c} = 3.53\left[1 + 12.5\left(\frac{T_c}{\omega_{\ln}}\right)^2 \ln\left(\frac{\omega_{\ln}}{2T_c}\right)\right],$$

SC energy **gap / T $_c$** ratio

$$\lambda = 2\int \alpha^2 F(\omega) d\omega/\omega$$

electron-phonon coupling constant

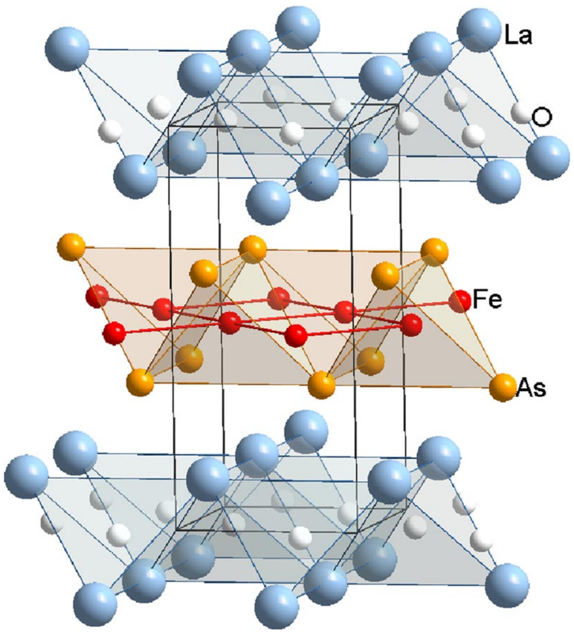
$$\ln\omega_{\ln} = (2/\lambda)\int \ln\omega\, \alpha^2 F(\omega)\frac{d\omega}{\omega}$$

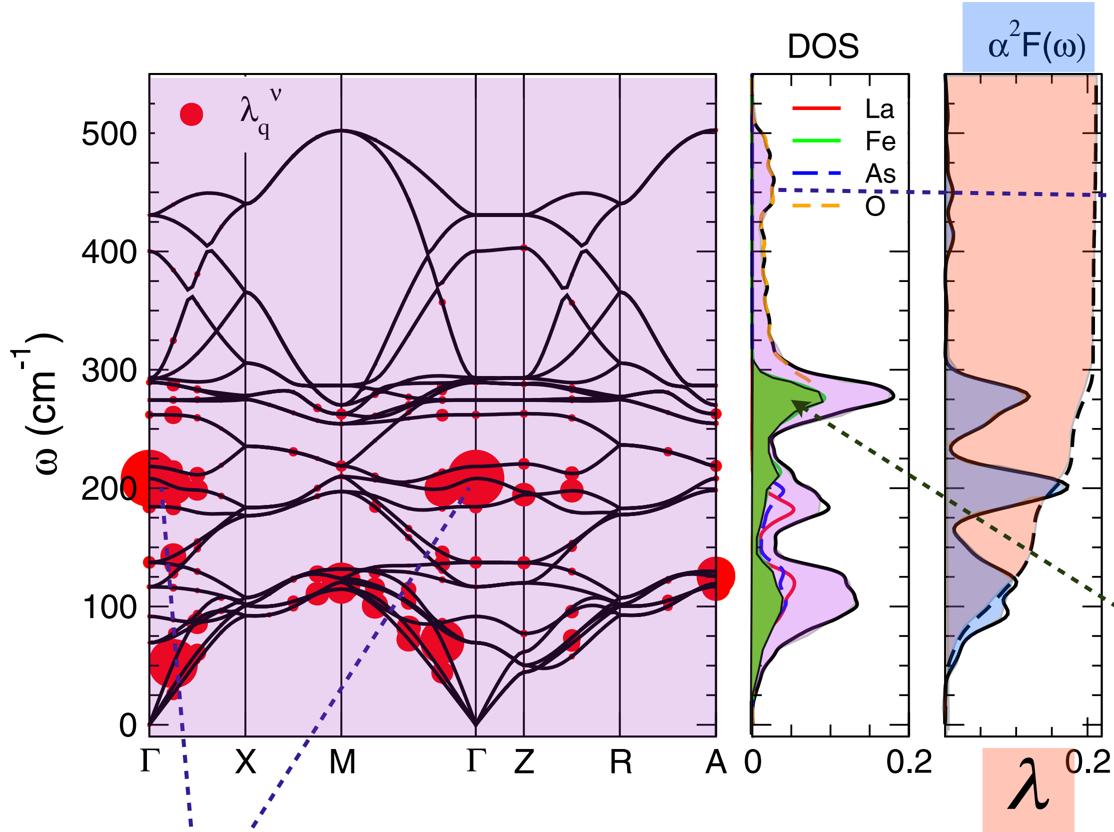
is the relevant phonon frequency

For pnictides values of λ is inconsistent with observed T_c. Estimated value of 0.2 is too small for the observed 26 K transition temperature.

$LaFeAsO_{1-x}F_x$

Boeri, Dolgov, Golubov, *Phys. Rev. Lett* **101**, 026403 (2008)





Oxygen modes do not contribute much to Eliashberg function

NRIXS: Element selective partial phonon dos

$$\lambda_{\nu\mathbf{q}} \equiv \frac{1}{\pi N(0)} \frac{\gamma_{\nu\mathbf{q}}}{\omega^2_{\nu\mathbf{q}}}$$

Electron-phonon linewidth

PHYSICAL REVIEW B **79**, 220511(R) (2009)

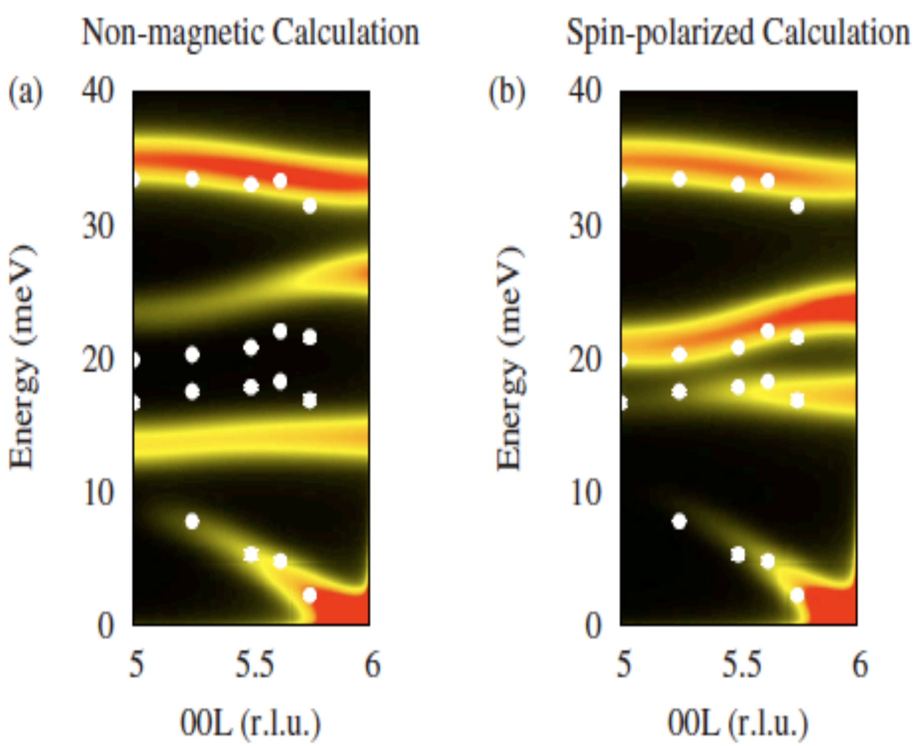
Influence of magnetism on phonons in $CaFe_2As_2$ as seen via inelastic x-ray scattering

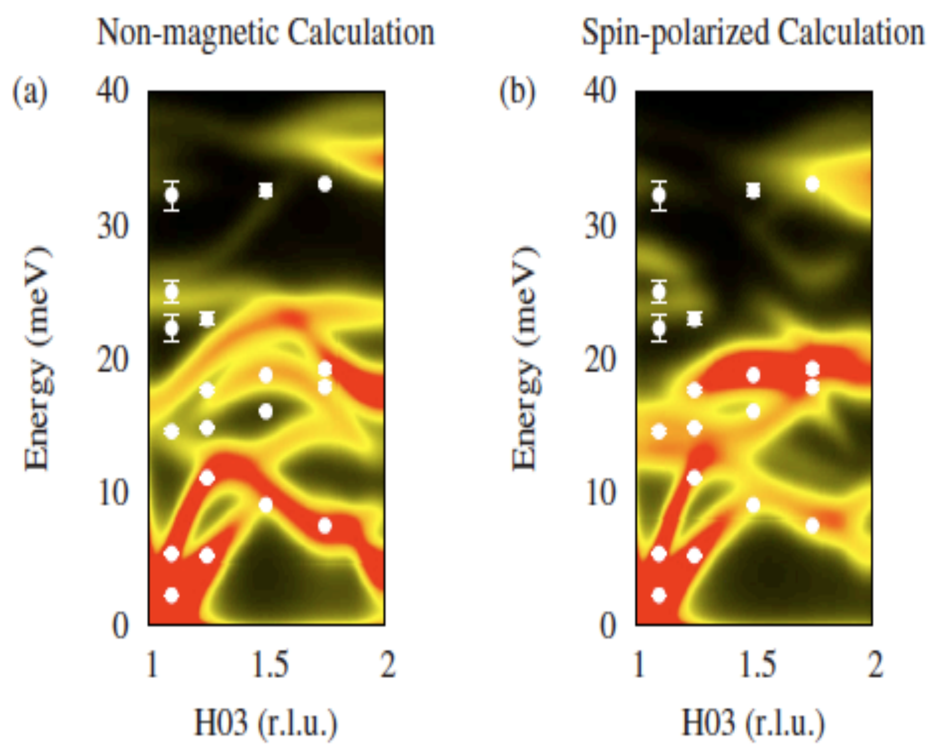
S. E. Hahn,* Y. Lee, N. Ni, P. C. Canfield, A. I. Goldman, R. J. McQueeney,† and B. N. Harmon
Department of Physics and Astronomy and Ames Laboratory, Iowa State University, Ames, Iowa 50010, USA

A. Alatas, B. M. Leu, and E. E. Alp
Advanced Photon Source, Argonne National Laboratory, Argonne, Illinois 60439, USA

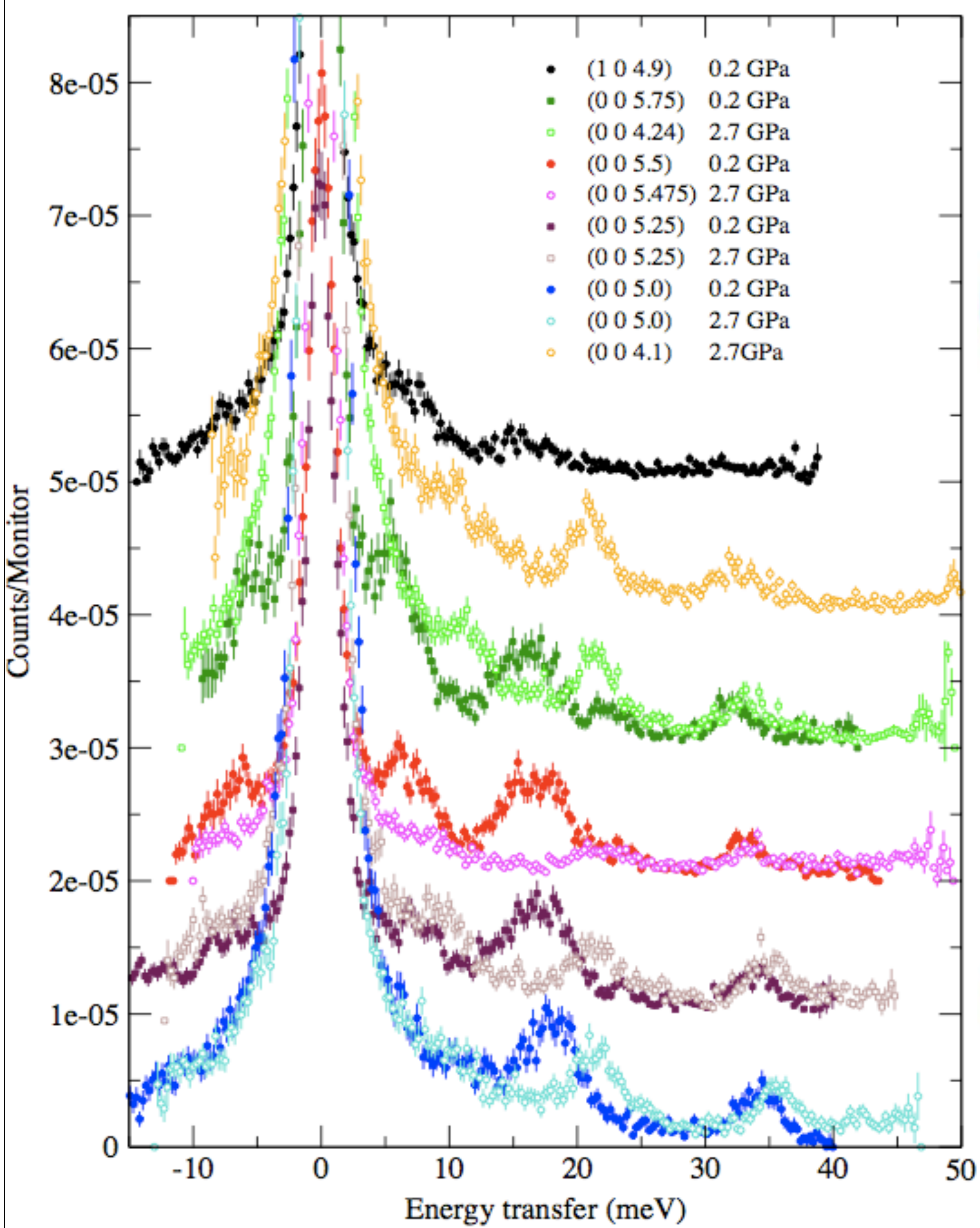
D. Y. Chung and I. S. Todorov
Materials Science Division, Argonne National Laboratory, Argonne, Illinois 60439, USA

M. G. Kanatzidis
Materials Science Division, Argonne National Laboratory, Argonne, Illinois 60439, USA
and Department of Chemistry, Northwestern University, Evanston, Illinois 60208, USA

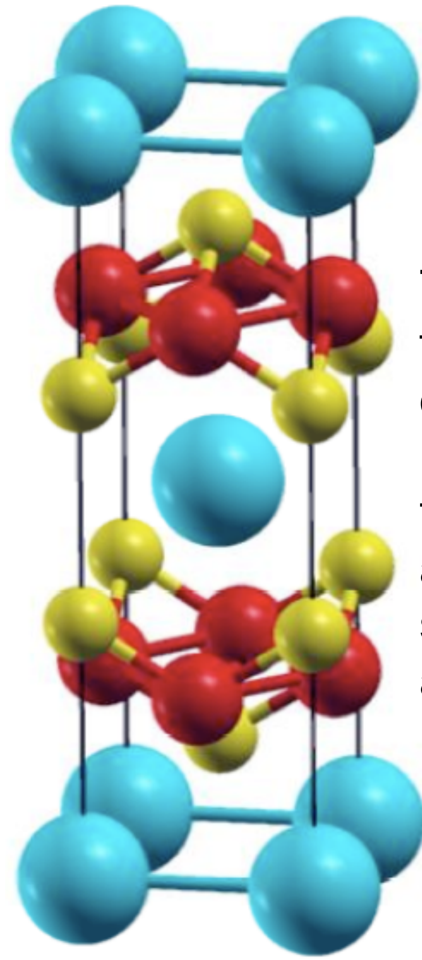


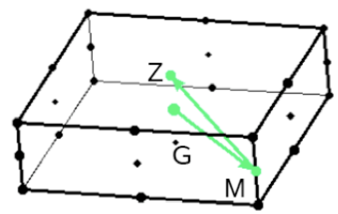


$CaFe_2As_2$ under pressure



I4/mmm



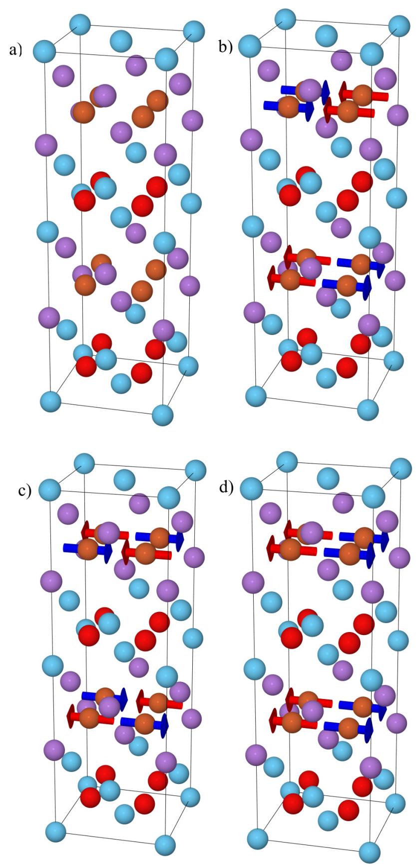


There is a phase transition from magnetically ordered orthorhombic phase to a nonmagnetic "collapsed" tetragonal phase, accompanied by a significant volume change at 0.3 GPa.

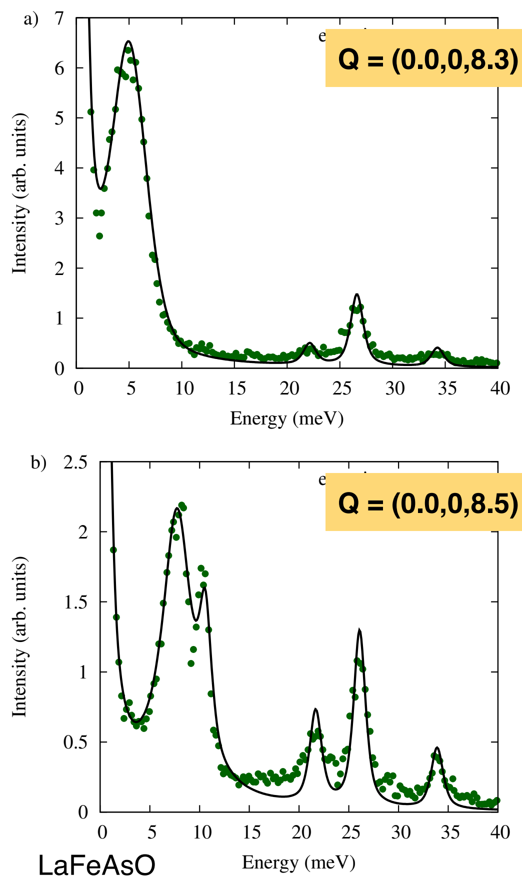
Pnictides: A scientific opportunity for IXS & NRVS:

S. E. Hahn, et al, Phys. Rev. B, 79, 220511 (2009) and Phys. Rev. B, (submitted, 2012)

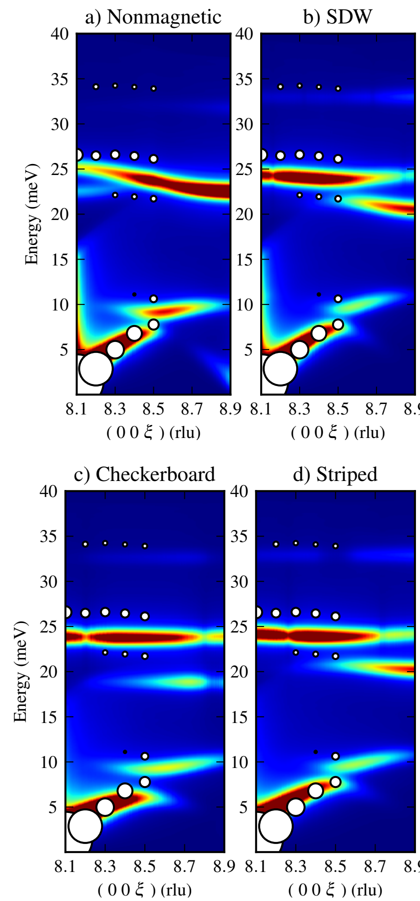
(A)

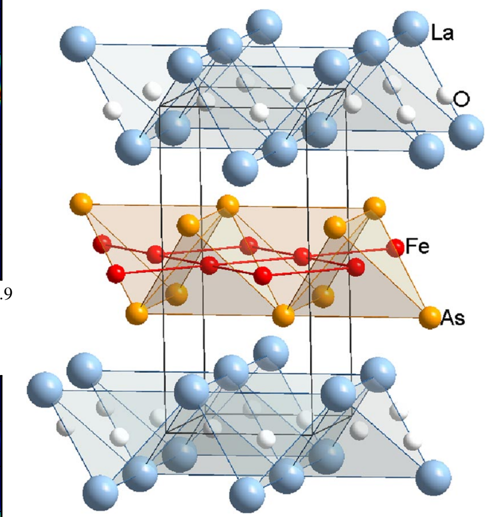


(B)



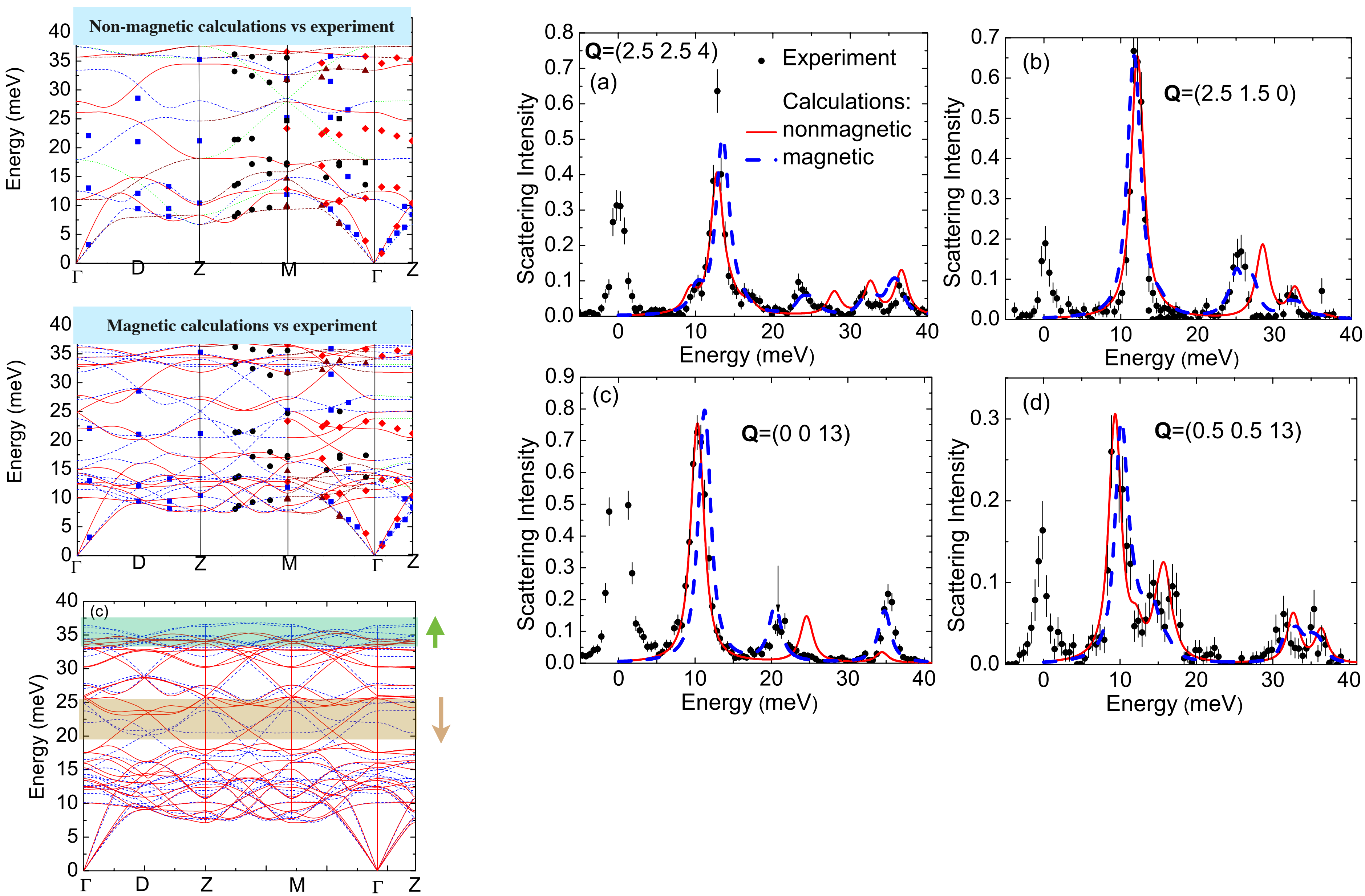
(C)



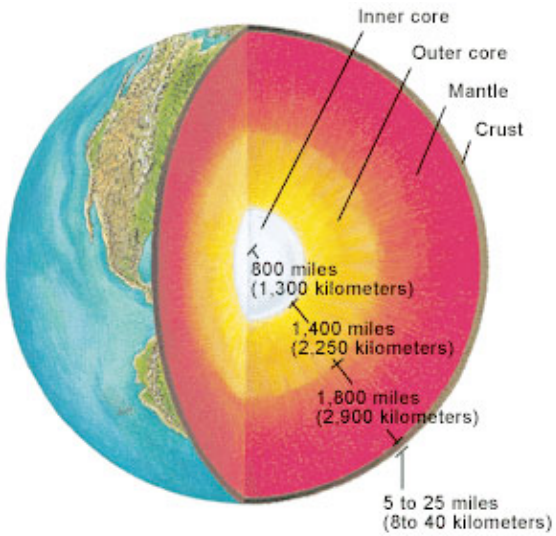


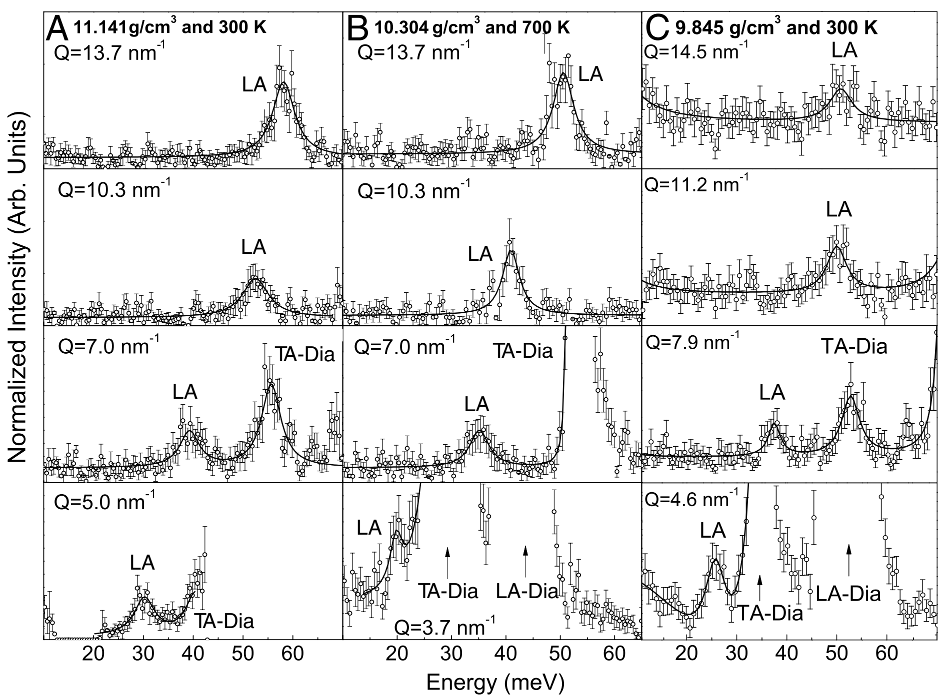
$BaFe_{1.8}Co_{0.2}As_2$

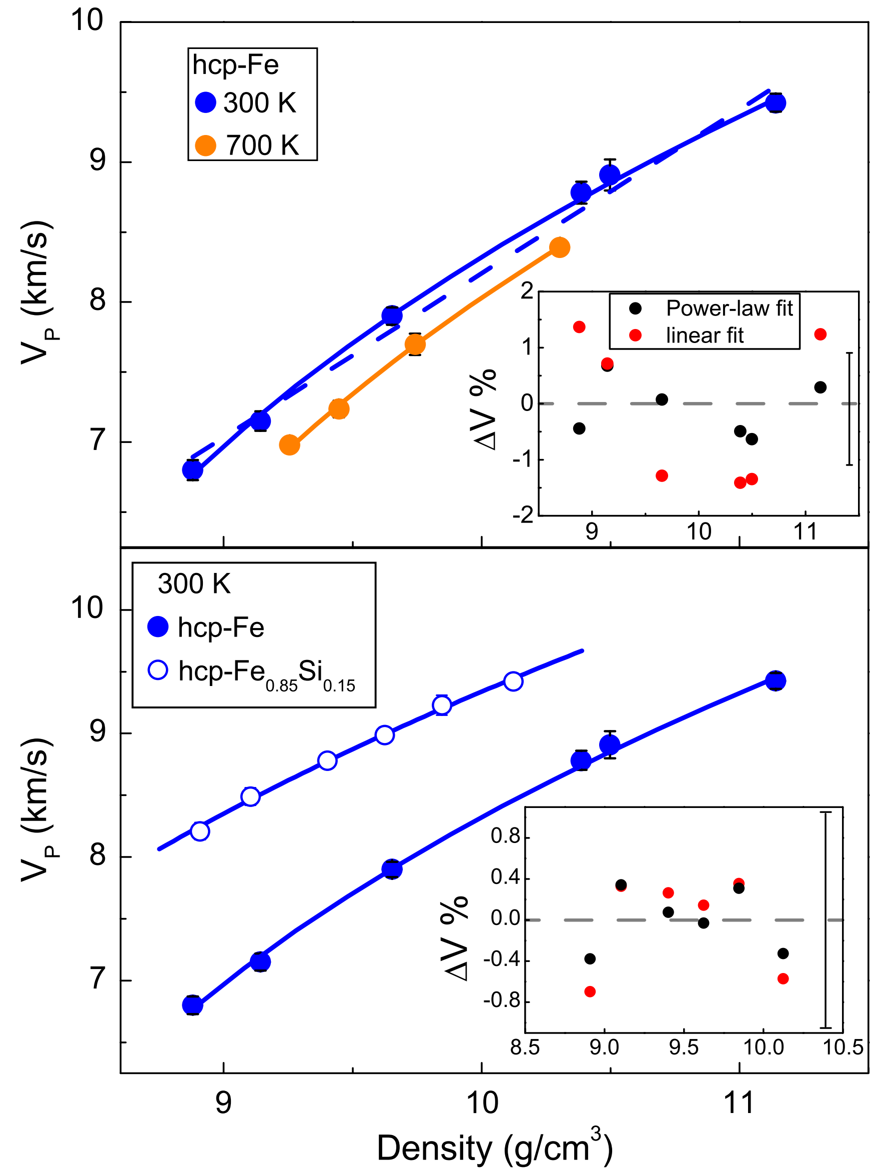
D. Reznik et al, *Phys. Rev B* **80**, 214534 (2009)



Sound velocity at the conditions of the Earth's core in iron alloys

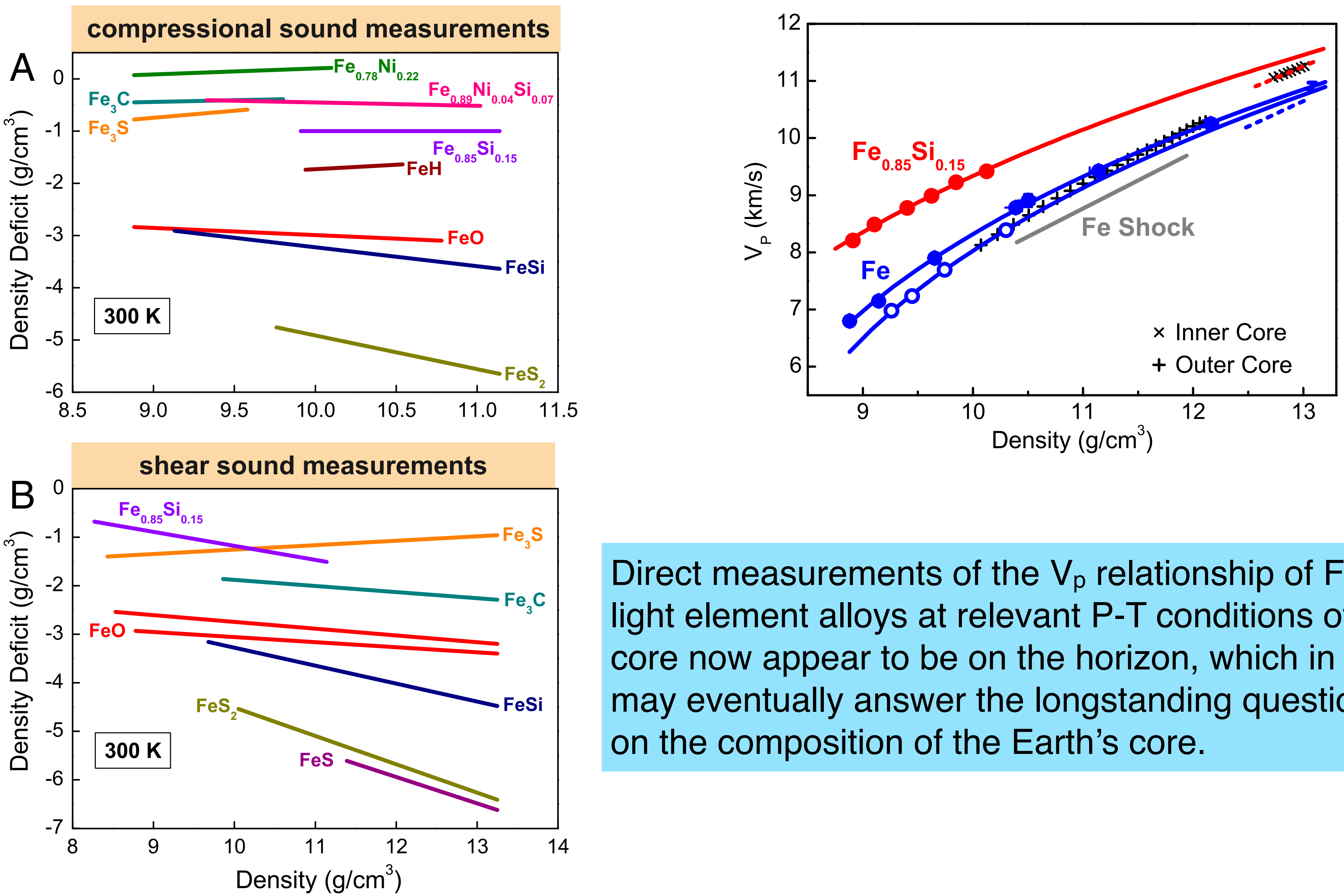






Z. Mao. et al, PNAS, 2012

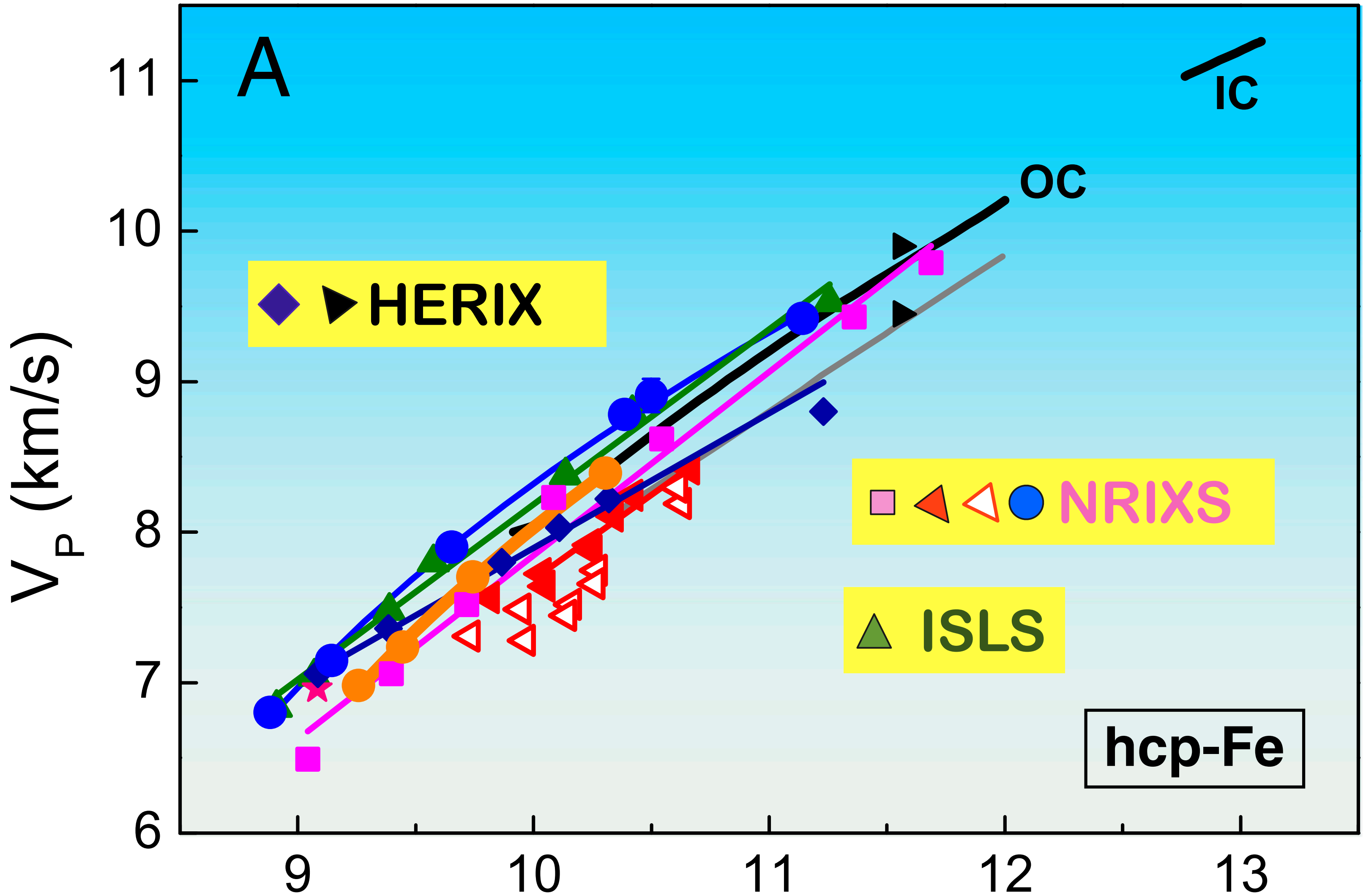
Sound velocity at the conditions of the Earth's core in iron alloys



Direct measurements of the V_P relationship of Fe-light element alloys at relevant P-T conditions of the core now appear to be on the horizon, which in turn may eventually answer the longstanding question on the composition of the Earth's core.

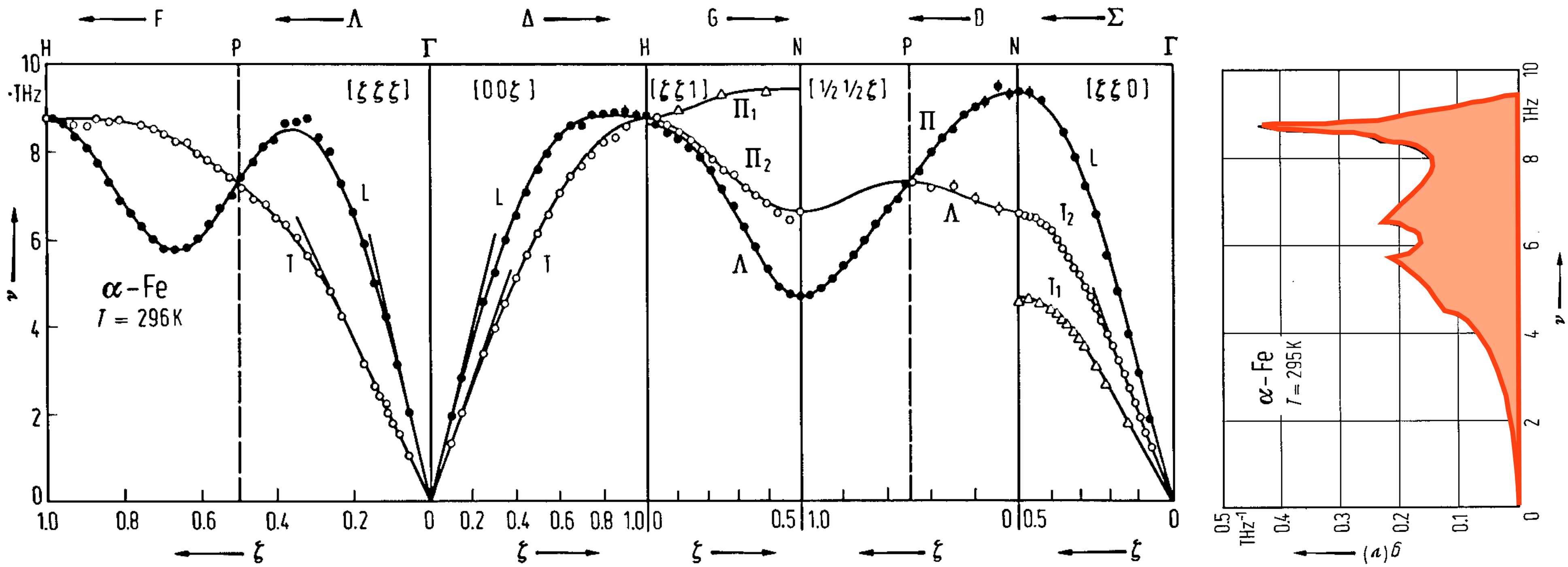
Z. Mao. et al, PNAS, 2012

Sound velocity at the conditions of the Earth's core in iron alloys



ISLS : impulsive stimulated light scattering

Dispersion relations and phonon density of states α -iron (bcc)

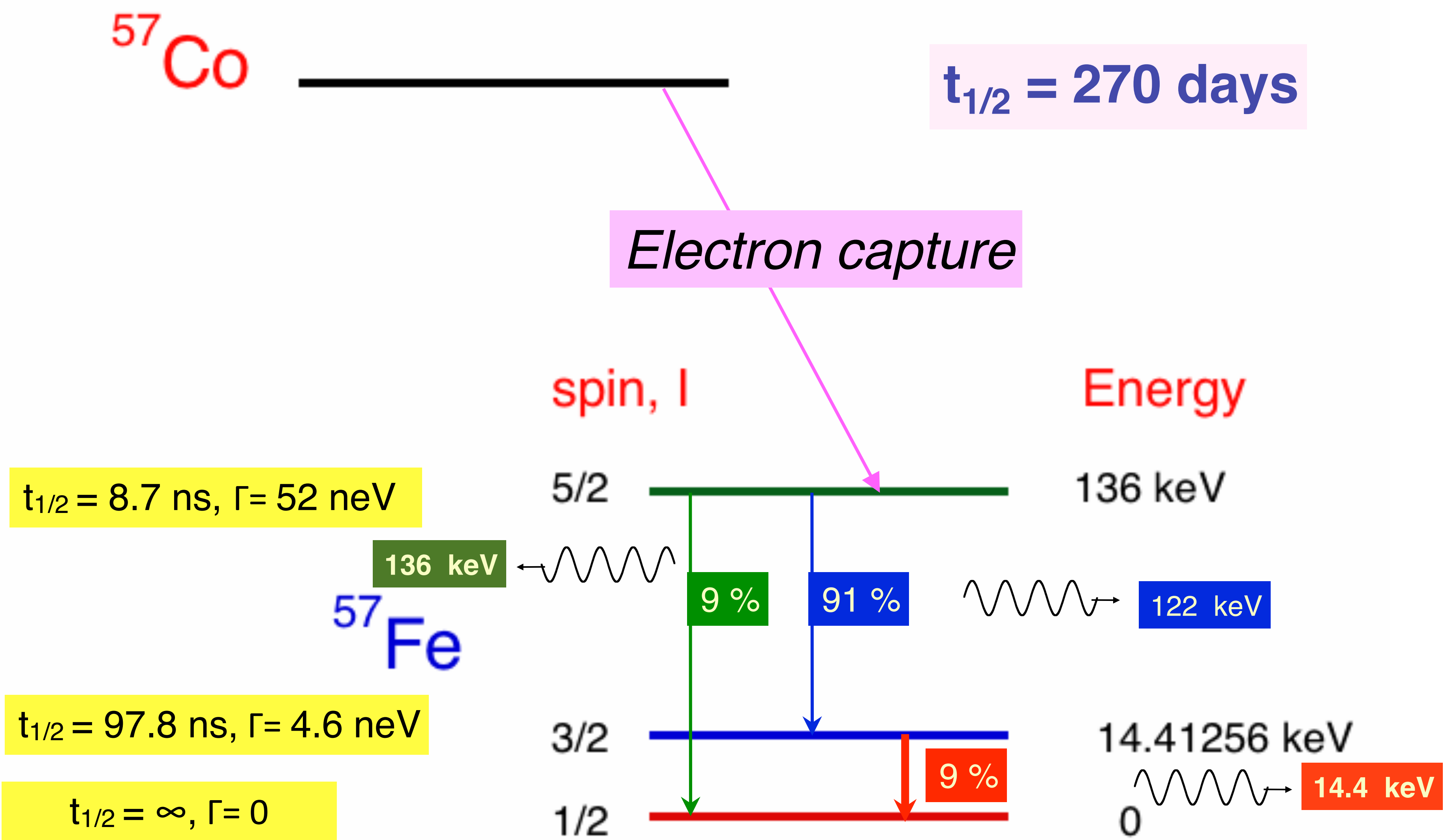


V. J. Minkiewicz, G. Shirane, and R. Nathans, Phys. Rev. 162 (1967) 528, and
Landolt-Börnstein, New Series, Group III, Vol 13, Eds. K.-H Hellwege, and J. L. Olsen, Springer Verlag, Berlin (1981) p. 53-56.

a few questions

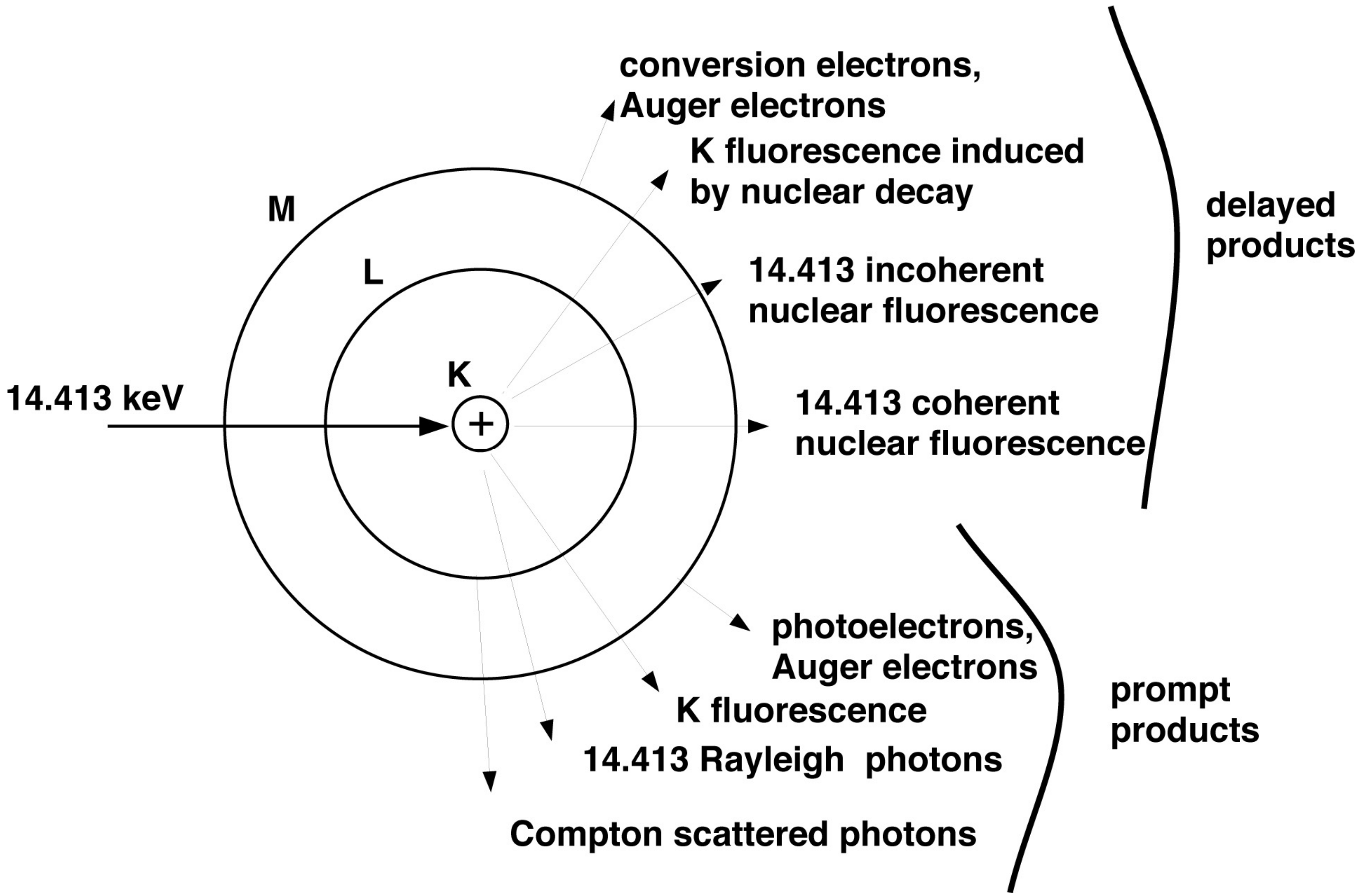
- Can one measure phonon dispersion and/or phonon dos
  - from a monolayer?
  - at a buried interface?
  - from nanosized particles on the surface?
  - at 3 Mbar and at 4 K to 5000K extreme conditions?
  - from a nanogram sample?
  - in a way that is element and isotope selective?
  - in a way that can be completely tested by DFT, i.e. both the frequency and amplitude of vibrations are determined

Characteristics of a Mössbauer nuclei

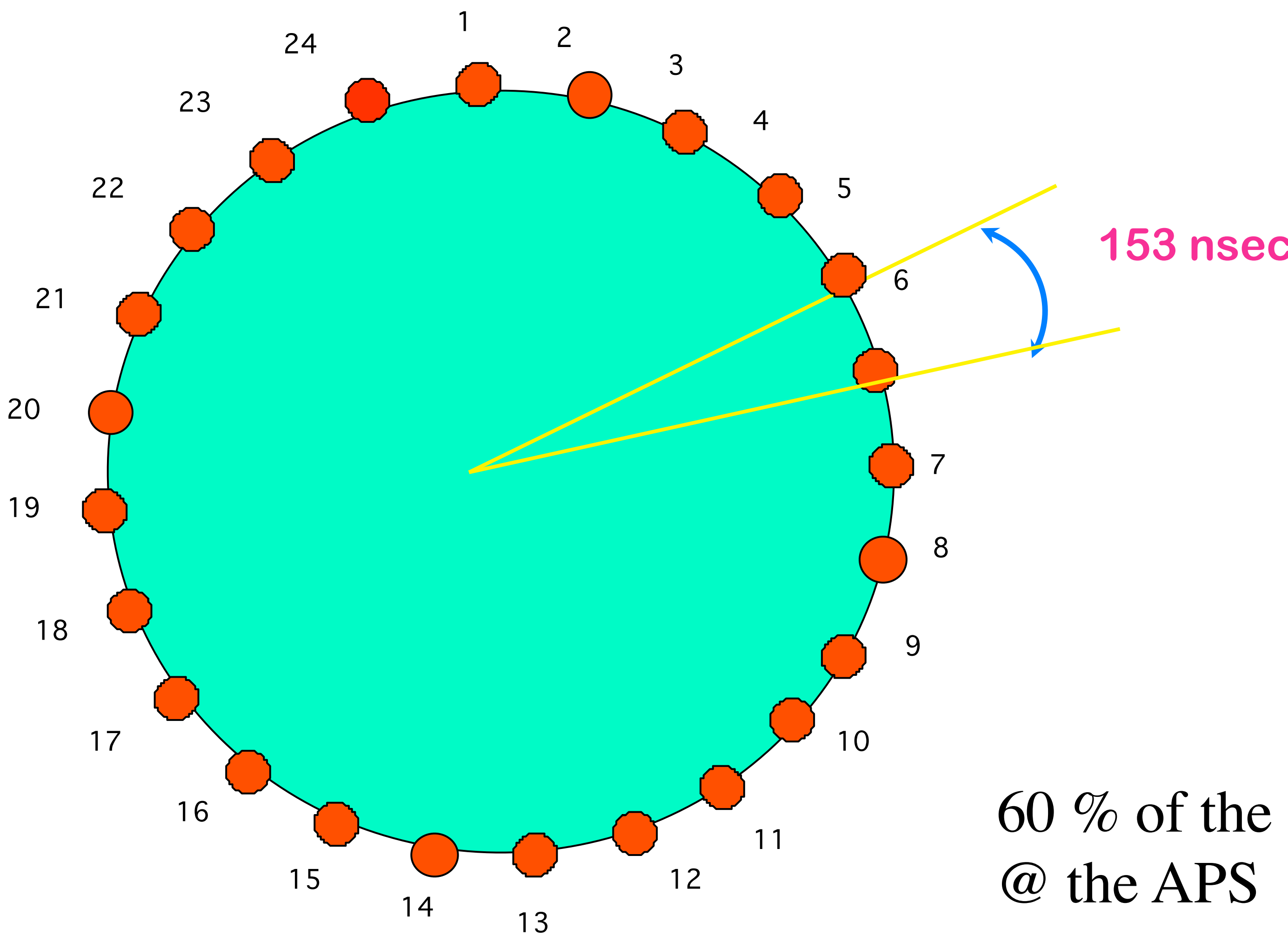


Transitions to ground state with a relatively low energy is what makes a nuclei a Mössbauer nuclei

Nuclear Resonance and Fallout in ^{57}Fe-decay



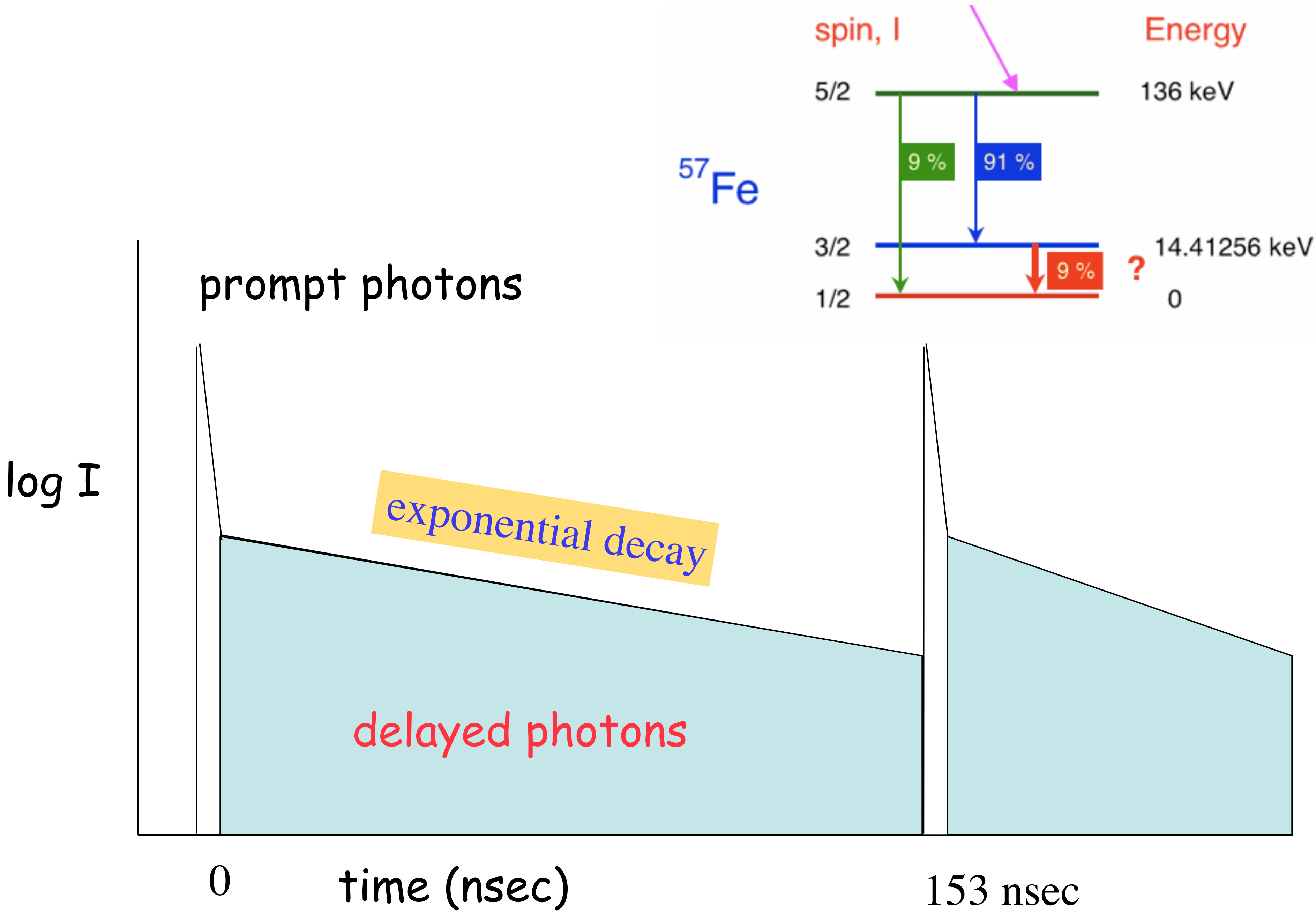
Standard Time structure @ APS

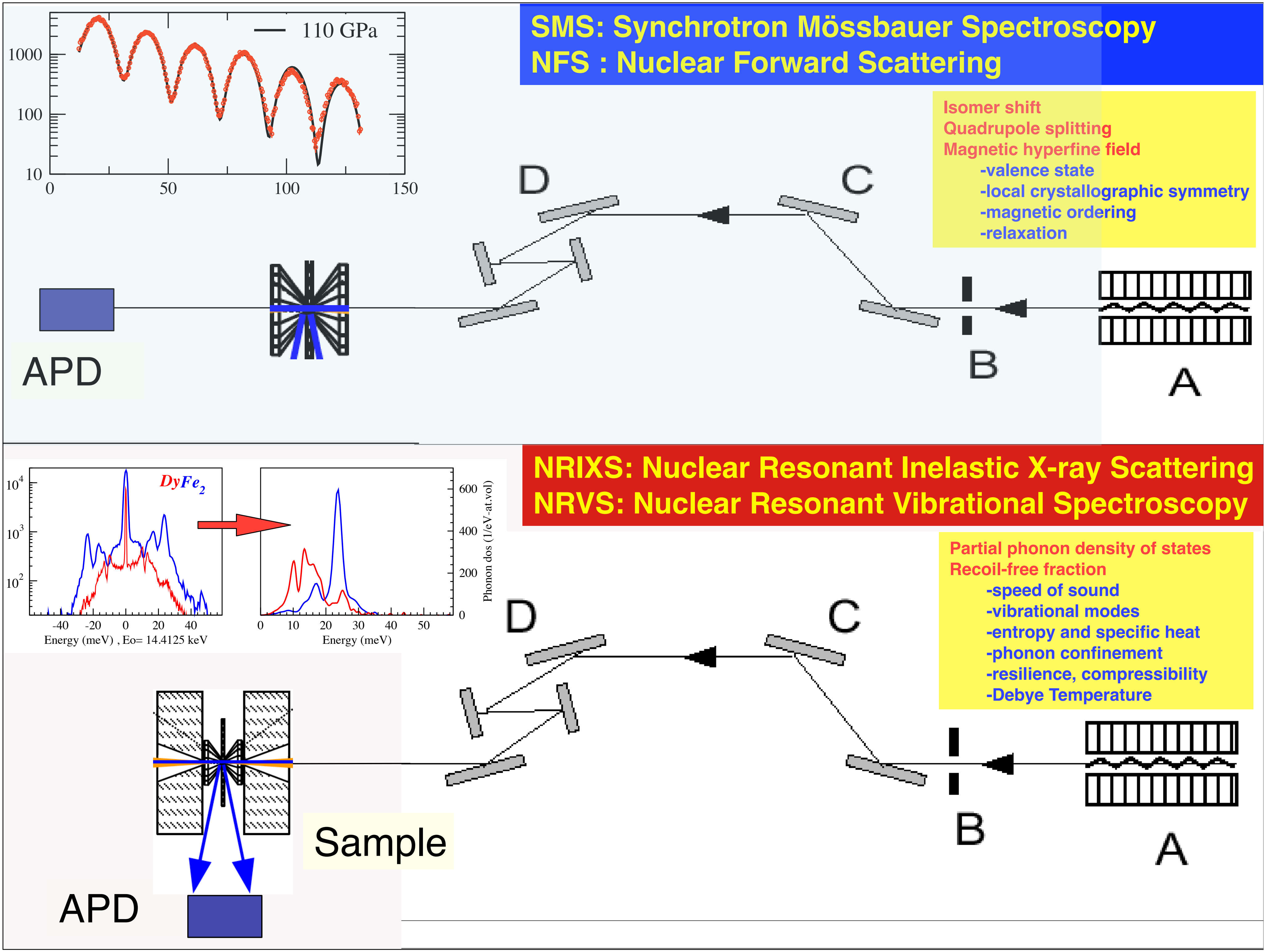


60 % of the time
@ the APS

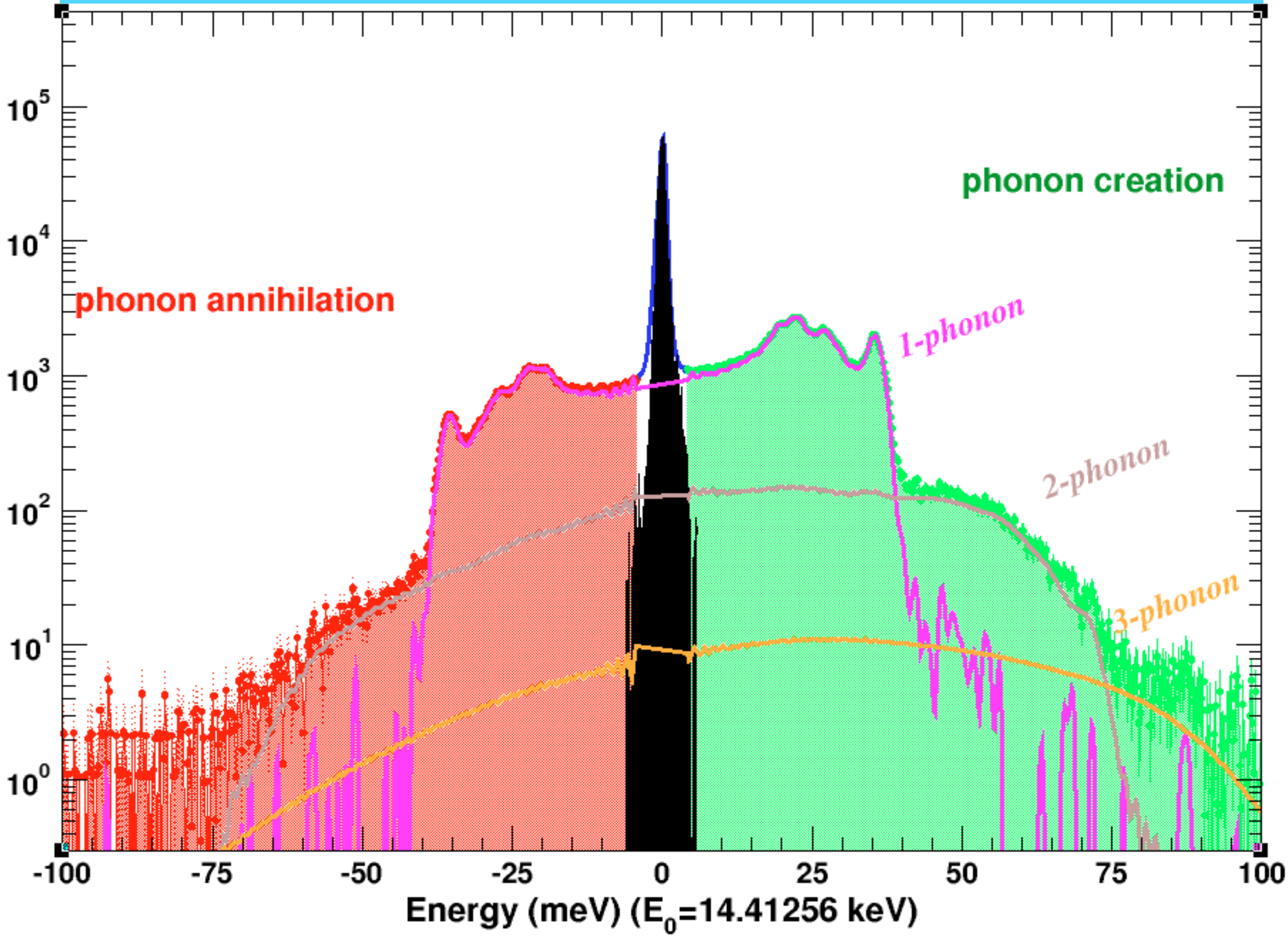
1 revolution=3.68 μsec =>1296 buckets

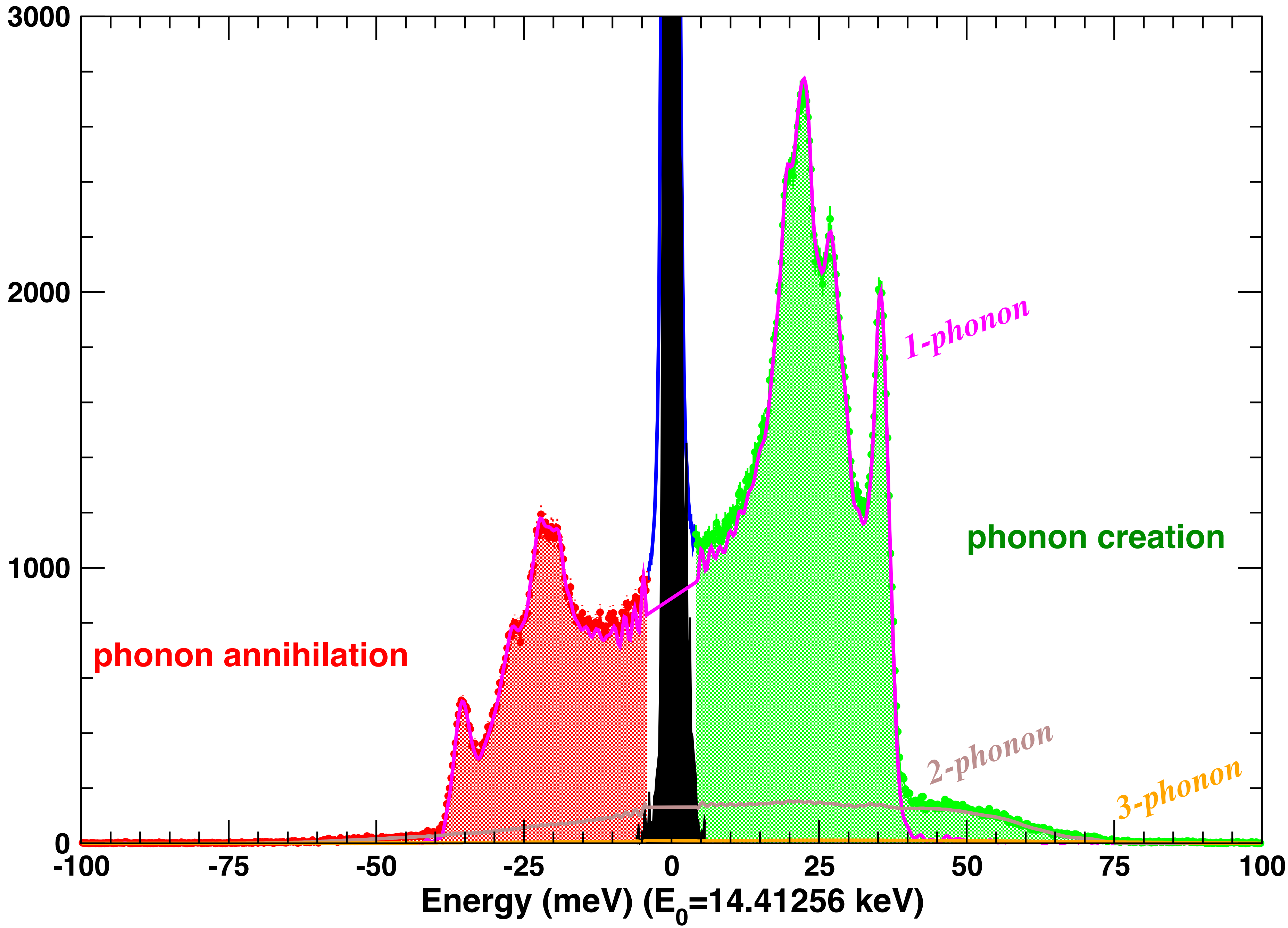
Detection of nuclear decay




SMS: Synchrotron Mössbauer Spectroscopy
NFS : Nuclear Forward Scattering
110 GPa
1000
100
10
0
50
100
150
Isomer shift
Quadrupole splitting
Magnetic hyperfine field
-valence state
-local crystallographic symmetry
-magnetic ordering
-relaxation
D
C
B
A
APD
NRIXS: Nuclear Resonant Inelastic X-ray Scattering
NRVS: Nuclear Resonant Vibrational Spectroscopy
DyFe2
10^4
10^3
10^2
-40 -20 0 20 40
Energy (meV) , Eo= 14.4125 keV
0 10 20 30 40 50
Energy (meV)
600
400
200
0
Phonon dos (1/eV-at.vol)
Partial phonon density of states
Recoil-free fraction
-speed of sound
-vibrational modes
-entropy and specific heat
-phonon confinement
-resilience, compressibility
-Debye Temperature
D
C
B
A
Sample
APD

Multi-phonon decomposition

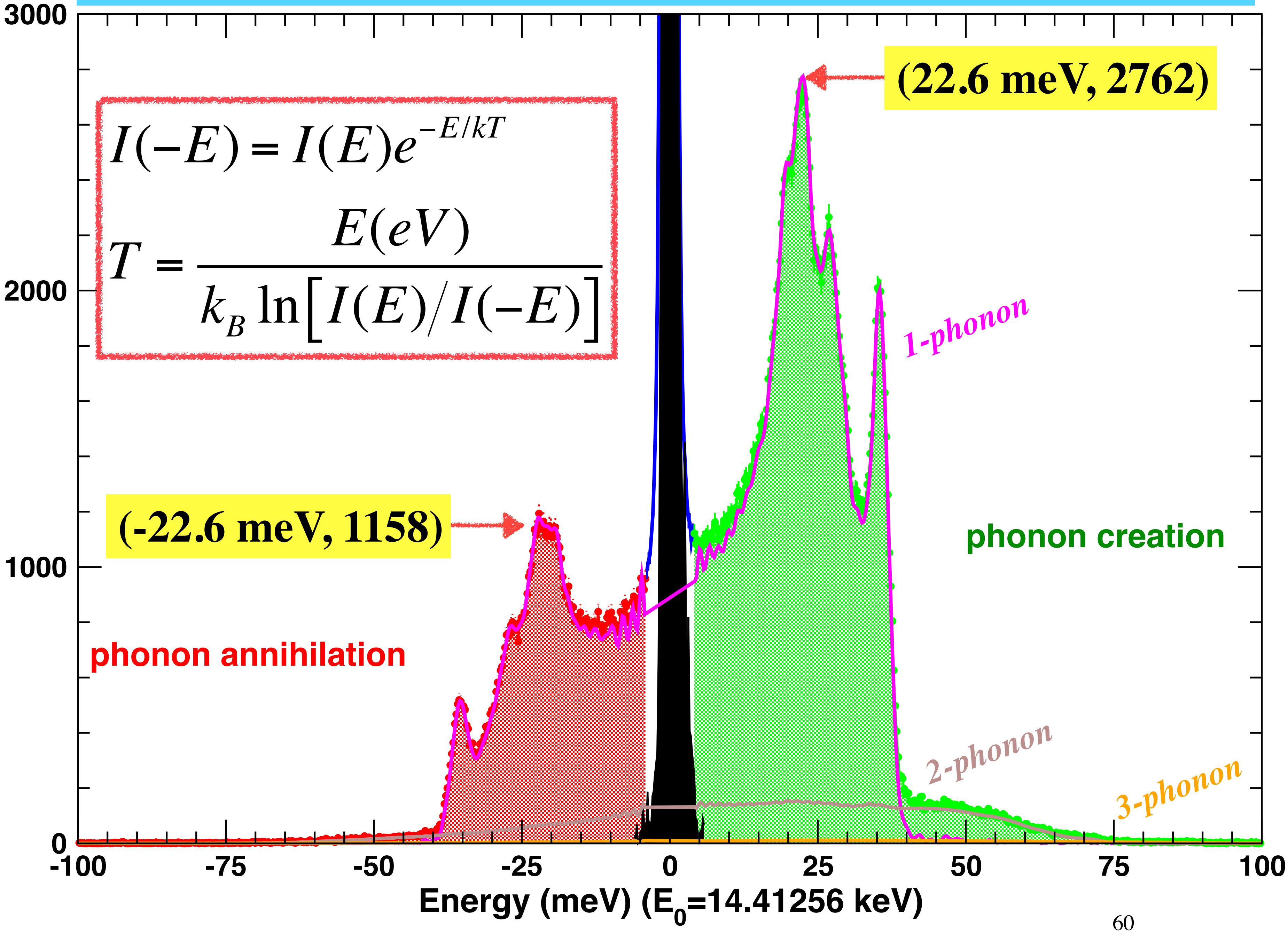



3000
2000
1000
0
-100
-75
-50
-25
0
25
50
75
100
Energy (meV) (E_0=14.41256 keV)
1-phonon
phonon creation
phonon annihilation
2-phonon
3-phonon

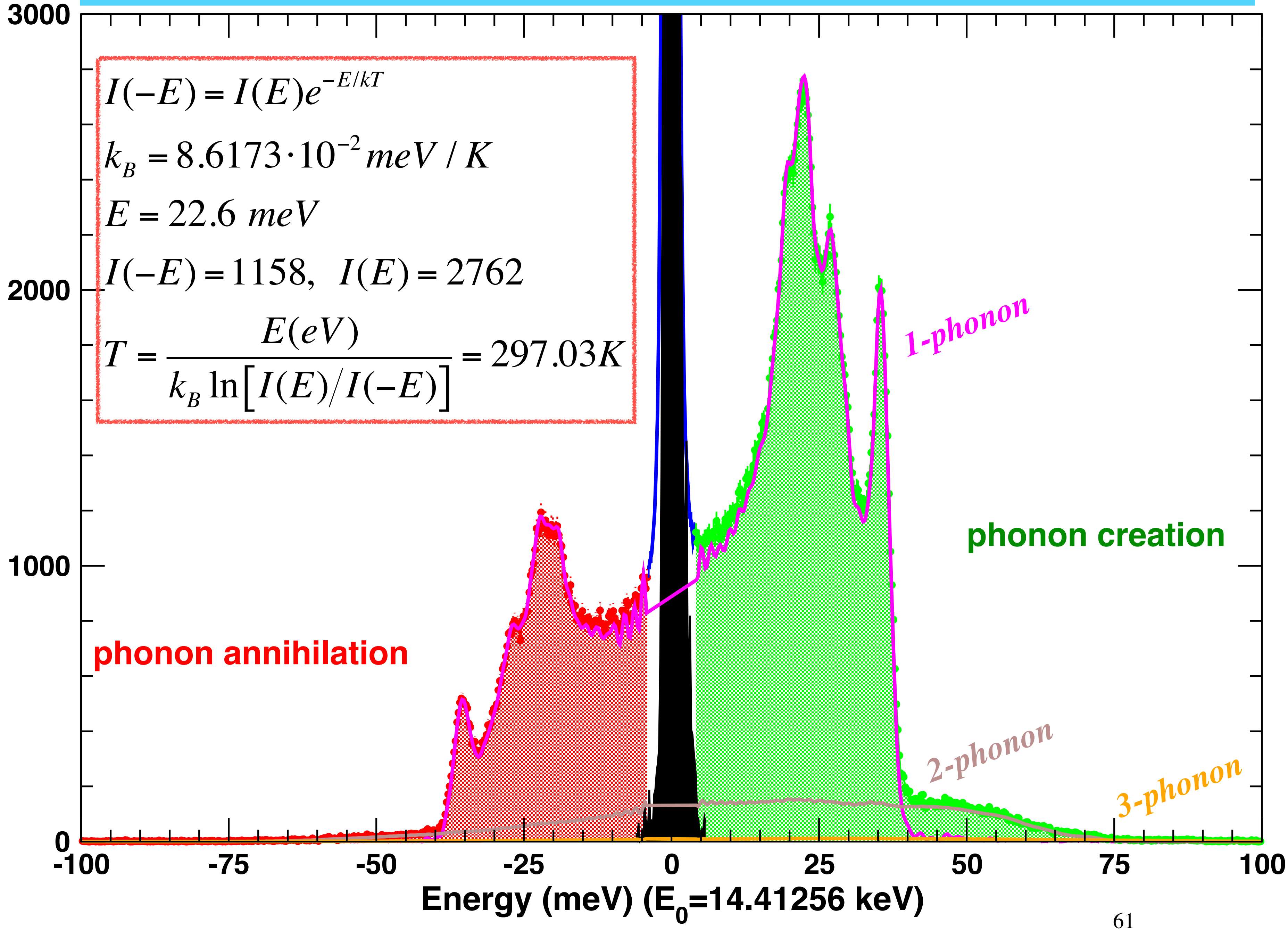
Detailed Balance

$$I(-E) = I(E)e^{-E/kT}$$

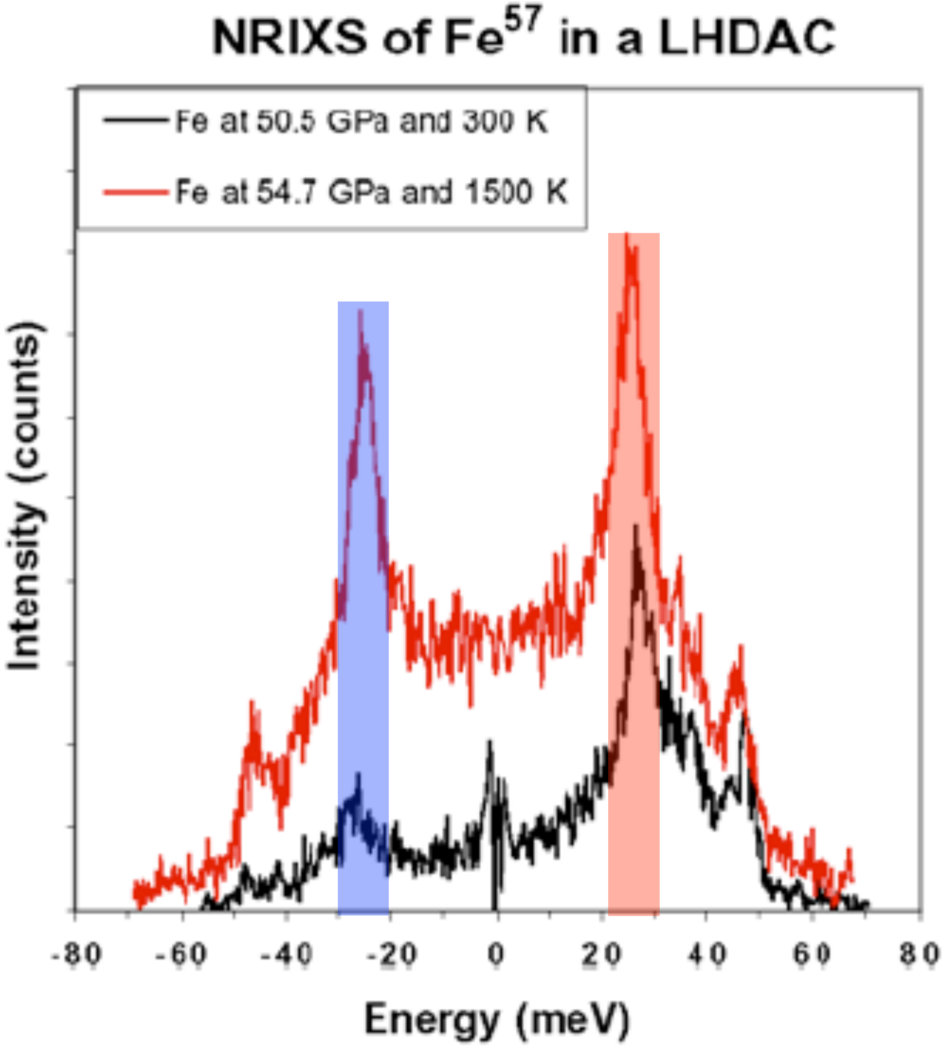
$$T = \frac{E(eV)}{k_B \ln\left[I(E)/I(-E)\right]}$$

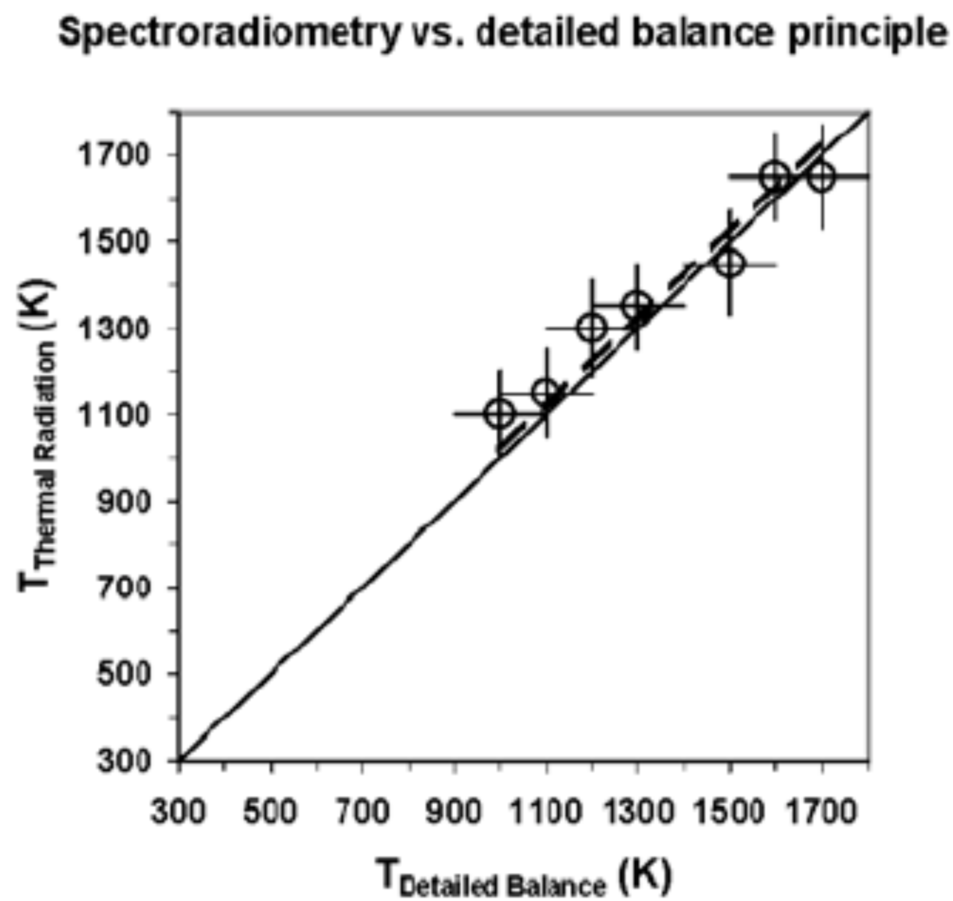


Detailed Balance



How to measure temperature in a DAC ?



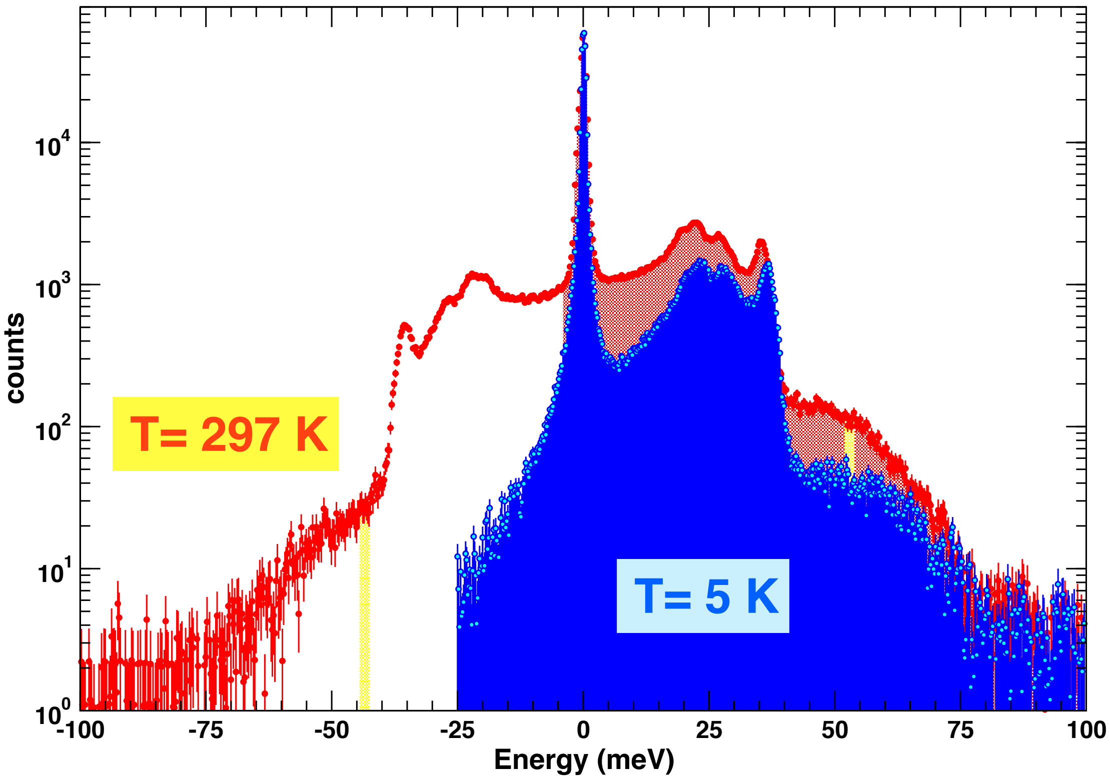


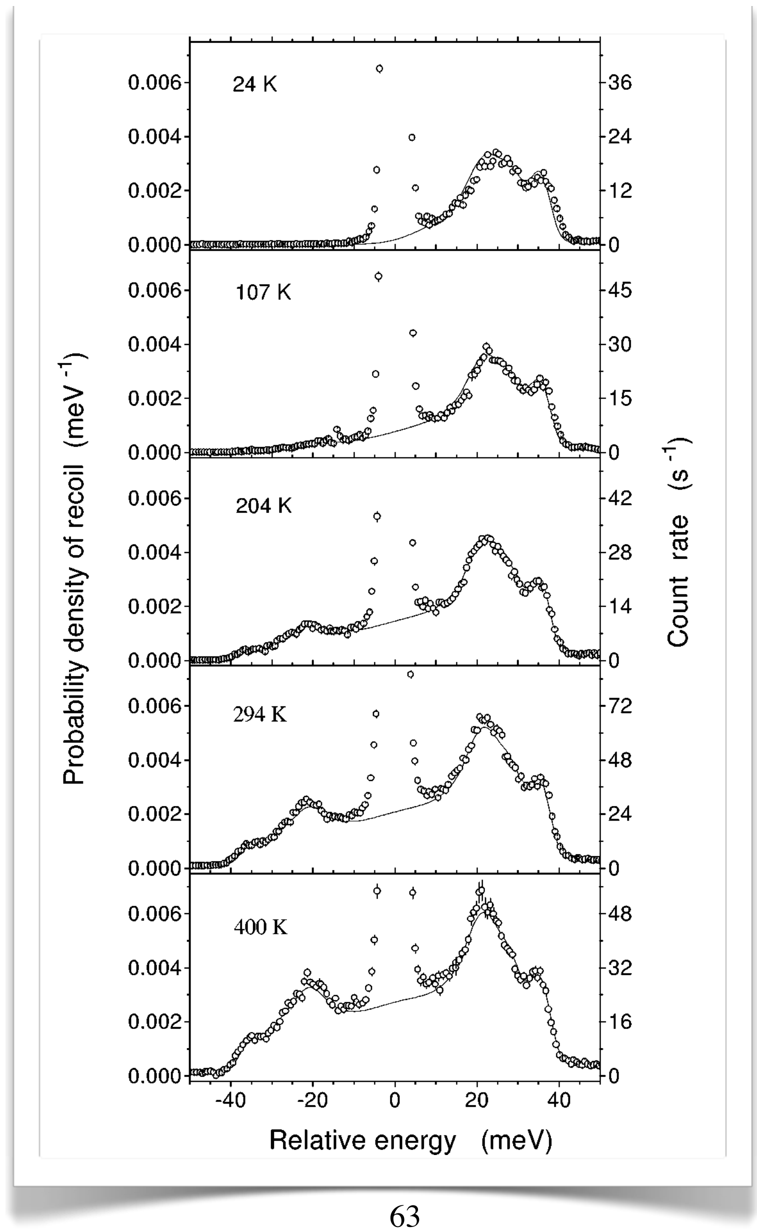
J.F. Lin, et al, Geophys. Res. Lett., 31 (2004) L13611

$$I(E) = I(-E)e^{(E/kT)}$$

$$\int I(E)dE = \int I(-E)e^{(E/kT)}dE$$

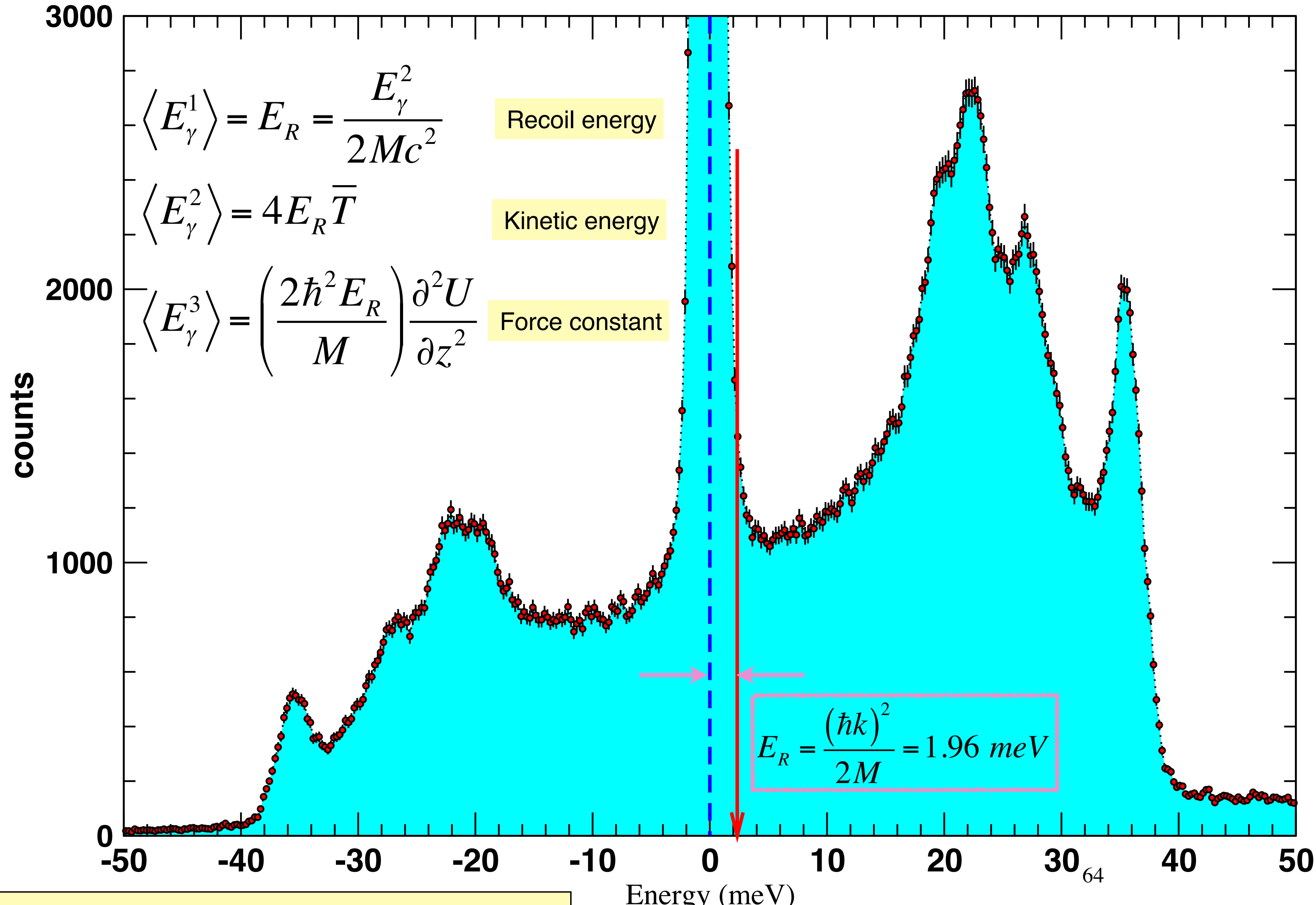
Temperature dependence of phonon excitation probability





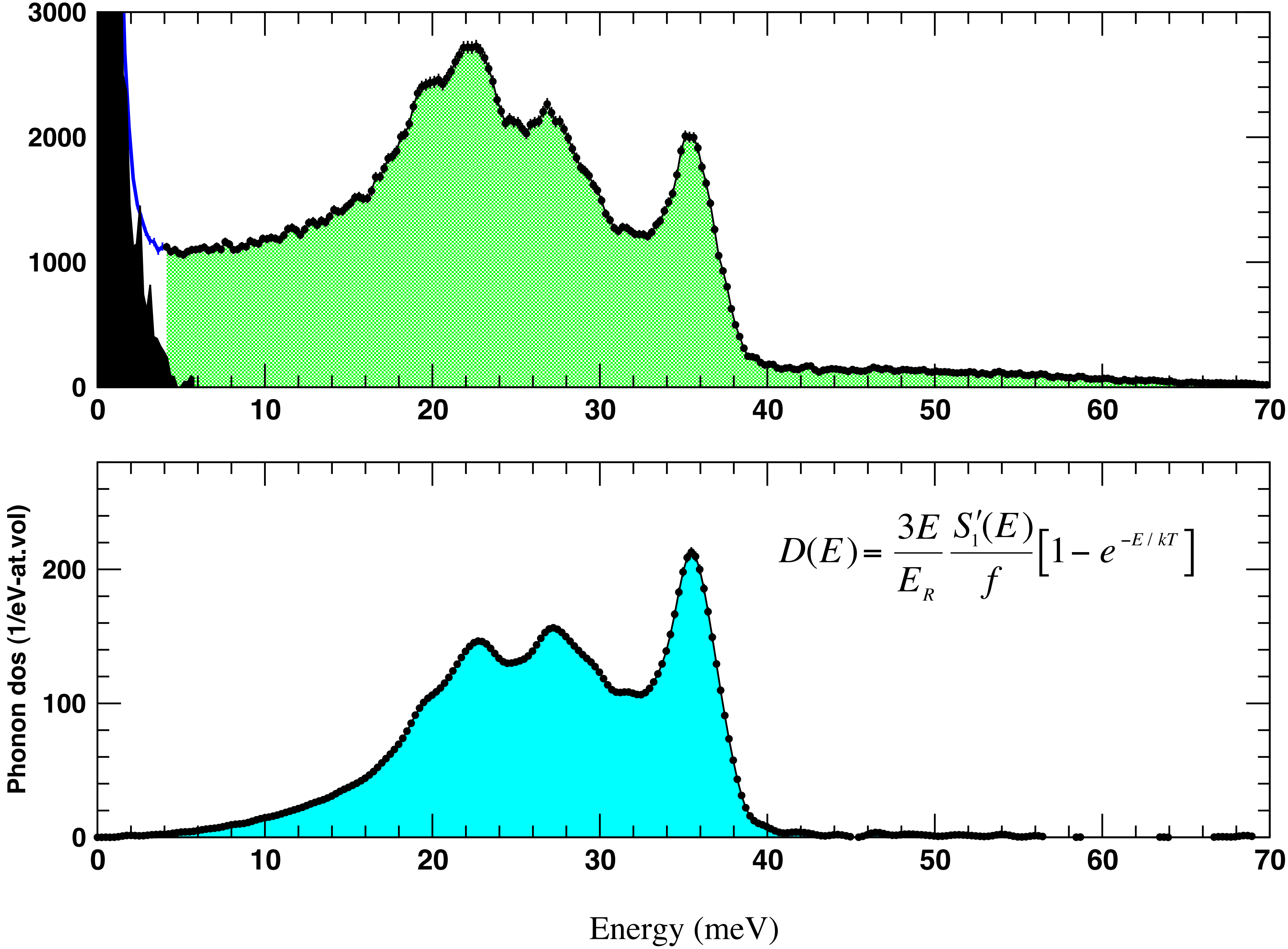
Chumakov, et al, Phys. Rev. B 54 (1996) 9596.

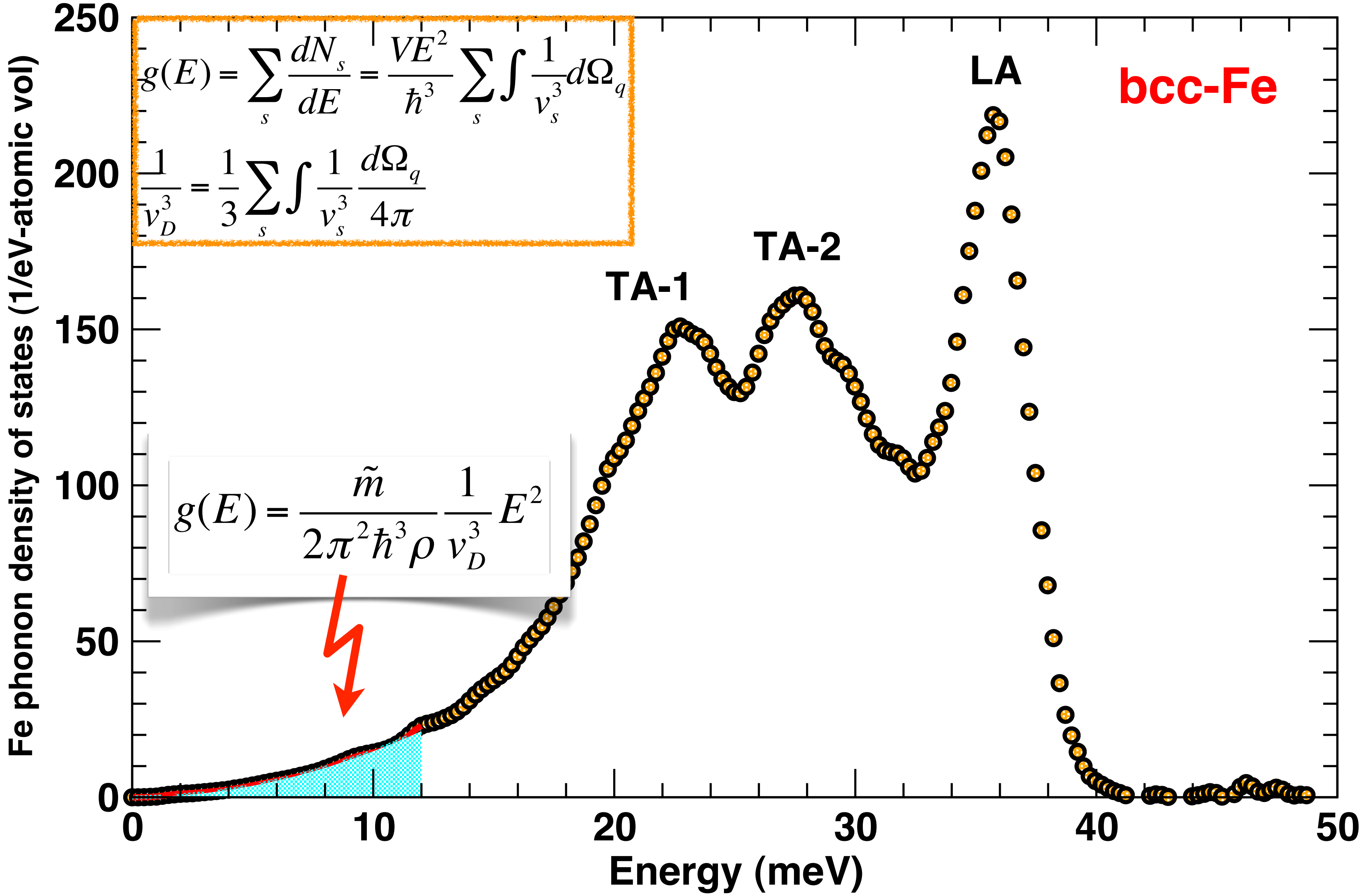
Lipkin's sum rules related to phonon excitation probability



H. Lipkin, Phys. Rev. B, **52** (1995) 10073

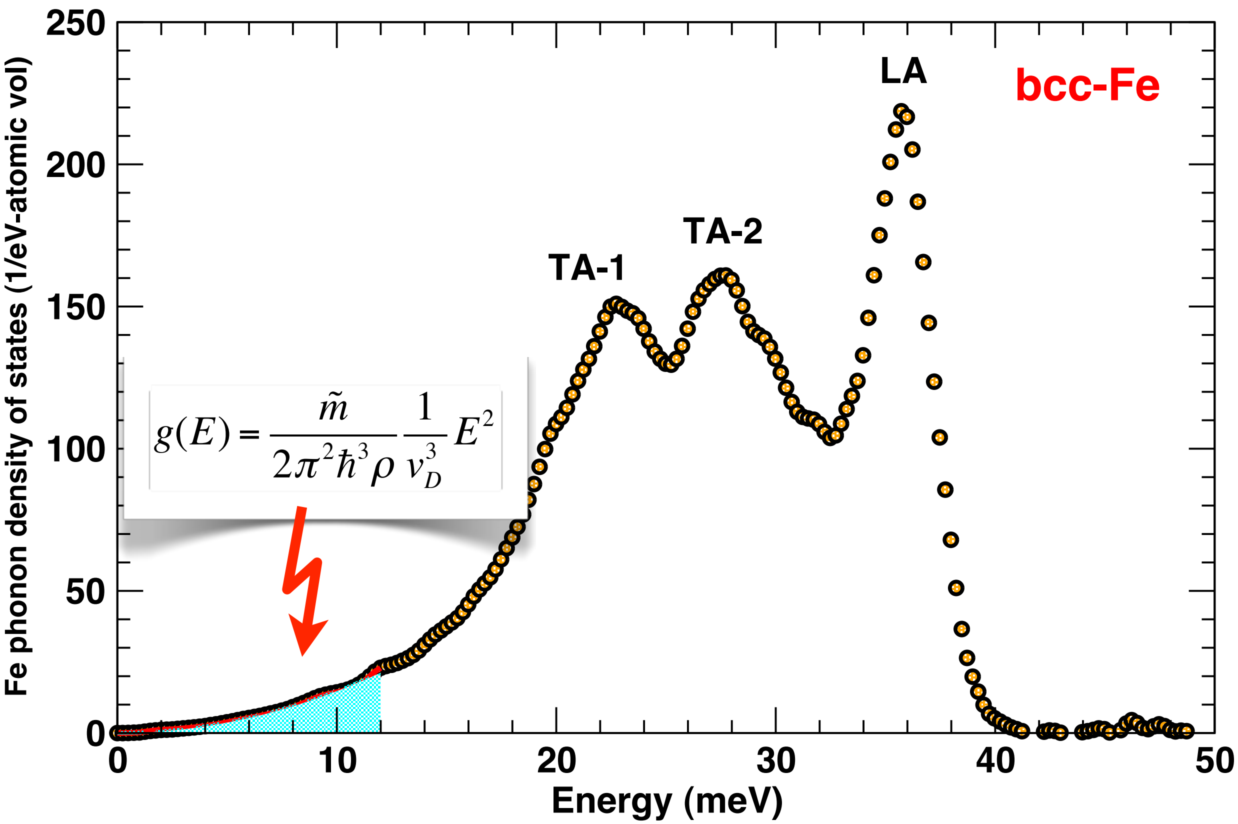
Extraction of phonon density of states





$g(E) = \sum_s \frac{dN_s}{dE} = \frac{VE^2}{\hbar^3} \sum_s \int \frac{1}{v_s^3} d\Omega_q$
$\frac{1}{v_D^3} = \frac{1}{3} \sum_s \int \frac{1}{v_s^3} \frac{d\Omega_q}{4\pi}$
$g(E) = \frac{\tilde{m}}{2\pi^2 \hbar^3 \rho} \frac{1}{v_D^3} E^2$
bcc-Fe
LA
TA-1
TA-2
Fe phonon density of states (1/eV-atomic vol)
Energy (meV)
0
50
100
150
200
250
0
10
20
30
40
50

Measurement of v_D, Debye sound velocity allows to resolve longitudinal and shear sound velocity, provided that bulk modulus and density, is independently and simultaneously measured by x-ray diffraction.



K (GPa)	ρ (g/cc)	V_D (m/s)	V_P (m/s)	V_S (m/s)	G (GPa)
165 ± 1	8.01	3510 ± 12	5813 ± 13	3146 ± 11	79.3 ± 0.6

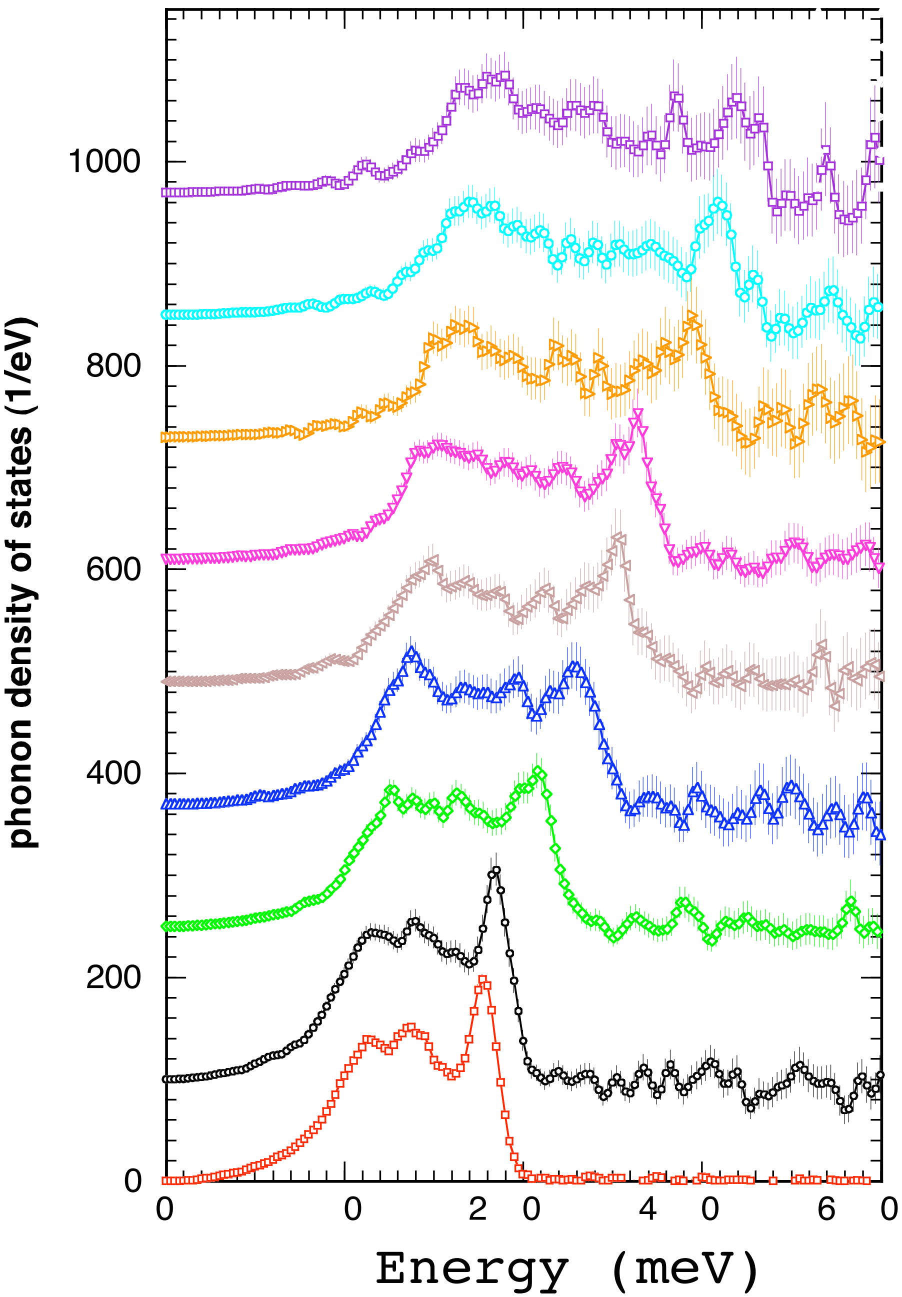
$$\frac{K_S}{\rho} = V_P^2 - \frac{4}{3}V_S^2$$

$$\frac{G}{\rho} = V_S^2$$

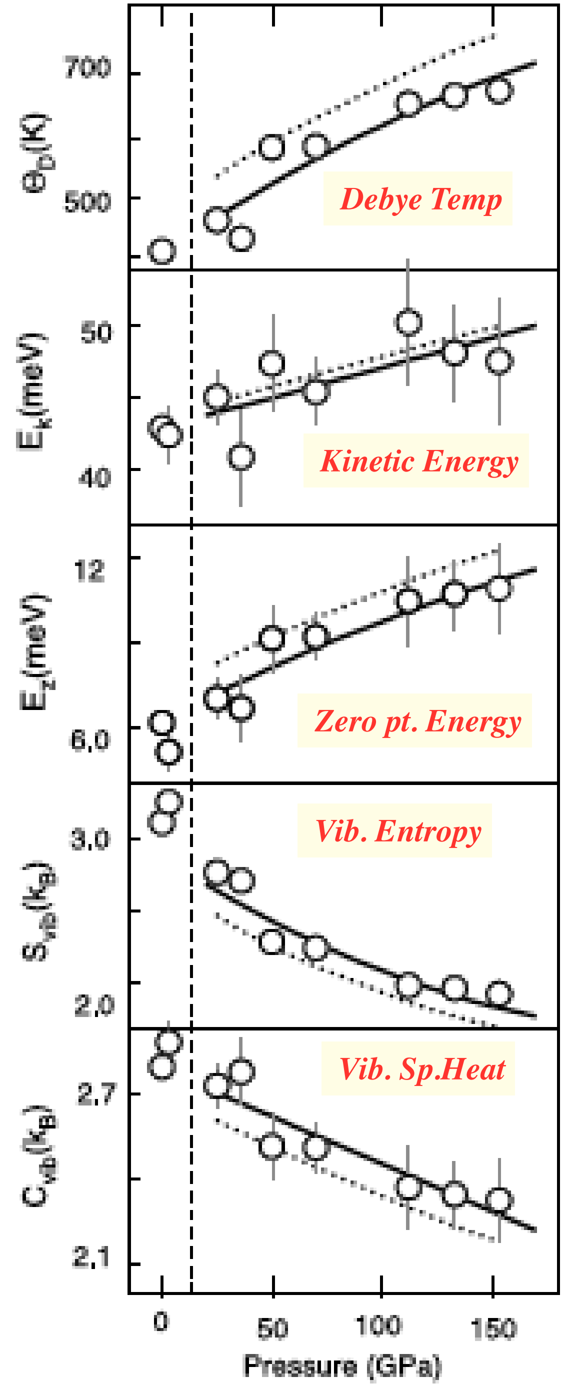
$$\frac{3}{V_D^3} = \frac{1}{V_P^3} + \frac{2}{V_S^3}$$

K_S : adiabatic bulk modulus
G : shear modulus
V_P : compression wave velocity
V_S : shear wave velocity
V_D : Debye sound velocity
Ρ : density

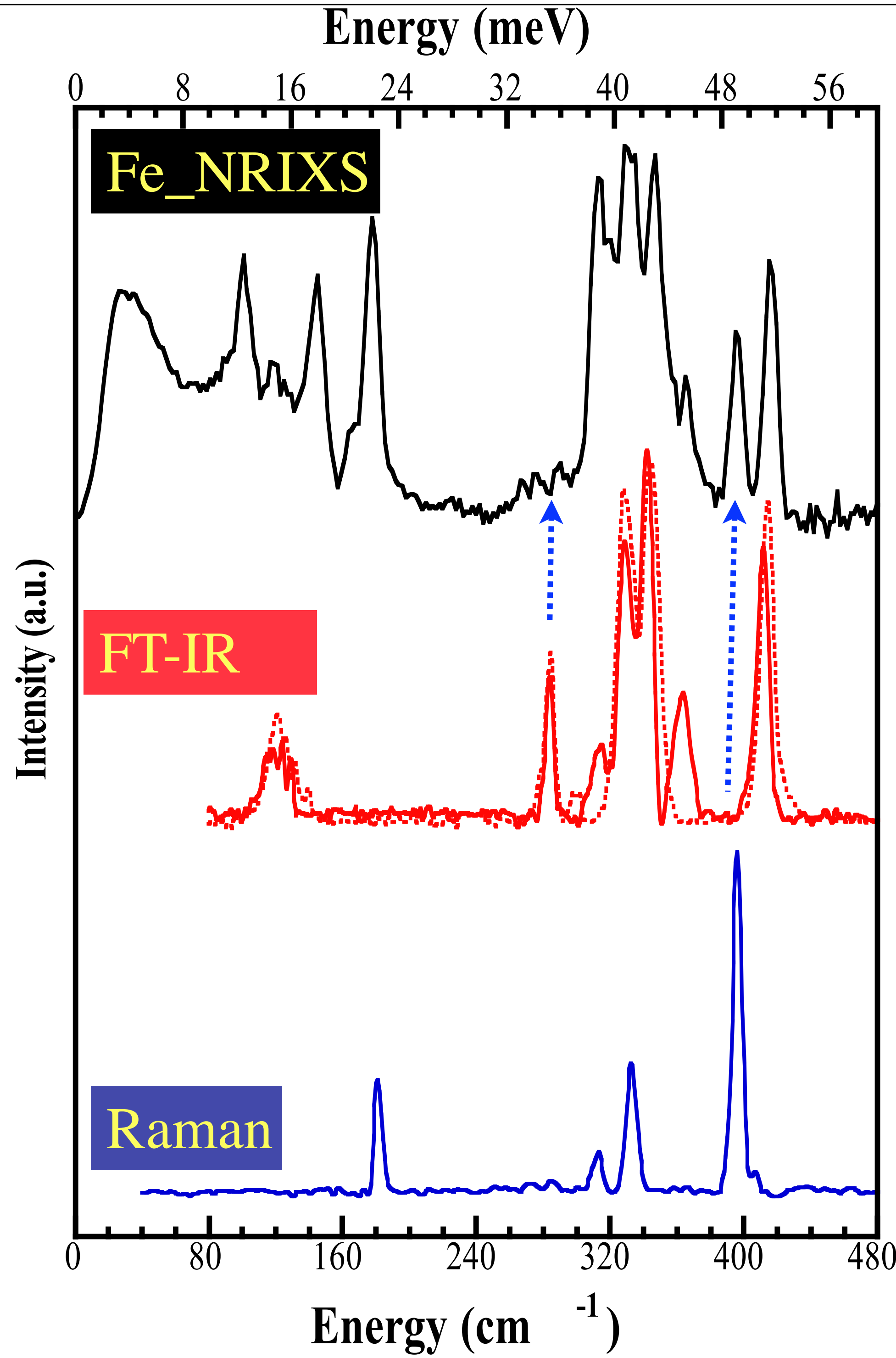
Phonon density of states of iron under high pressure



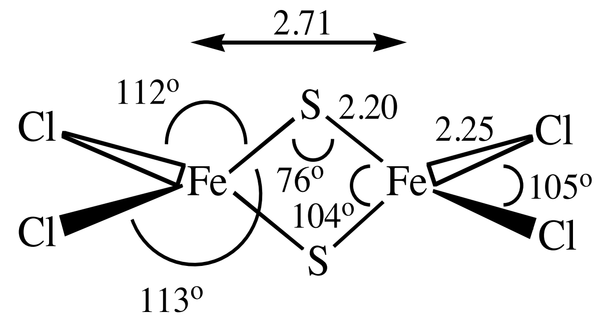
H.K. Mao, et al, Science, 292 (2001) 914



Property	Information content
Lamb-Mössbauer Factor, or recoil-free fraction	$\boldsymbol{f_{LM}}$, recoil free fraction obtained from density of states, $\boldsymbol{g(E)}$: $f_{LM} = \exp\left(-E_R \int \frac{g(E)}{E} \cdot \coth \frac{\beta E}{2} dE\right)$
Second order Doppler shift	$\boldsymbol{\delta_{SOD} = -E_0 \frac{< v^2 >}{2c^2}}$
Average kinetic energy	Extracted from second moment of energy spectrum: $T = \frac{1}{4E_R}\left\langle (E - E_R)^2 \right\rangle$
Average force constant	Extracted from third moment of energy spectrum: $\frac{\partial^2 U}{\partial z^2} = \frac{m}{2\hbar^2}\left\langle E^3 \right\rangle$
Phonon density of states	Extracted one-phonon absorption probability, $\boldsymbol{S_1(E)}$: $g(E) = \frac{E}{E_R} \tanh(\beta E/2)(S_1(E) + S_1(-E))$
Specific heat (vibrational part only)	$C_V = 3k_B \int_0^\infty (\beta E/2)^2 \operatorname{csch}(\beta E)\, g(E) dE$
Vibrational entropy	$S_V = 3k_B \int_0^\infty \left\{ \frac{\beta E}{2} \coth(\beta E) - \ln\left[2\sinh(\beta E)\right] \right\} g(E) dE$
Debye sound velocity (aggregate sound velocity)	From low-energy portion of the density of states: $g(E) = \frac{3V}{2\pi \hbar^3 v_D^3} E^2$
Mode specific vibrational amplitude	Contribution of mode α of atom j to zero-point fluctuation [11,12]: $\left\langle r_{j\alpha}^2 \right\rangle_0 = \frac{\hbar^2}{2m_j \omega_\alpha^2} e_{j\alpha}^2$
Mode specific Gruneisen constant	From pressure dependence of phonon frequencies ω_α of acoustic or optical modes: $\gamma_\alpha = -\frac{\partial \ln \omega_\alpha}{\partial \ln V}$
Temperature of the sample	From detailed balance between phonon occupation probability



$[NEt_4]_2[Fe_2S_2Cl_4]$.

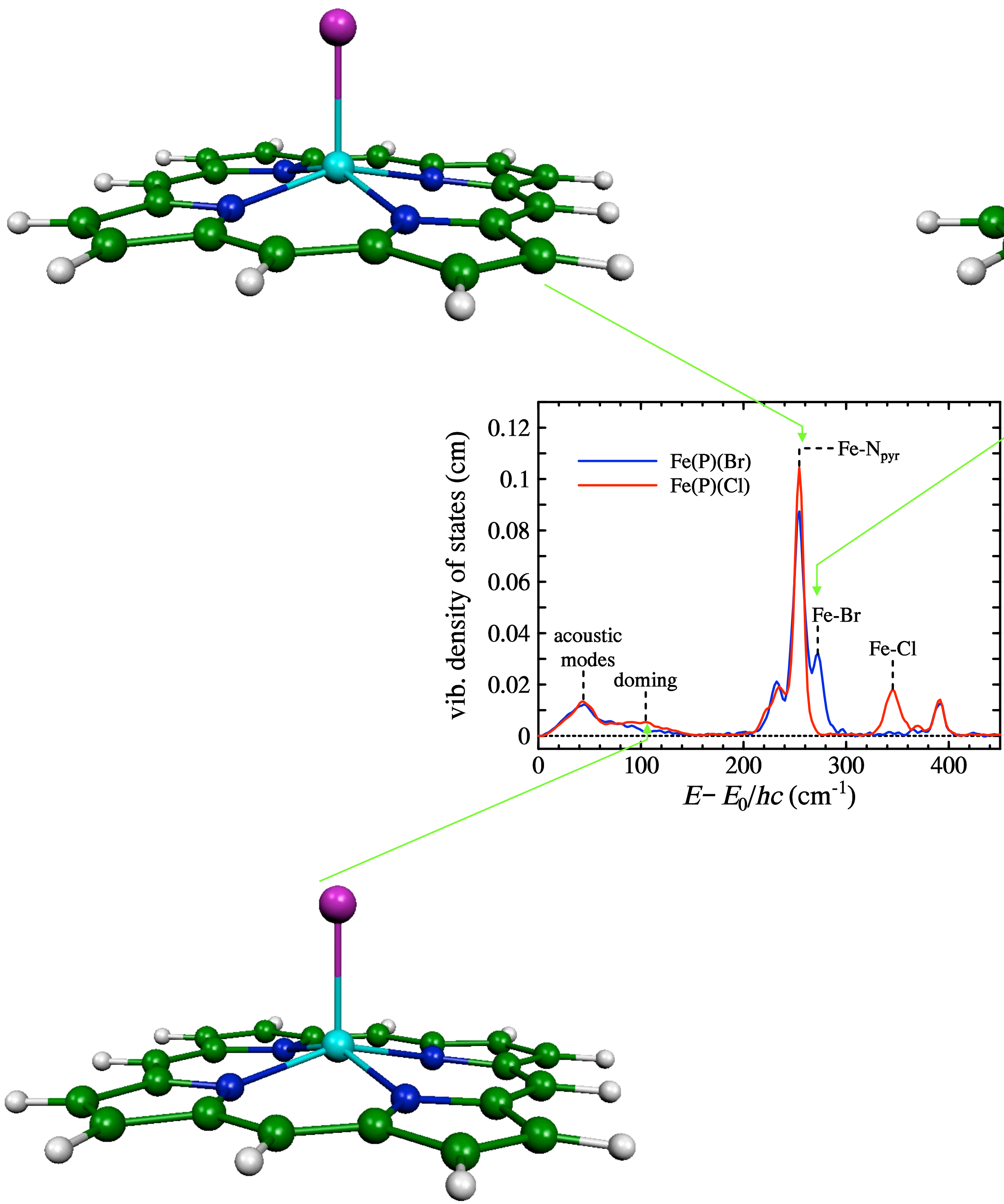


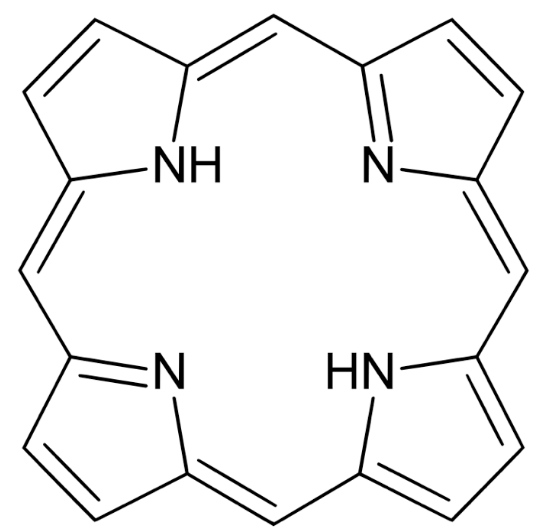
Some unique advantages of NRIXS

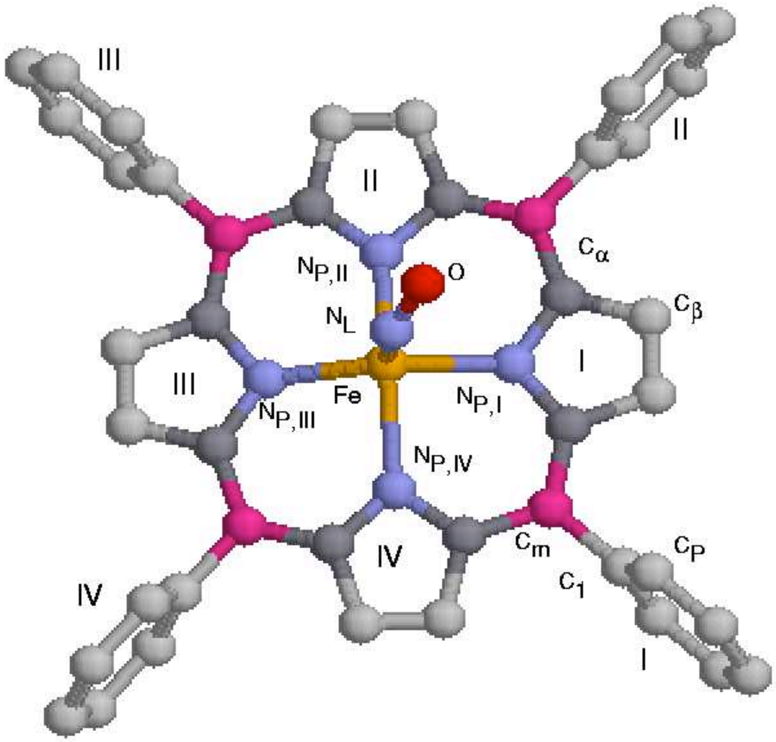
1. Low frequency motions: ~ total mass
2. No selection rule except motion of atoms along x-ray propagation
3. Peak intensity ~ mode participation ~ actual displacement
4. No matrix effects or limitations
5. Element and isotope selective
6. No unpredictable cancellations in scattering terms

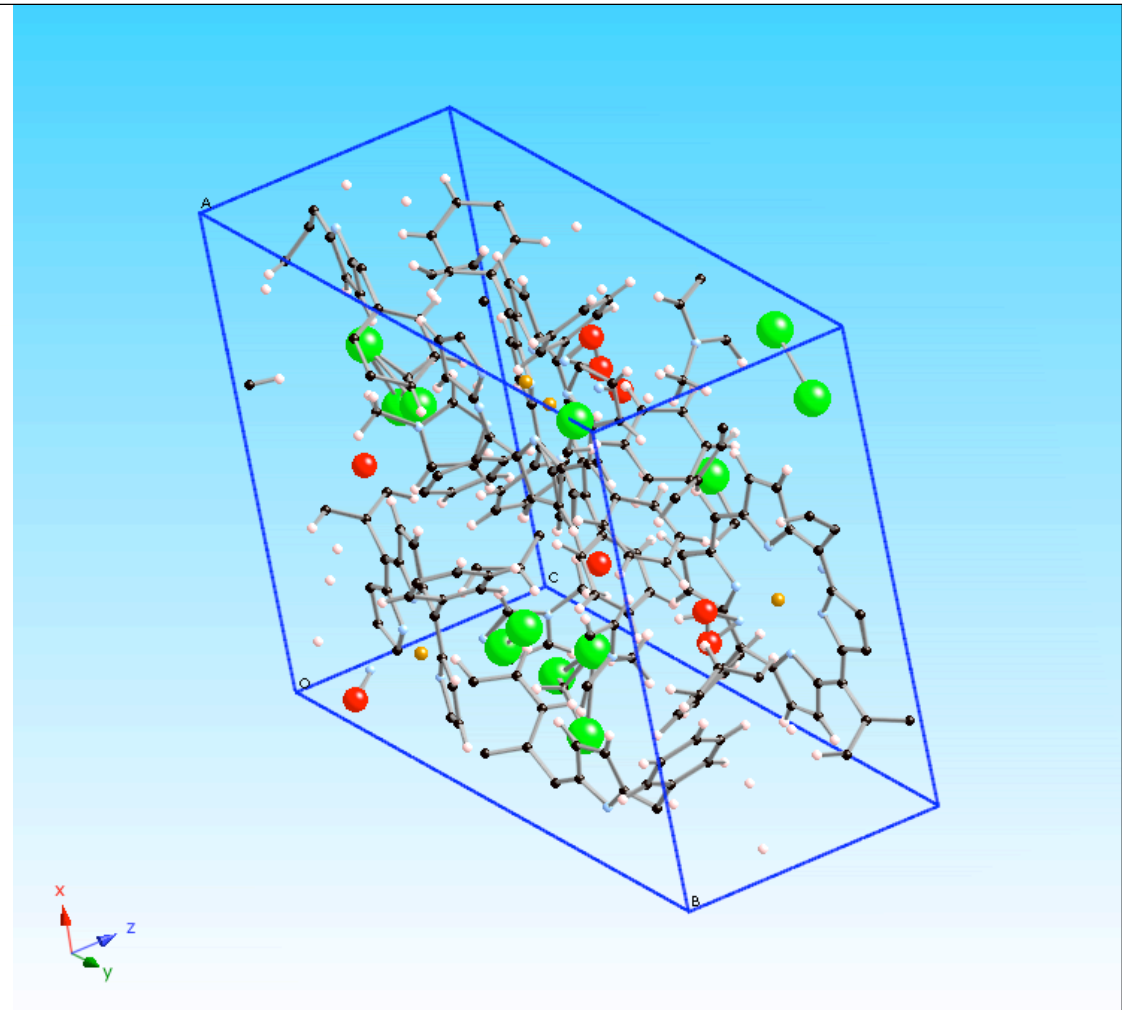
$$\phi_\alpha = \frac{1}{3}\frac{\bar{\nu}_R}{\bar{\nu}_\alpha} e^2_{j\alpha}(\bar{n}_\alpha + 1) f$$

Matt Smith, et al, Inorganic Chemistry, 2005, 44,5562

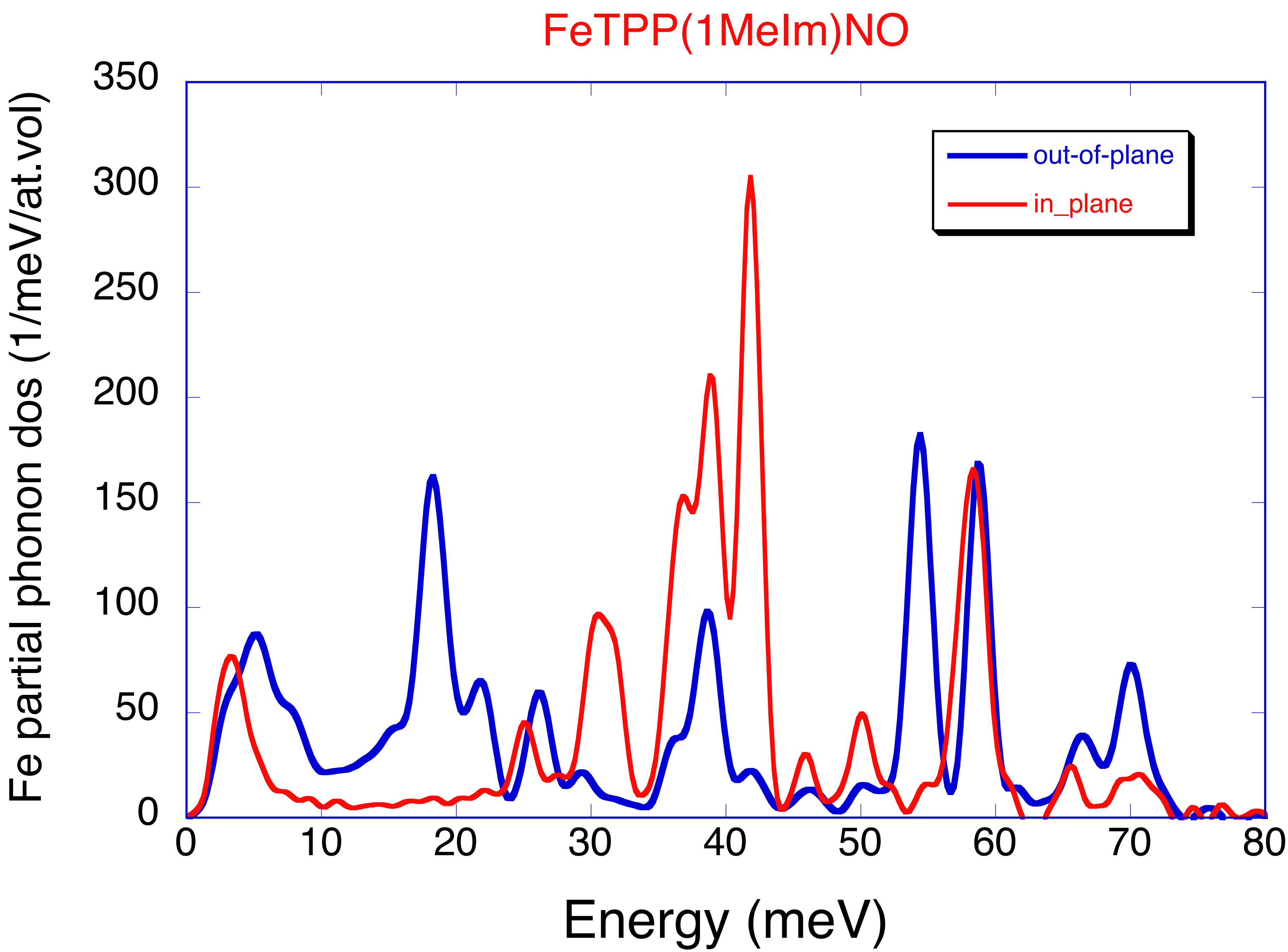

0.12
0.1
0.08
0.06
0.04
0.02
0
vib. density of states (cm)
Fe(P)(Br)
Fe(P)(Cl)
Fe-N$_{pyr}$
Fe-Br
Fe-Cl
acoustic modes
doming
0
100
200
300
400
$E - E_0/hc$ (cm^{-1})


NH
N
N
HN





Porphyrins:	A	B
Tetraphenylporphyrin (TPP)	Phenyl	H
Octaethylporphyrin (OEP)	H	Ethyl


FeTPP(1MeIm)NO
out-of-plane
in_plane
Fe partial phonon dos (1/meV/at.vol)
Energy (meV)
0
50
100
150
200
250
300
350
0
10
20
30
40
50
60
70
80

Materials Science & Physics

B. Roldan Cuenaya	Central Florida University
R. Hermann	Institut fuer Festkoerperforschung
J. Tse	University of Saskatchewan
D. Klug	National Research Council of Canada
R. Mc Queeney	Iowa State University-Ames Lab.
E. Tanis	University of Nevada at Las Vegas
O. Delaire	Oak Ridge National Laboratory
B. Fultz	California Institute of Technology
R. Rohlsberger	HASYLAB-DESY