Phonons by Inelastic X-Ray Scattering

Esen **Ercan** Alp
Advanced Photon Source, Argonne National Laboratory

alp@anl.gov

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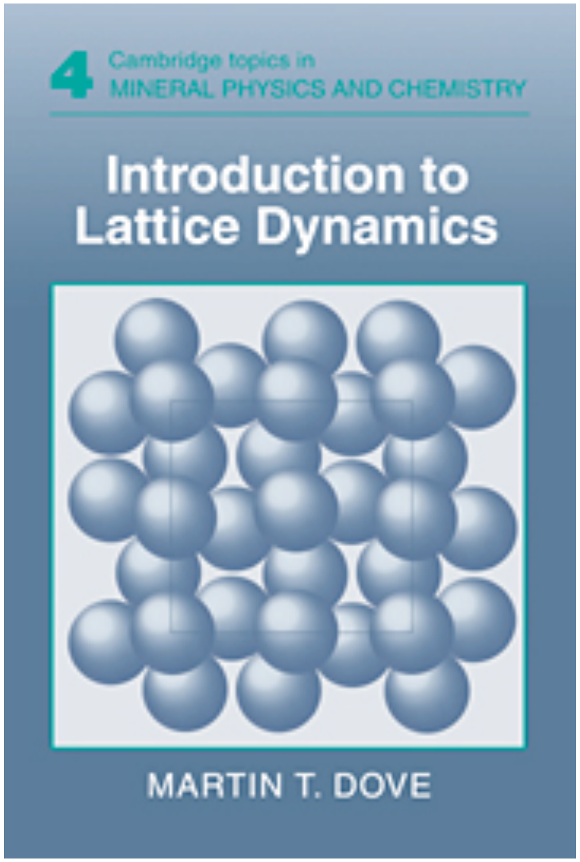
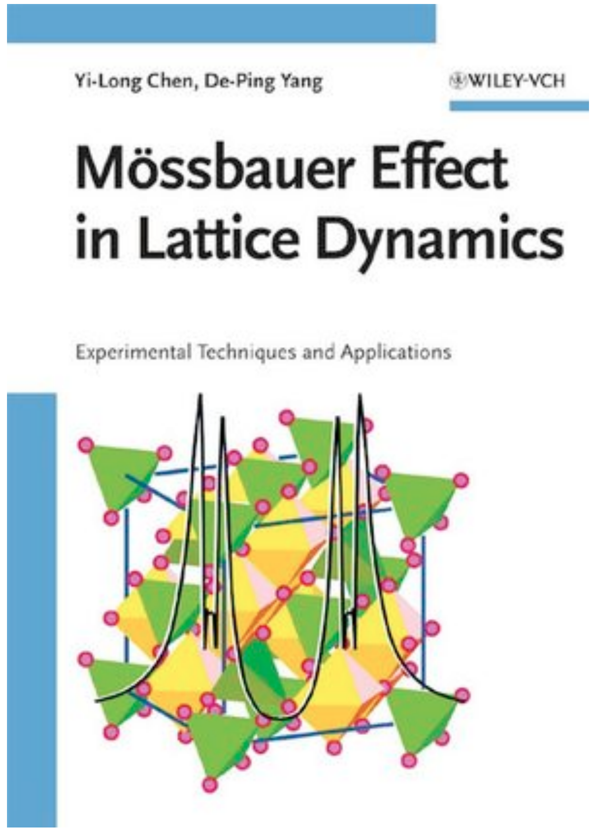
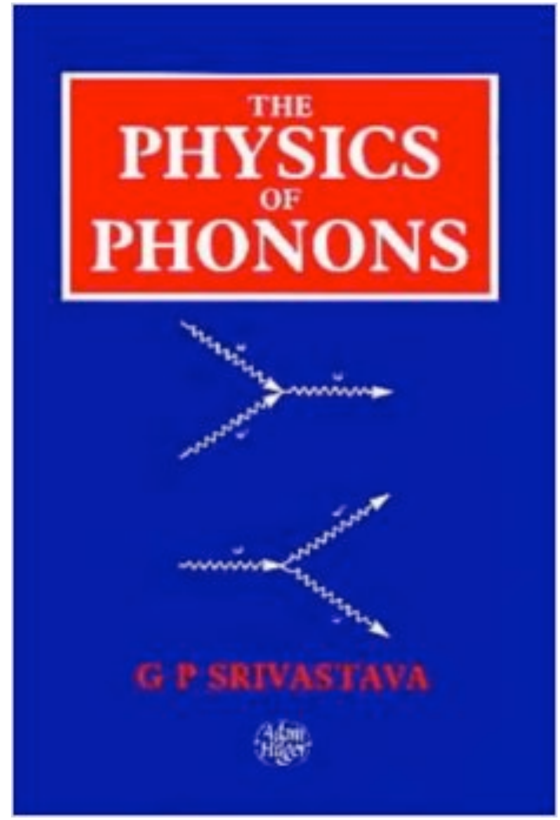
Lattice dynamics for beginners







Lattice dynamics for beginners

Lattice dynamics describes vibrations of atoms in condensed matter:

- crystalline solids
- glasses, and liquids

However, some of the convenience gained by symmetry or periodic lattice is lost for glasses and liquids. Also, effect of surfaces and defects are glowing short-comings of the classical model.

Lattice dynamics is a reflection of forces acting upon atoms and leads to

- sound velocity
- vibrational entropy
- specific heat
- force constant
- compression tensor
- Young's modulus
- stiffness and resilience
- Gruneisen constant
- viscosity

Imagine that you can measure all that for a micron sized sample, at 3 Mbar at 4000 K, in a way that is element selective, or even better isotope selective.

Many experimental techniques exist to study lattice dynamics

- sound velocity, deformation, thermal expansion,heat capacity….
- spectroscopic methods using light, x-rays and neutrons, and electrons
- point contact spectroscopy

Atomic motions are described as harmonic traveling waves, characterized by

- wavelength, λ
- angular frequency, ω
- momentum vector along the direction of propagation, $\vec{k} = \dfrac{\lambda}{2\pi}$

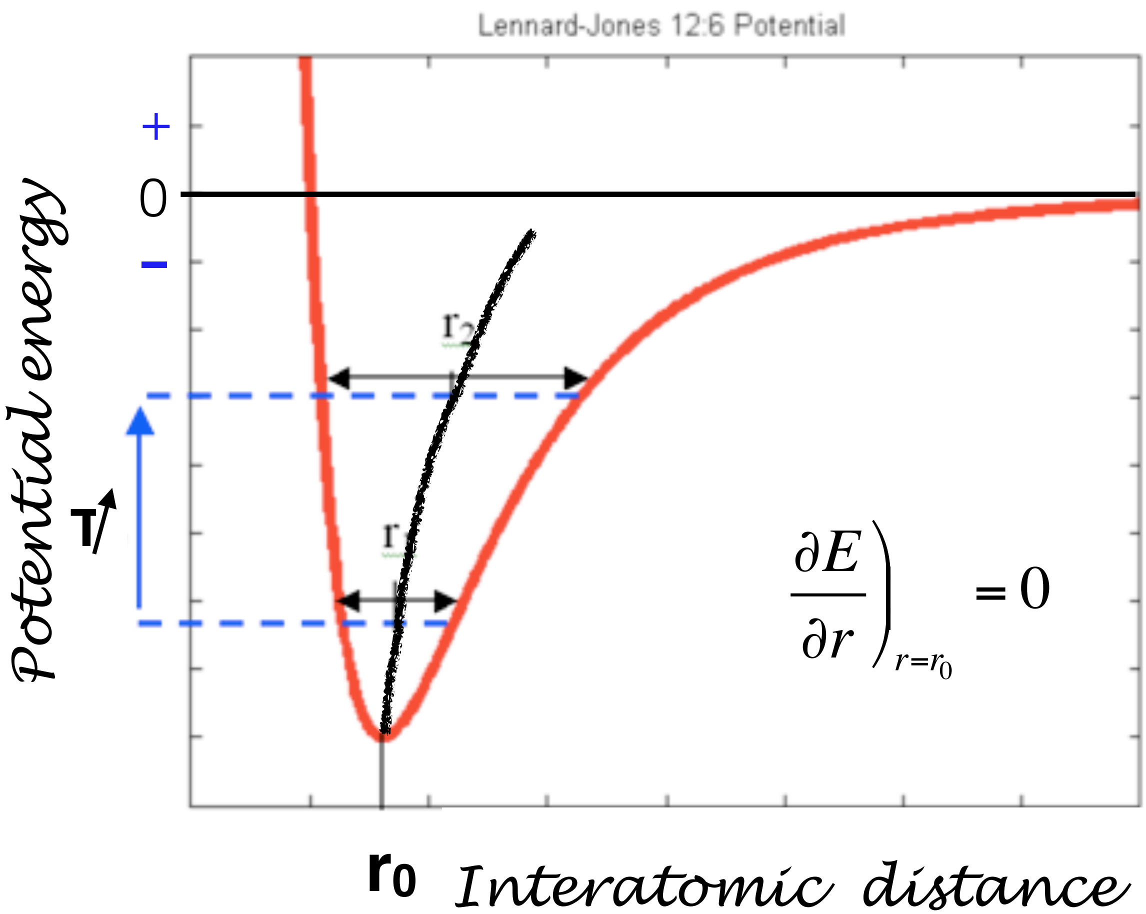
Two main approximations should be noticed:

- **Born-Oppenheimer (adiabiatic) approximation**

  - Motion of atoms are independent and decoupled from the electrons.
  - All electrons follow the nuclei. This can be justified by considering the time scales involved: 10^{-15} s (femto) for electrons, 10^{-12} s (pico) for nuclei

- **Harmonic approximation**

  - At equilibrium, attractive and repulsive forces are balanced.
  - When atoms move away from the equilibrium positions, they are forced to come back by restoring forces.
  - Magnitude of atomic displacements are small compared to interatomic distance.
  - All atoms in equivalent positions in every unit cell move together.



There should be no thermal expansion in the harmonic model.

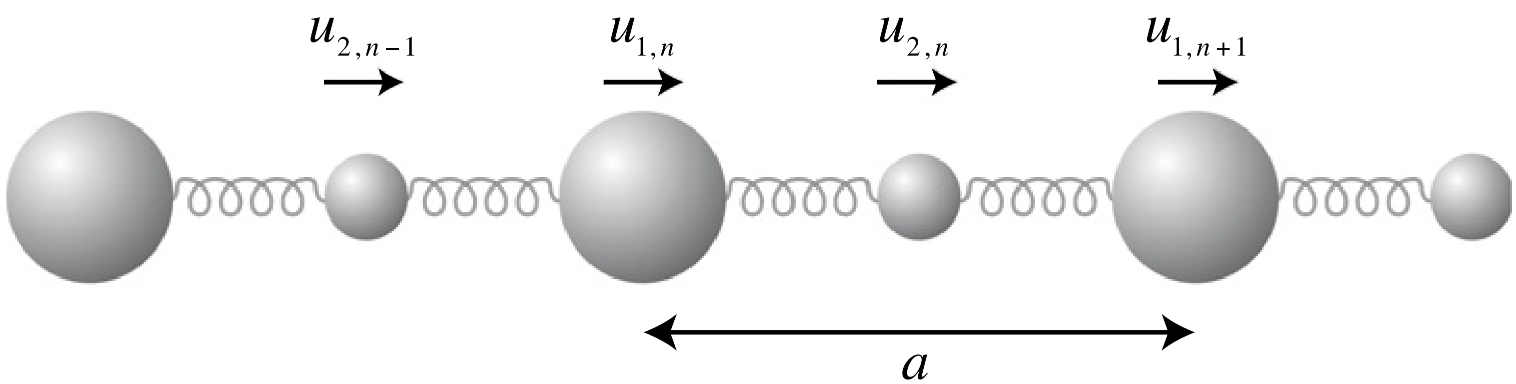
The fact that there is thermal expansion is an indication that the potential under which the atoms move is not harmonic.

However, harmonic model has so many convenient features that we adopt it to explain many features of atomic vibrations.

$$E(r) = E_0 + \frac{1}{2}\left.\frac{\partial^2 E}{\partial r^2}\right|_{r_0}(r-r_0)^2 + \frac{1}{3!}\left.\frac{\partial^3 E}{\partial r^3}\right|_{r_0}(r-r_0)^3 + \frac{1}{4!}\left.\frac{\partial^4 E}{\partial r^4}\right|_{r_0}(r-r_0)^4 + \cdots$$

ignoring these terms is the harmonic approximation

Diatomic infinite 1-D chain



$$\boxed{E = \frac{1}{2} J \sum_n (u_{1,n} - u_{2,n})^2 + \frac{1}{2} J \sum_n (u_{2,n} - u_{1,n+1})^2}$$

$$J = \frac{\partial^2 E}{\partial u_{1,n} \partial u_{2,n}}$$

Force constant (spring constant)

$$\boxed{\begin{aligned} u_{1,n}(t) &= \tilde{u}_1 \exp(i(kna - \omega t)) \\ u_{2,n}(t) &= \tilde{u}_2 \exp(i(kna - \omega t)) \end{aligned}}$$

Time dependent displacement of two atoms
in terms of relative displacement of each atom

$$E_{1,n} = \frac{1}{2}J(u_{1,n} - u_{2,n})^2 + \frac{1}{2}J(u_{1,n} - u_{2,n-1})^2$$

$$E_{2,n} = \frac{1}{2}J(u_{2,n} - u_{1,n})^2 + \frac{1}{2}J(u_{2,n} - u_{1,n+1})^2$$

Energy

$$f_{1,n} = -\frac{\partial E_{1,n}}{\partial u_{1,n}} = -J(u_{1,n} - u_{2,n}) - J(u_{1,n} - u_{2,n-1})$$

$$f_{2,n} = -\frac{\partial E_{2,n}}{\partial u_{2,n}} = -J(u_{2,n} - u_{1,n}) - J(u_{2,n} - u_{1,n+1})$$

Force as derivative of energy

$$\ddot{u}_{1,n}(t) = -\omega^2 \tilde{u}_1 \exp i\,(kna - \omega t) = -\omega^2 u_{1,n}(t)$$

$$\ddot{u}_{2,n}(t) = -\omega^2 \tilde{u}_2 \exp i\,(kna - \omega t) = -\omega^2 u_{2,n}(t)$$

Acceleration

$$m_1 \ddot{u}_{1,n}(t) = -m_1 \omega^2 u_{1,n}(t) = -J(2u_{1,n}(t) - u_{2,n}(t) - u_{2,n-1}(t))$$

$$m_2 \ddot{u}_{2,n}(t) = -m_2 \omega^2 u_{2,n}(t) = -J(2u_{2,n}(t) - u_{1,n}(t) - u_{1,n+1}(t))$$

Newton's eq^n of motion

$$e_1 = m_1^{1/2}\tilde{u}_1; \quad e_2 = m_2^{1/2}\tilde{u}_2$$

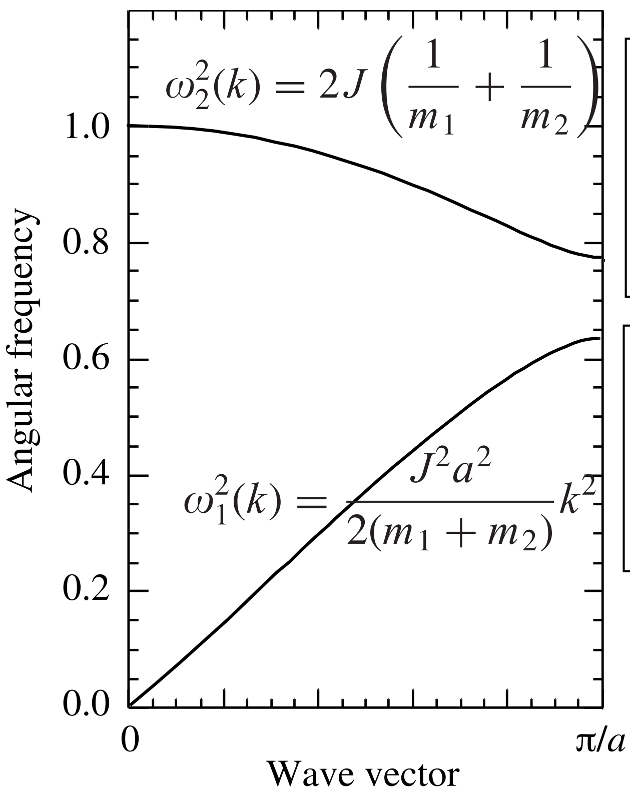
Mass normalized displacements (real)

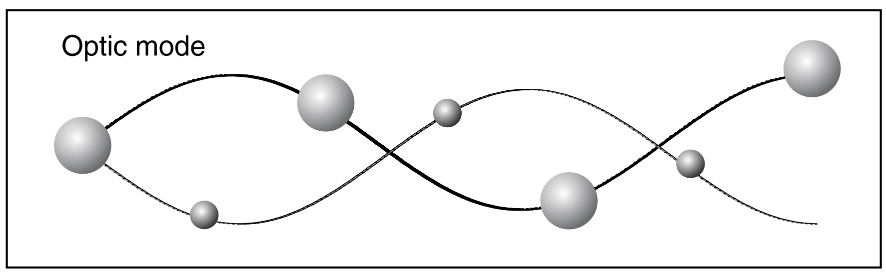
$$\omega^2 \begin{pmatrix} e_1 \\ e_2 \end{pmatrix} = \mathbf{D}(k) \cdot \begin{pmatrix} e_1 \\ e_2 \end{pmatrix}$$

Matrix form of Newton's eq^{n} of motion

$$\mathbf{D}(k) = \begin{pmatrix} 2J/m_1 & -J\left(1+\exp(-ika)\right)/\sqrt{m_1 m_2} \\ -J\left(1+\exp(+ika)\right)/\sqrt{m_1 m_2} & 2J/m_2 \end{pmatrix}$$

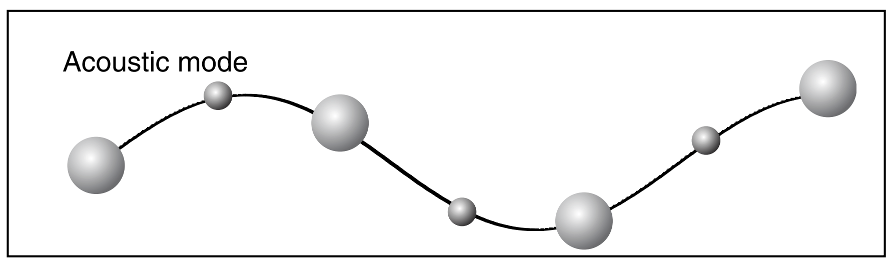
Eigen solutions





out-of-phase

$$m_1^{1/2} e_1 = -m_2^{1/2} e_2$$



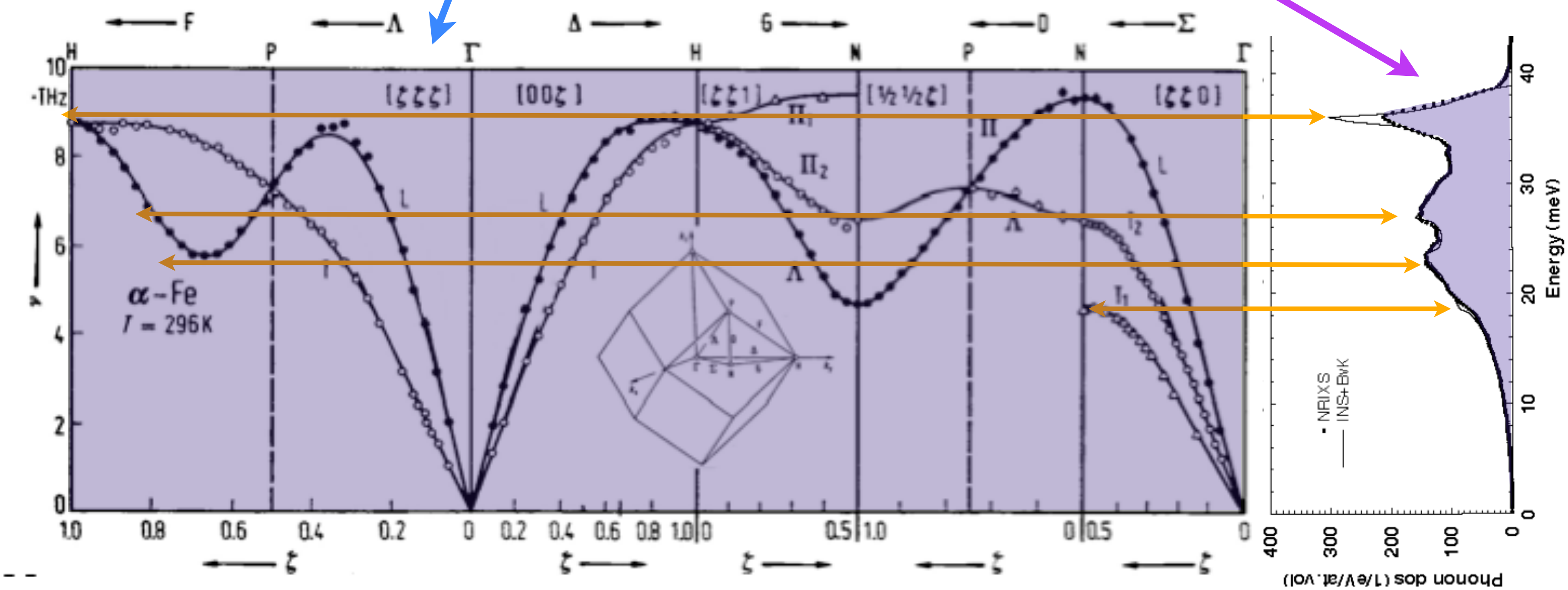
$$m_1^{-1/2} e_1 = m_2^{-1/2} e_2$$

in-phase

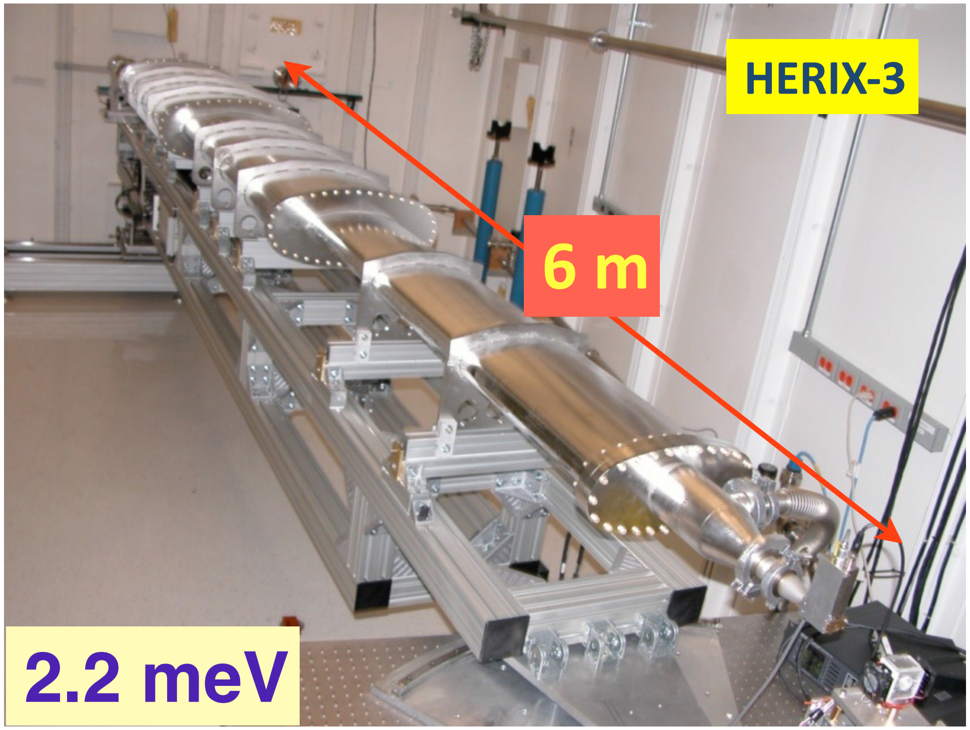
Inelastic X-Ray Scattering: A plethora of different techniques

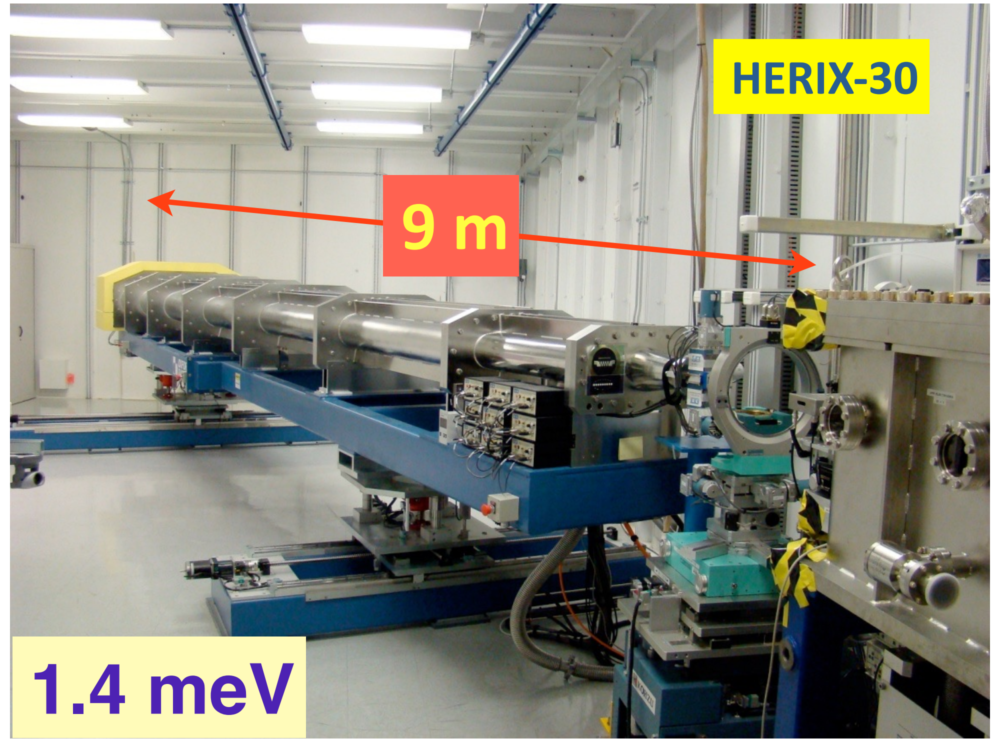
IXS

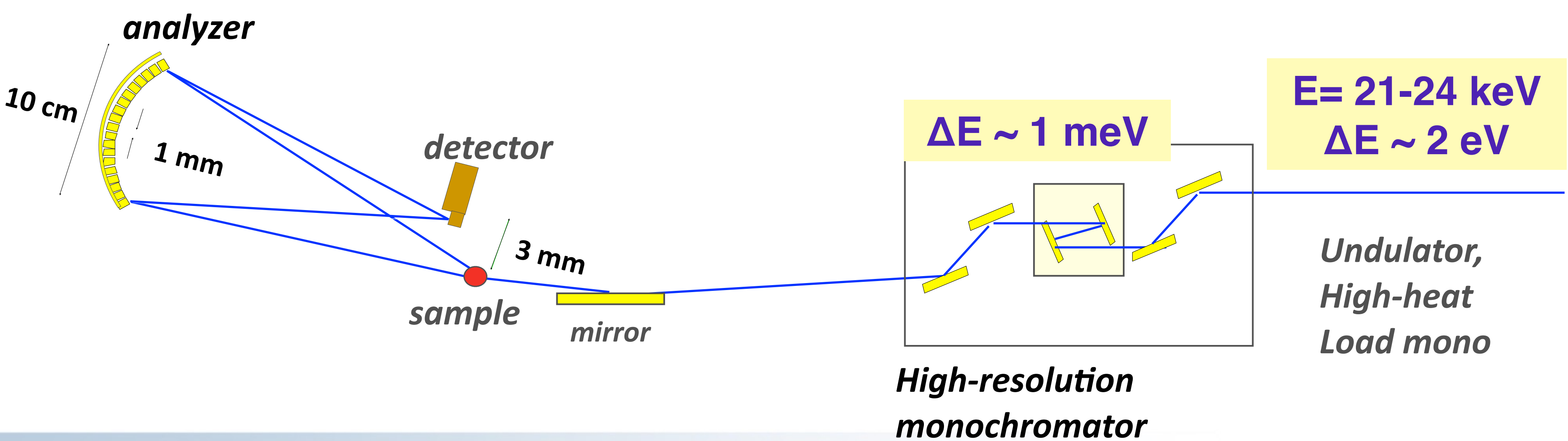
- **Non-Resonant**
  - **ΔE ~ meV**
    IXS
- **Resonant**
  - **ΔE ~ 1 meV**
    Nuclear resonant

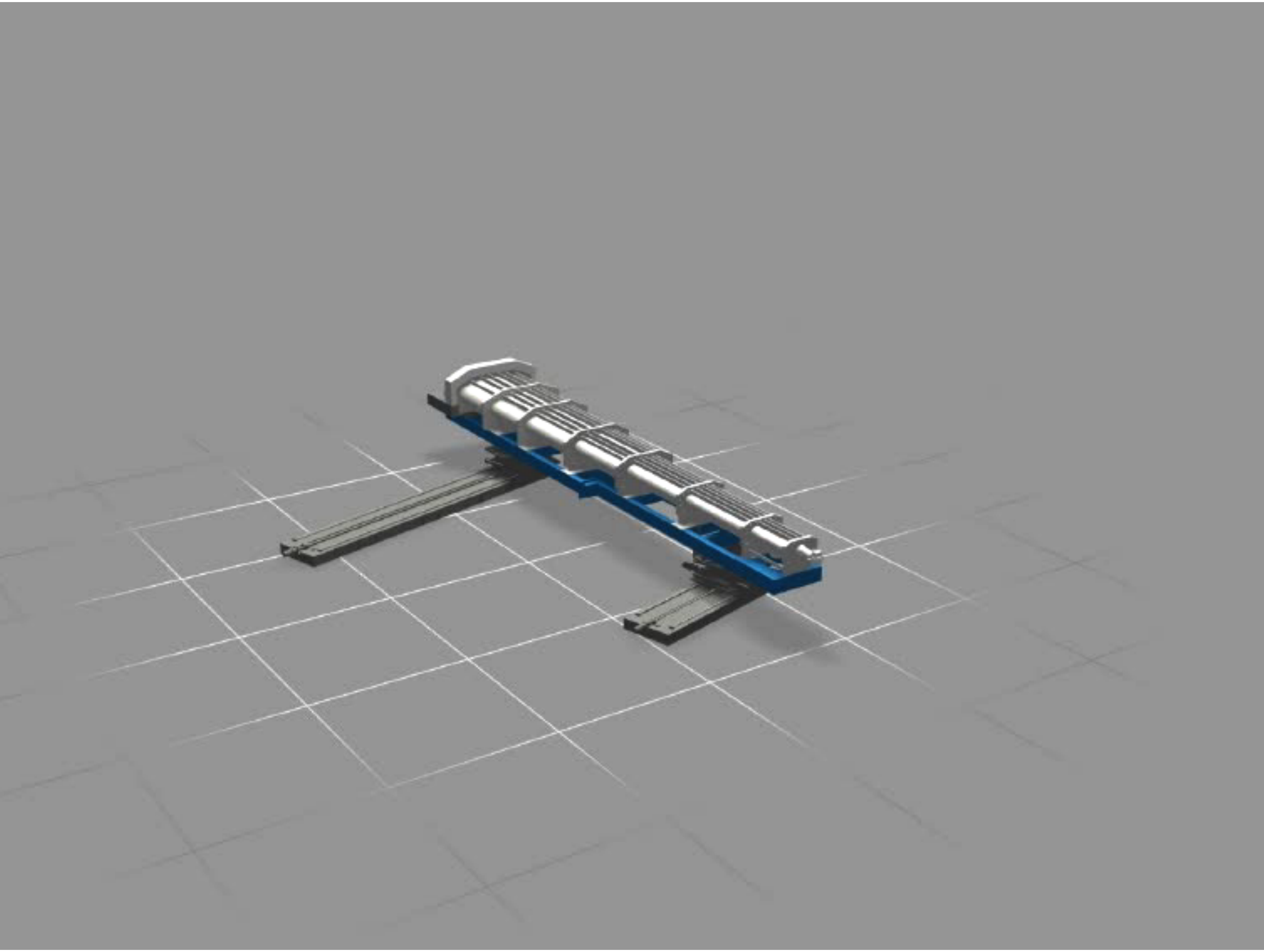


HERIX-3 and HERIX-30









What is being measured ?

$$\frac{d^2\sigma}{d\Omega\, d\omega} = \underbrace{r_0^2 \frac{\omega_f}{\omega_i} \left|\mathbf{e}_i \cdot \mathbf{e}_f\right|}_{\text{Thomson cross section}} \underbrace{N \sum_{i,f} \left| \left\langle i \middle| \sum e^{i\mathbf{Q}\mathbf{r}_\mathbf{j}} \middle| f \right\rangle \right|^2 \delta(E_f - E_i - \hbar\omega)}_{\text{Dynamical structure factor } S(Q,w)}$$

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

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

Atomic form factor

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

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

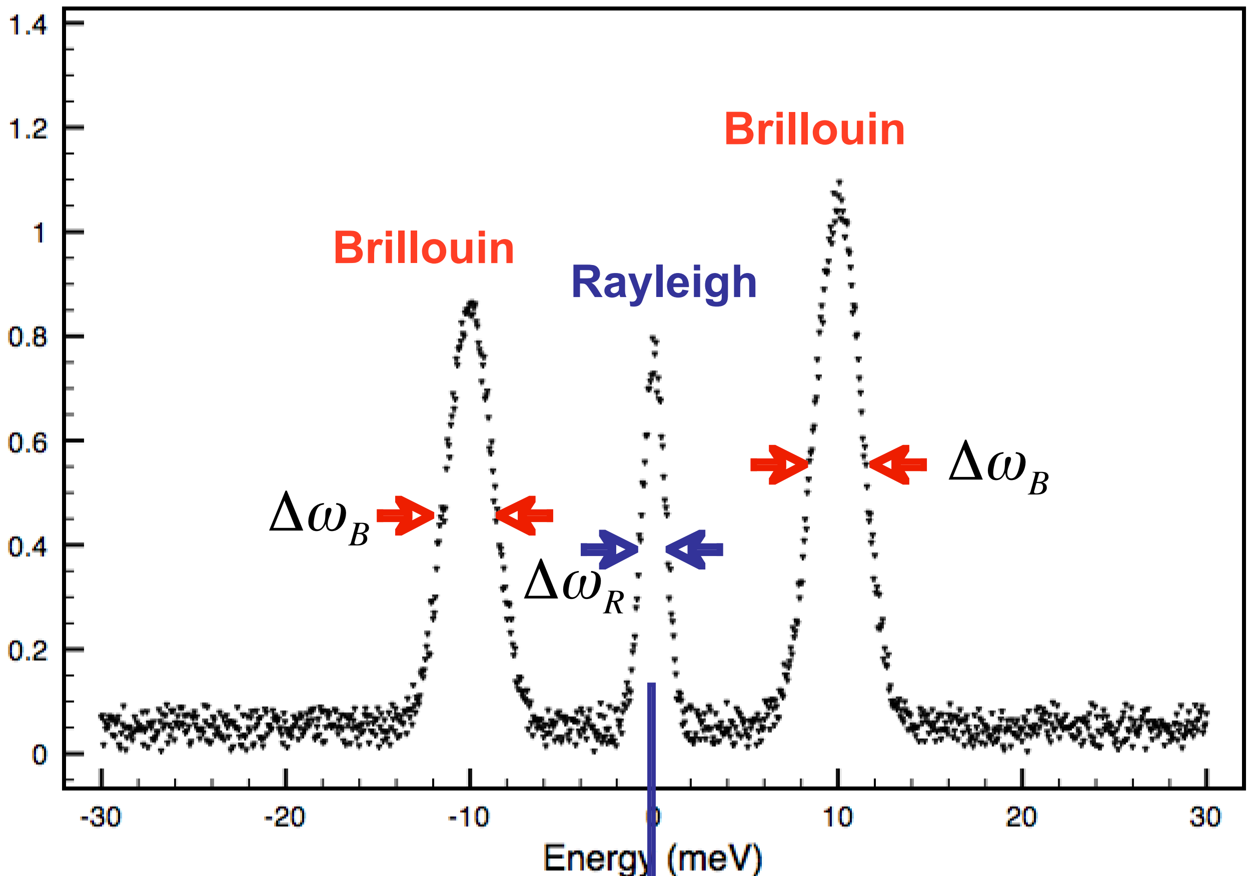
Phase of the scattering amplitude

phonon frequency

Polarization factor between momentum transfer and phonon's polarization vector

delta-function in ω

External probe-photon



$\omega - \omega_B$ $\omega + \omega_B$

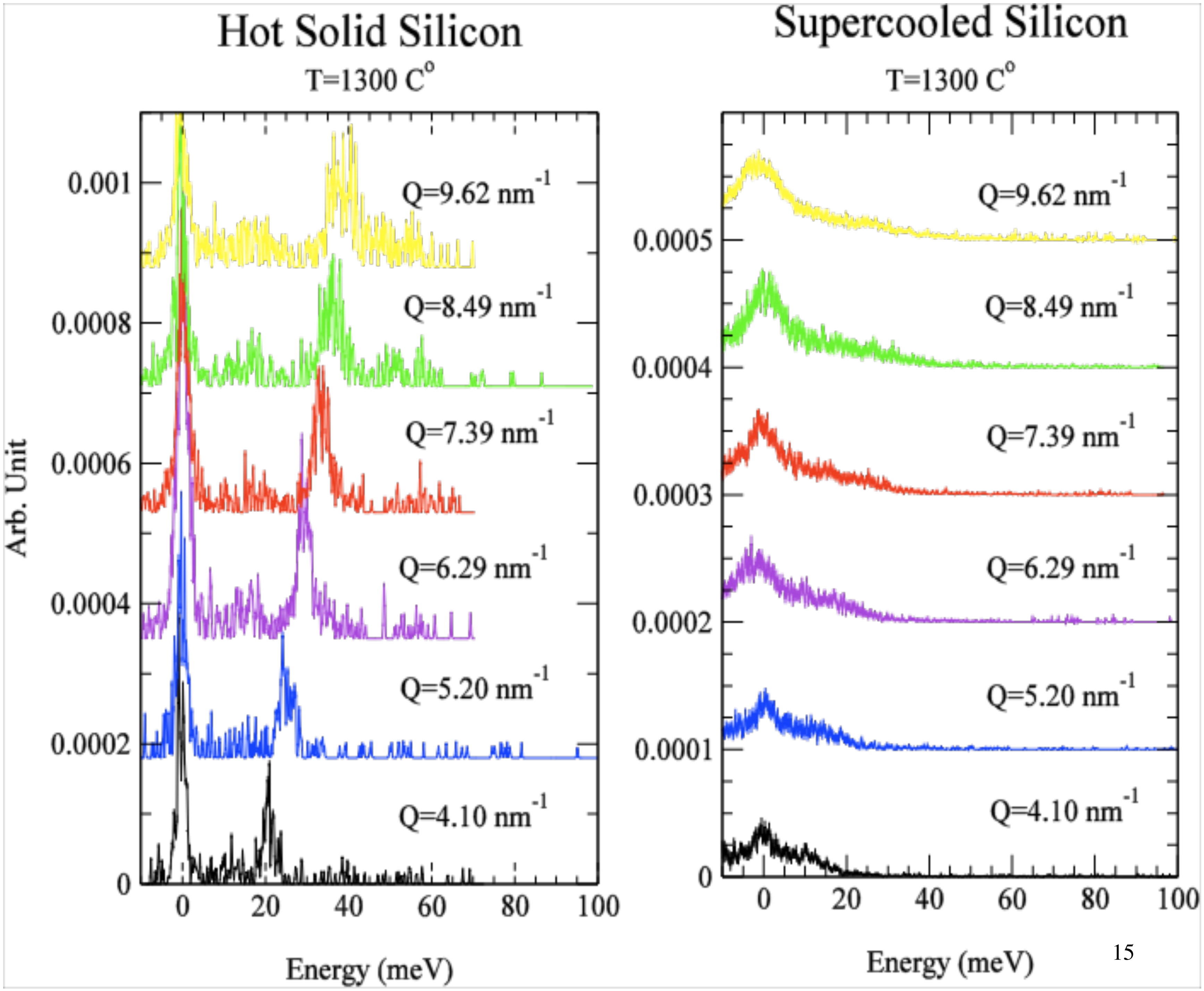
Entropy fluctuations, $\Delta\omega_R \sim \alpha q^2$

Concentration fluctuations $\Delta\omega_R \sim D q^2$

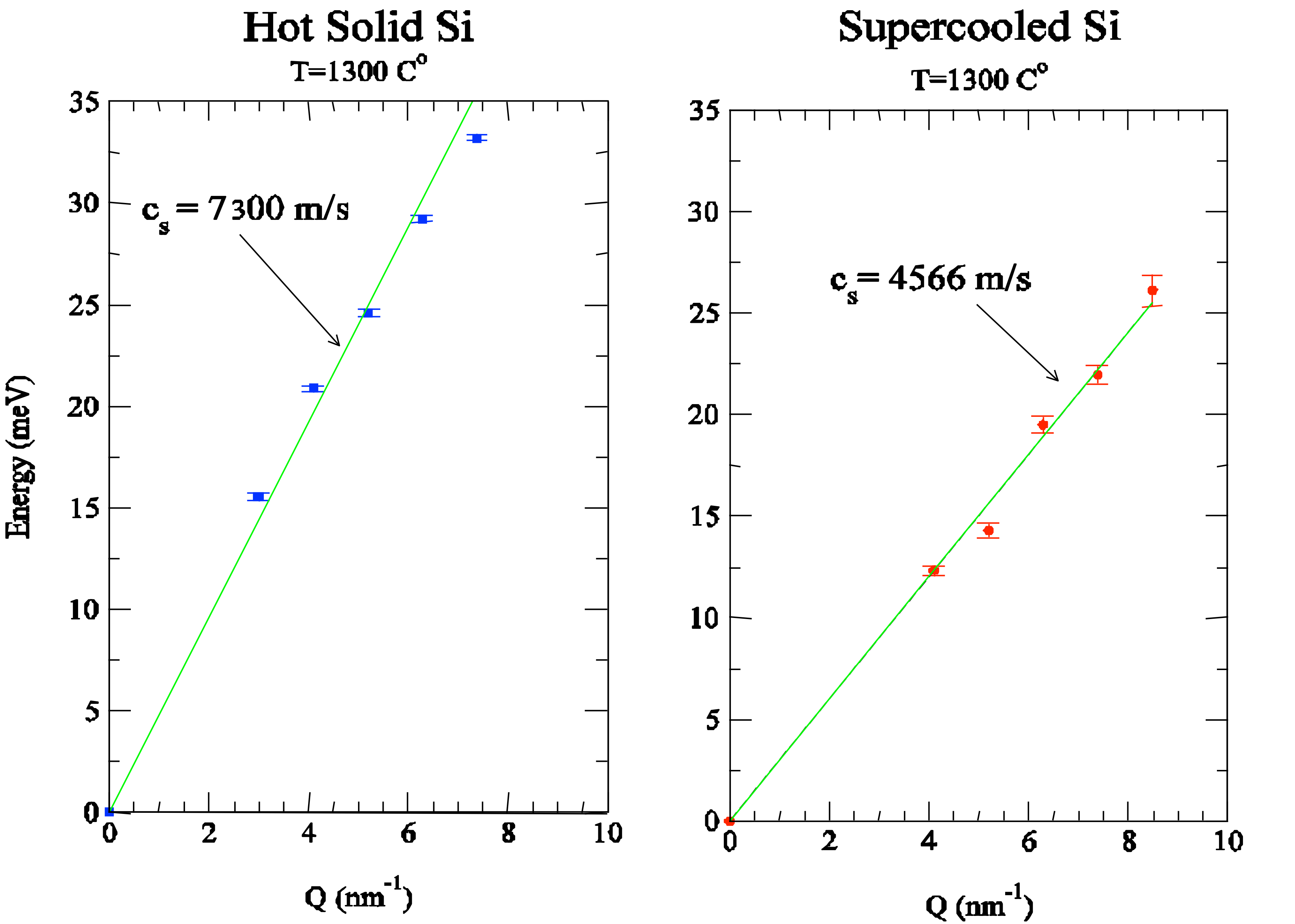
Pressure fluctuations

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

$$\Delta\omega_B \sim V q^2$$



Hot Solid Silicon
T=1300 C°
Supercooled Silicon
T=1300 C°
Q=9.62 nm-1
Q=8.49 nm-1
Q=7.39 nm-1
Q=6.29 nm-1
Q=5.20 nm-1
Q=4.10 nm-1
Arb. Unit
0.001
0.0008
0.0006
0.0004
0.0002
0
0.0005
0.0004
0.0003
0.0002
0.0001
0
0
20
40
60
80
100
Energy (meV)
Energy (meV)


Hot Solid Si
T=1300 C°
c_s = 7300 m/s
Energy (meV)
Q (nm^-1)
35
30
25
20
15
10
5
0
0
2
4
6
8
10
Supercooled Si
T=1300 C°
c_s = 4566 m/s
Q (nm^-1)

Where is quantum mechanics in all of this?

$$E_{1,n} = \frac{1}{2}J(u_{1,n} - u_{2,n})^2 + \frac{1}{2}J(u_{1,n} - u_{2,n-1})^2$$

$$E_{2,n} = \frac{1}{2}J(u_{2,n} - u_{1,n})^2 + \frac{1}{2}J(u_{2,n} - u_{1,n+1})^2$$

Diatomic model

$$E = \frac{1}{4}\sum_{n,n'}\sum_{j,j'}\phi_{n,n'}^{j,j'}\left(u_{j,n} - u_{j',n'}\right)^2 = \frac{1}{2}\sum_{n,n'}\sum_{j,j'}u_{j,n}\Phi_{n,n'}^{j,j'}u_{j',n'}$$

Generalized model

j, j': atoms in the unit cell

n, n': unit cells in the crystal

$\phi_{j,j'}^{n,n'}$: differential of individual bond energy with respect to displacement

$\Phi_{j,j'}^{n,n'}$: differential of overall bond energy of all lattice

$$\boxed{u_{j\ell}(t) = \frac{1}{\sqrt{Nm_j}} \sum_{\mathbf{k},\lambda} \mathbf{e}_{\mathbf{k},\lambda} \exp(i\mathbf{k}\cdot\mathbf{r}_{j\ell})\, Q(\mathbf{k},\lambda,t)}$$

Fourier relationship between real space and time and reciprocal space and time

$\mathbf{e}_{\mathbf{k},\lambda}$: mode eigenvector

$Q(\mathbf{k},\lambda,t)$: normal mode coordinate

$$\boxed{\dot{u}_{j\ell}(t) = \frac{-i}{\sqrt{Nm_j}} \sum_{\mathbf{k},\lambda} \omega_{\mathbf{k},\lambda}\mathbf{e}_{\mathbf{k},\lambda} \exp(i\mathbf{k}\cdot\mathbf{r}_{j\ell})\, Q(\mathbf{k},\lambda,t)}$$

Velocity

$$\boxed{\frac{1}{2}\sum_{j,\ell} m_j \left|\dot{\mathbf{u}}_{j\ell}\right|^2 = \frac{1}{2}\sum_{\mathbf{k},\lambda} \omega^2_{\mathbf{k},\lambda} \left|Q\left(\mathbf{k},\lambda\right)\right|^2}$$

Kinetic energy

$$\boxed{\frac{1}{2}\sum_{\substack{j,j'\\ \ell,\ell'}} \mathbf{u}^T_{j\ell}\cdot\Phi^{j,j'}_{\ell,\ell'}\cdot\mathbf{u}_{j'\ell'} = \frac{1}{2}\sum_{\mathbf{k},\lambda} \omega^2_{\mathbf{k},\lambda} \left|Q\left(\mathbf{k},\lambda\right)\right|^2}$$

Potential energy (via Virial theorem)

$$\boxed{\frac{1}{2}\sum_{j,\ell} m_j \left|\dot{\mathbf{u}}_{j\ell}\right|^2 + \frac{1}{2}\sum_{\substack{j,j'\\ \ell,\ell'}} \mathbf{u}^T_{j\ell}\cdot\Phi^{j,j'}_{\ell,\ell'}\cdot\mathbf{u}_{j'\ell'} = \sum_{\mathbf{k},\lambda} \omega^2_{\mathbf{k},\lambda} \left|Q\left(\mathbf{k},\lambda\right)\right|^2.}$$

Total energy, in terms of normal mode coordinates

$$\boxed{\omega^2 \mathbf{e} = \mathbf{D}(\mathbf{k}) \cdot \mathbf{e} \quad \Rightarrow \quad \omega^2 = \mathbf{e}^{\mathrm{T}} \cdot \mathbf{D}(\mathbf{k}) \cdot \mathbf{e}}$$

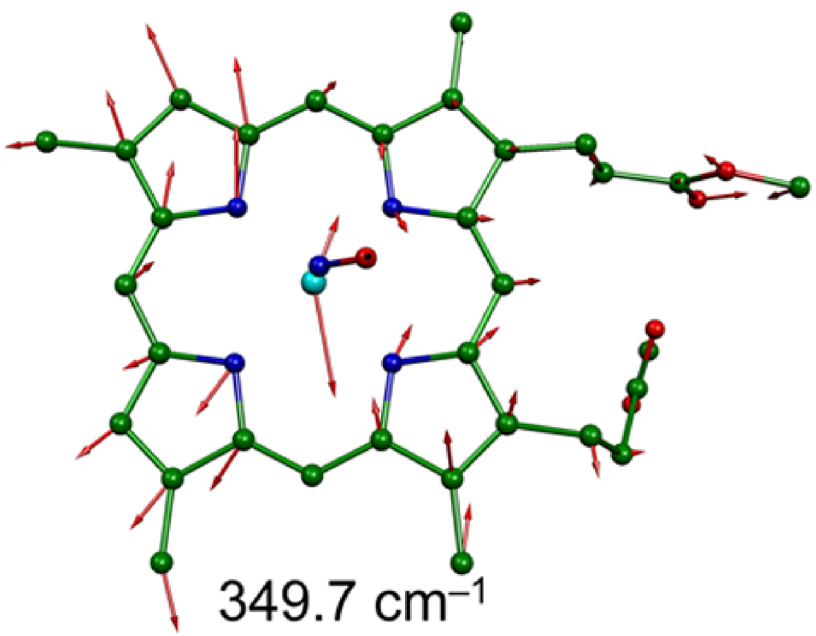
Eigenvalue eq^n.

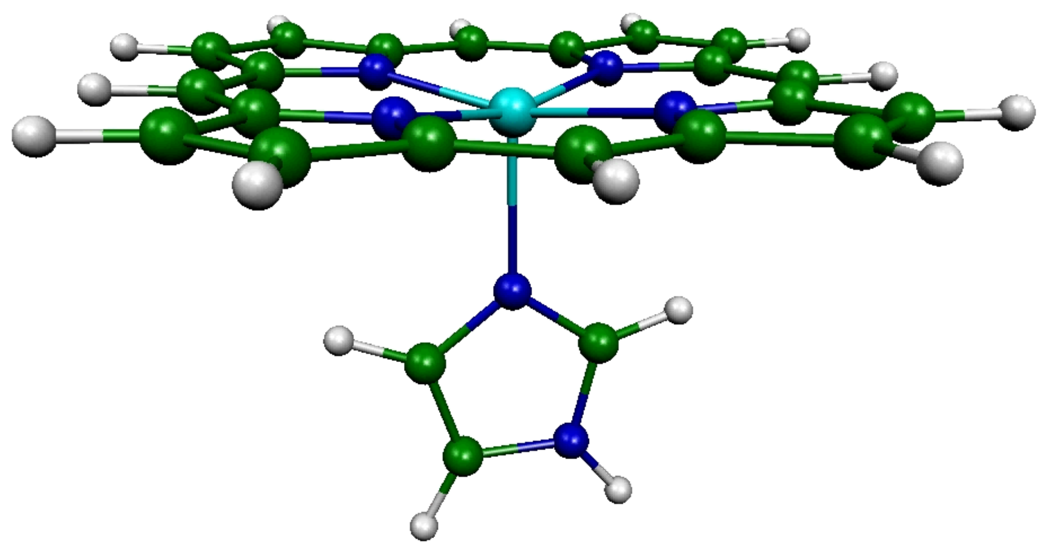
$$\boxed{D_{j,j'}(\mathbf{k}) = \frac{1}{\sqrt{m_j m_{j'}}} \sum_{n'} \Phi_{0,n'}^{j,j'} \exp\left(i\mathbf{k} \cdot (\mathbf{r}_{j,0} - \mathbf{r}_{j',n'})\right)}$$

Dynamical matrix

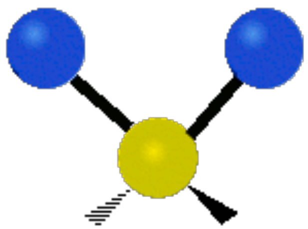
$$\boxed{\mathbf{e}_\lambda^{\mathrm{T}} \cdot \mathbf{e}_\lambda = 1; \quad \mathbf{e}_{\lambda'}^{\mathrm{T}} \cdot \mathbf{e}_\lambda = \delta_{\lambda',\lambda}}$$

Eigenvalues are orthonormal..

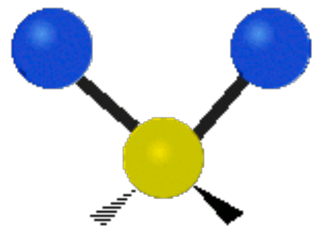




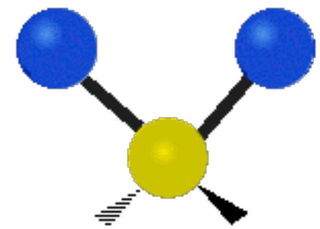
symmetrical stretching



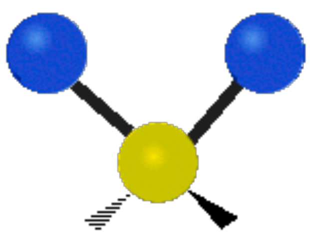
asymmetrical stretching



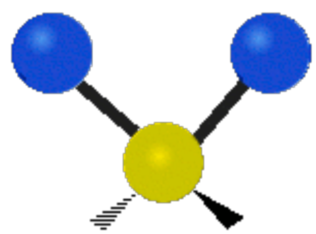
scissoring



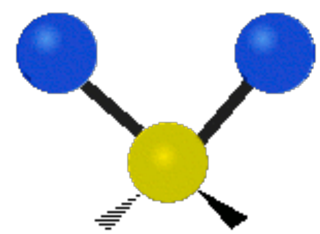
rocking

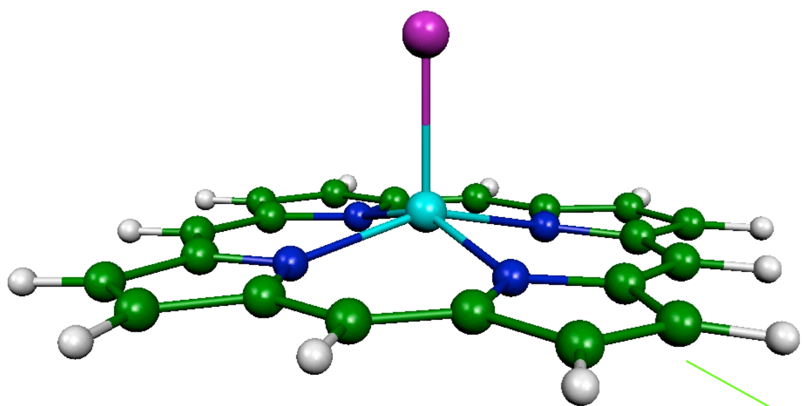


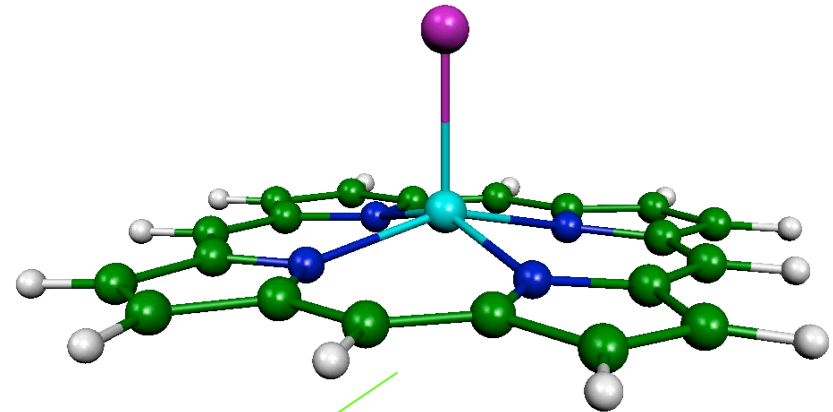
wagging

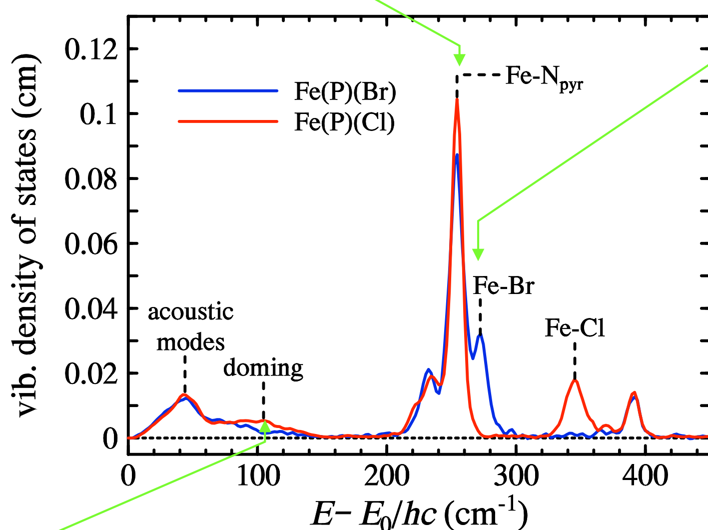


twisting

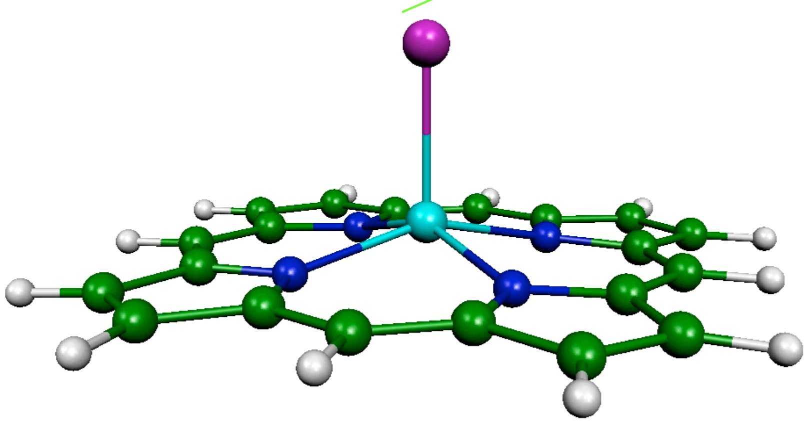


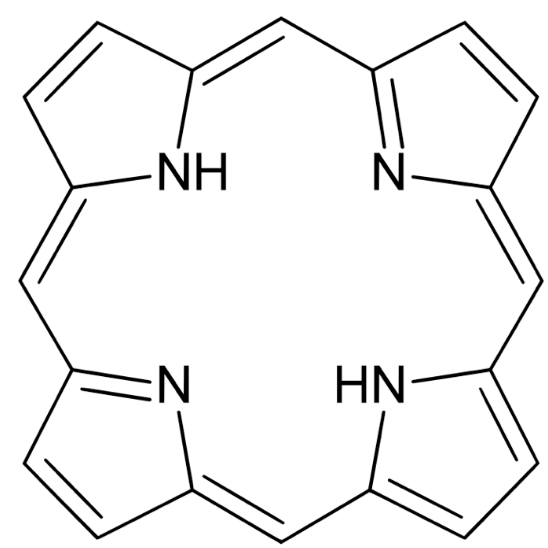






Fe(P)(Br)
Fe(P)(Cl)
Fe-N$_{pyr}$
Fe-Br
Fe-Cl
acoustic modes
doming
vib. density of states (cm)
$E - E_0/hc$ (cm^{-1})
0.12
0.1
0.08
0.06
0.04
0.02
0
0
100
200
300
400





NH
N
N
HN

PHONONS (cont'd)

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega$$

Energy of a single oscillation as a function of number of phonons. The second term +1/2 is the "zero-point" energy.

$$E = \sum_{\mathbf{k},\lambda} \omega^2_{\mathbf{k},\lambda} \left| Q(\mathbf{k},\lambda) \right|^2 = \sum_{\mathbf{k},\lambda} \left(n_{\mathbf{k},\lambda} + \frac{1}{2} \right) \hbar\omega_{\mathbf{k},\lambda}.$$

Total energy, in terms of normal mode coordinates

$$\langle n(\omega_{\mathbf{k},\lambda}) \rangle = \frac{1}{\exp(\hbar\omega_{\mathbf{k},\lambda}/k_B T) - 1}$$

Bose-Einstein statistics for average number of modes at a given temperature

$$\mathcal{H} = \frac{1}{2}\sum_{j,\ell} m_j \left| \dot{\mathbf{u}}_{j\ell} \right|^2 + \frac{1}{2}\sum_{\substack{j,j' \\ \ell,\ell'}} \mathbf{u}^T_{j\ell} \cdot \Phi^{j,j'}_{\ell,\ell'} \cdot \mathbf{u}_{j'\ell'}$$

Hamiltonian of the system:

$\mathcal{H}$=Kin. En. + Pot. En

Phonon density of states

Many thermodynamic functions like free energy, specific heat, and entropy are additive functions of phonon density of states.

This stems from the notion that the normal modes do not interact in the harmonic approximation.

Phonon density of states is the number of modes in a unit energy interval.

$$\boxed{c_v(T) = 3Nk\int \frac{\hbar^2\omega^2 e^{\hbar\omega/kT}}{(kT)^2(1-e^{\hbar\omega/kT})^2}\cdot g(\omega)\cdot d\omega}$$

Vibrational specific heat

Phonon density of states is a key ingredient for many thermodynamic properties

If we choose to write in terms of energy, $E = \hbar\omega, \quad \beta = 1/k_B T$

$$c_v(T) = 3k_B \int (\beta E/2)^2 \operatorname{csc}h(\beta E) \cdot g(E) \cdot dE$$

Vibrational specific heat

$$S_v(T) = 3k_B \int_0^\infty \{\beta E/2 \bullet \cot h(\beta E) - \ln[2 \sin h(\beta E)]\} \cdot g(E) \cdot dE$$

Vibrational entropy

$$f_{LM} = e^{-E_R \int \{g(E)/2\}.\coth(\beta E/2)} dE$$

Lamb-Mössbauer factor

$$g(E) = \frac{3m}{2\pi^2 \hbar^3 \rho v_D^3} E^2$$

Debye Sound velocity

$$\langle F \rangle = \frac{M}{\hbar^2} \int_0^\infty E^2 g(E) dE$$

Average restoring force constant

PHONON's: $\phi\omega\nu\acute{\eta}$ (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.

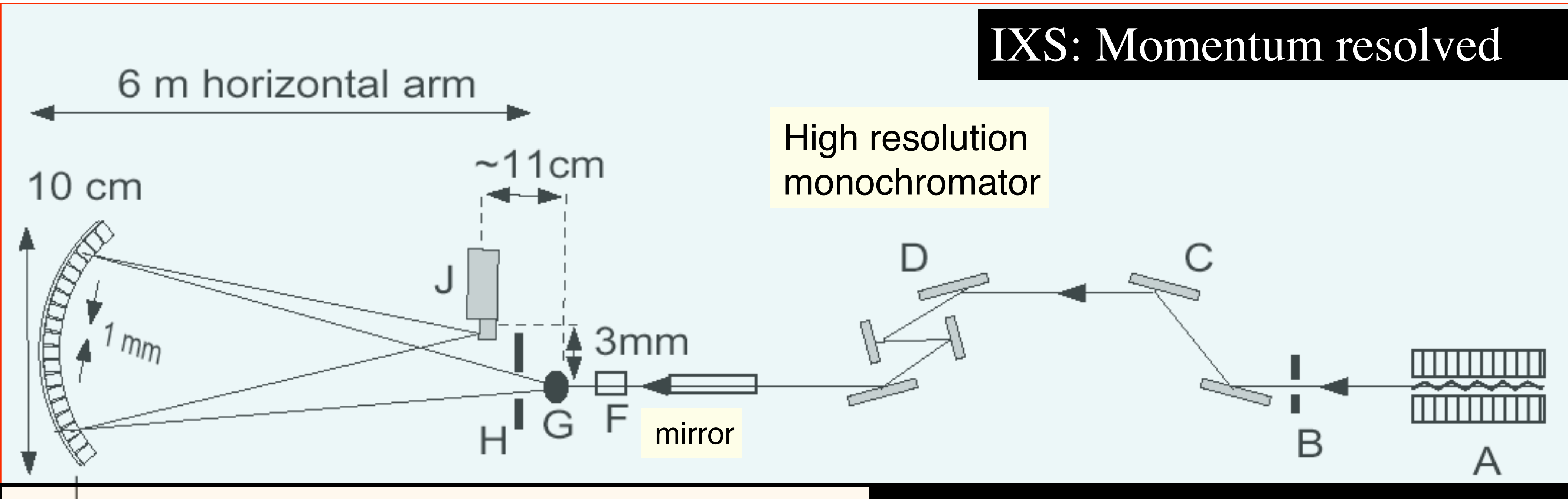
• Phonons are bosons, and they are not conserved. They can be created or annihilated during interactions with neutrons or photons.

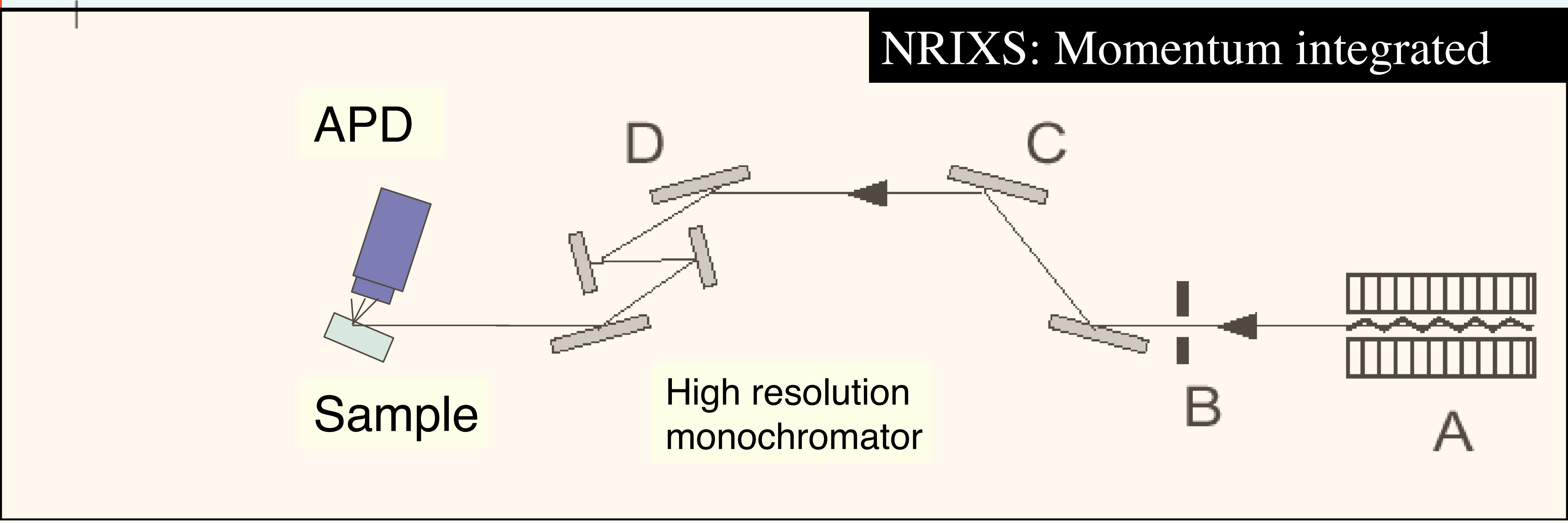
• They can be detected by Brillouin scattering (acoustic), Raman scattering, FTIR (optical).

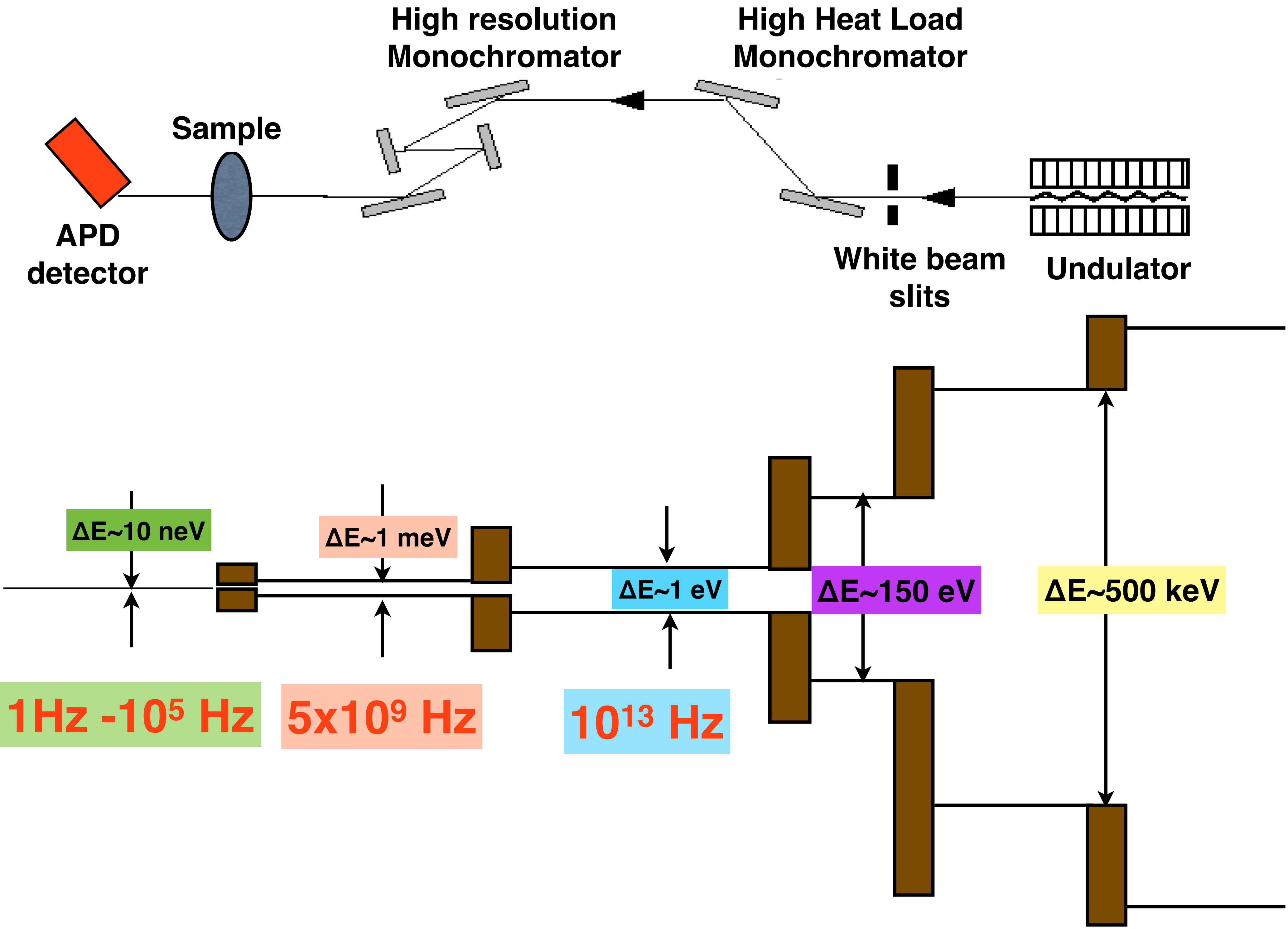
• Their dispersion throughout the BZ can ONLY be monitored with x-rays (IXS), or neutrons (INS).

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

Inelastic X-Ray Scattering: two approaches






High resolution Monochromator
High Heat Load Monochromator
Sample
APD detector
White beam slits
Undulator
ΔE~10 neV
ΔE~1 meV
ΔE~1 eV
ΔE~150 eV
ΔE~500 keV
1Hz -10⁵ Hz
5x10⁹ Hz
10¹³ Hz

And, some thermodynamics

$$\mathcal{Z} = \frac{1}{1 - \exp(-\beta\hbar\omega)}$$

Partition function

$$F = -k_B T \ln \mathcal{Z}$$

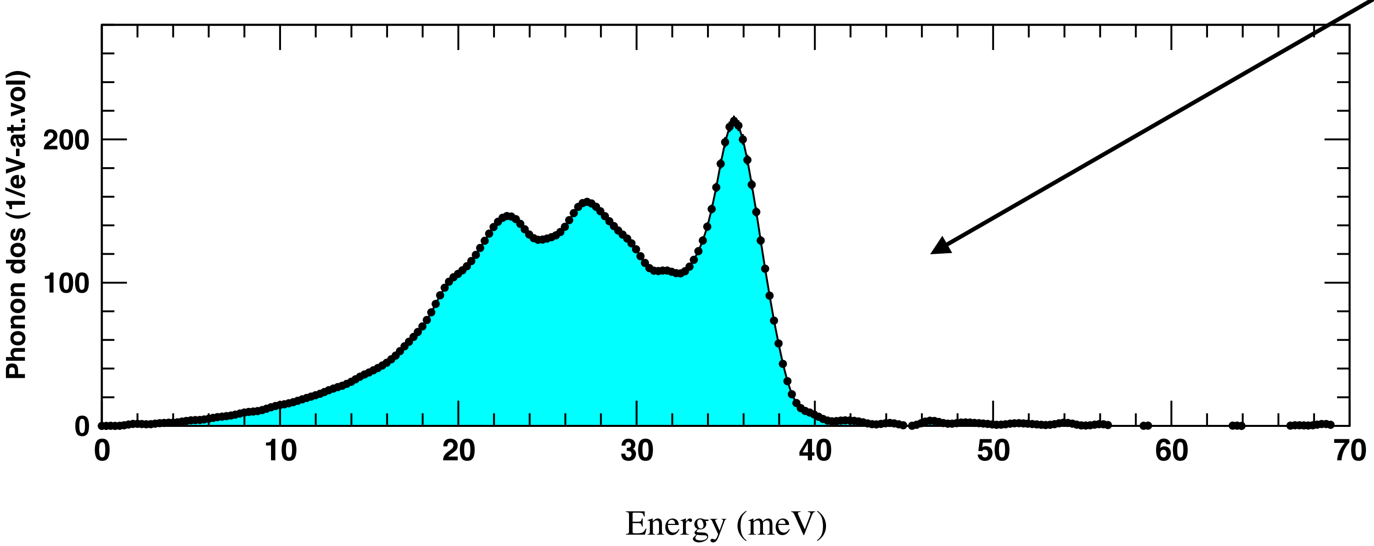
Free energy

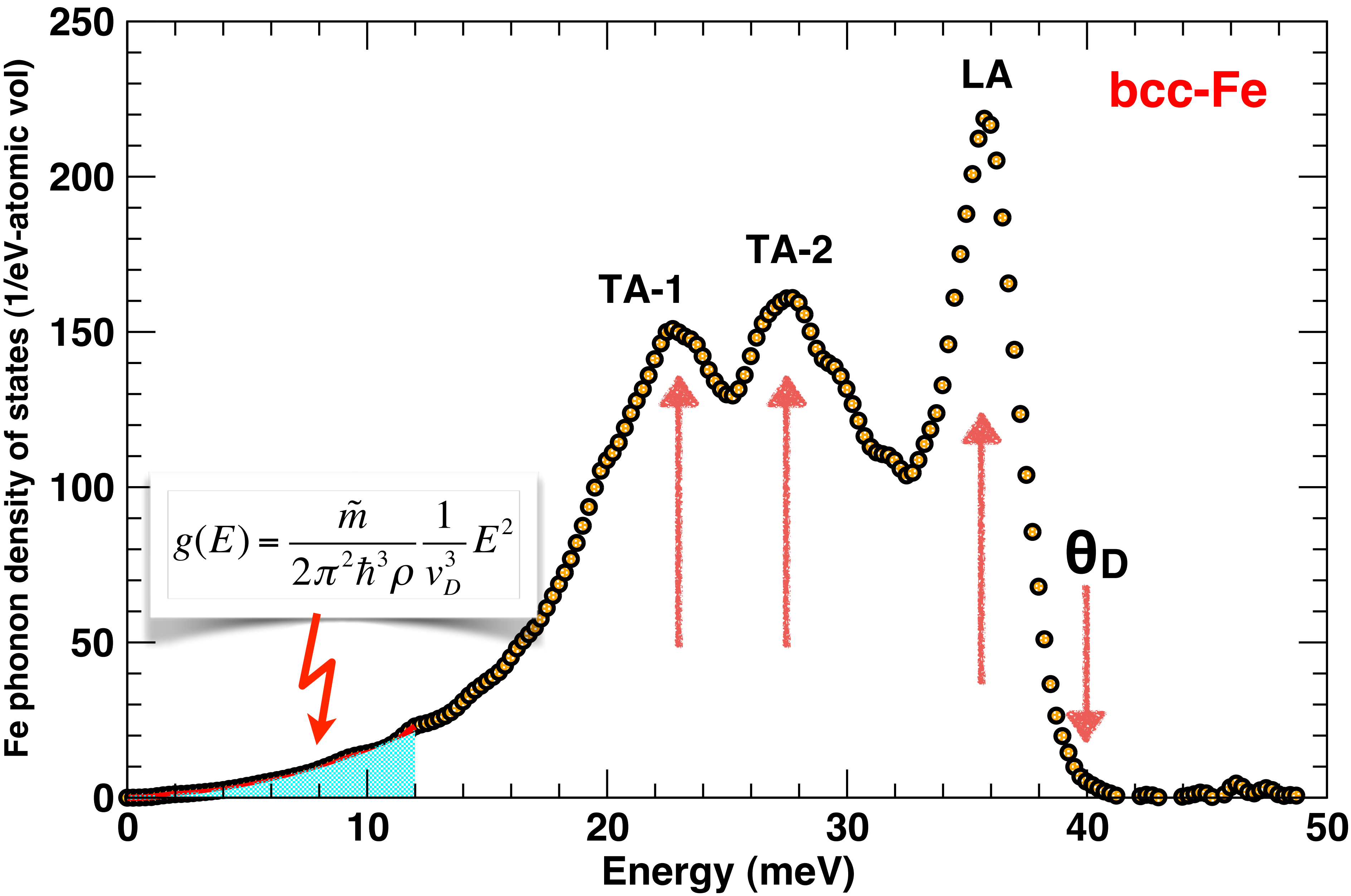
$$C = -T\frac{\partial^2 F}{\partial T^2}$$

Heat capacity

$$E = \sum_{\mathbf{k},\lambda}\left(\langle n(\omega_{\mathbf{k},\lambda})\rangle + \frac{1}{2}\right)\hbar\omega_{\mathbf{k},\lambda} \equiv \int\left(\langle n(\omega)\rangle + \frac{1}{2}\right)\hbar\omega\, g(\omega)\,\mathrm{d}\omega.$$

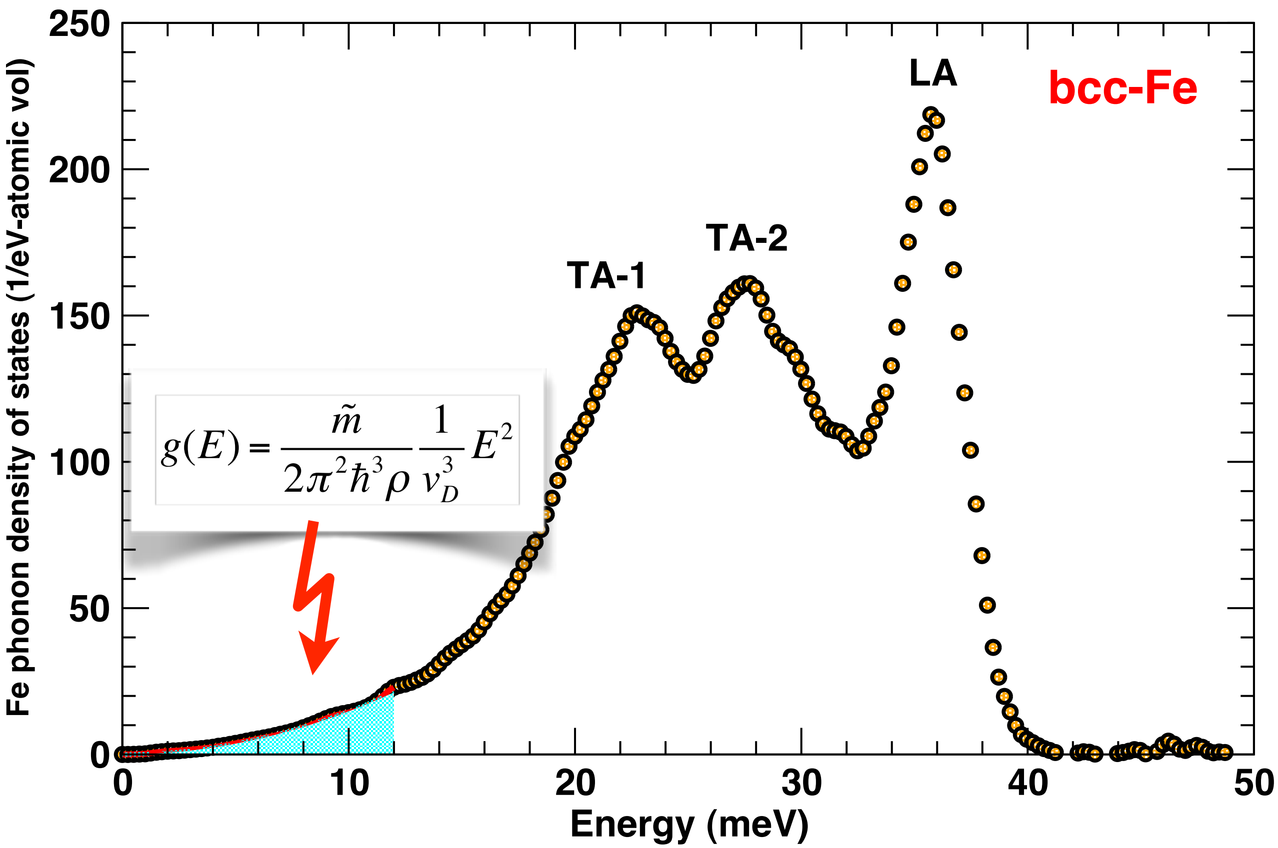
Energy in terms of ***phonon density of states***





bcc-Fe
LA
TA-1
TA-2
θ_D
$$g(E)=\frac{\tilde{m}}{2\pi^2\hbar^3\rho}\frac{1}{v_D^3}E^2$$
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

P : density

Phonon density of states

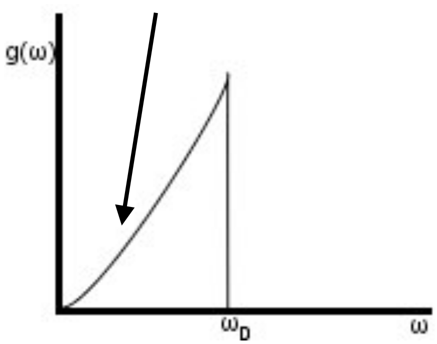
$$\boxed{g(k)\,\mathrm{d}k = \frac{V}{(2\pi)^3}\,4\pi k^2\,\mathrm{d}k.}$$

Number of wave vectors in a spherical shell of radius k per unit volume of reciprocal space.

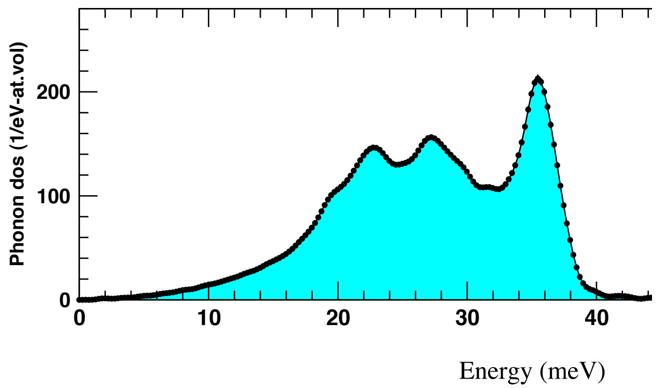
$$\boxed{g(\omega) = \frac{3V}{2\pi^2 c^3}\omega^2}$$

Phonon density of states has a quadratic dependence on frequency, and inversely proportional to the cube of sound velocity.

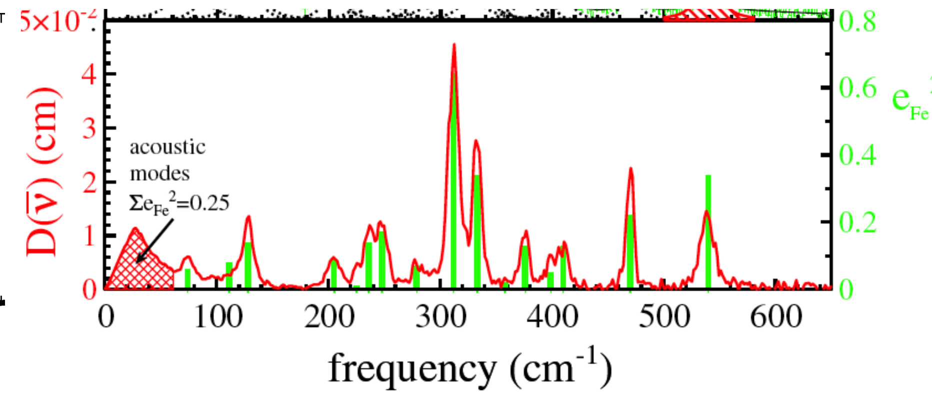
Debye model



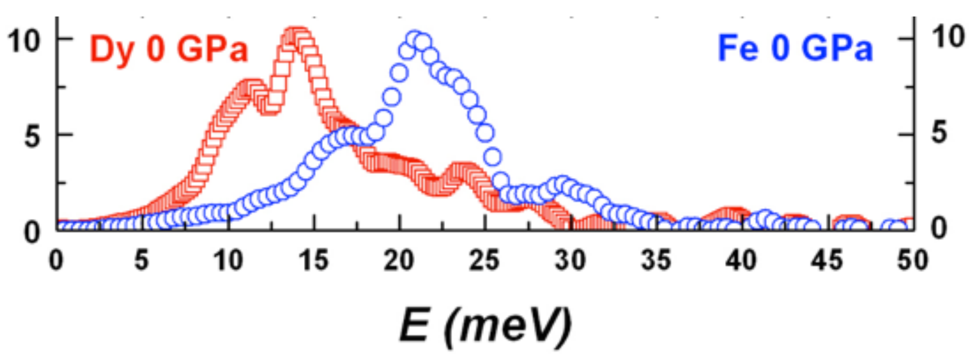
pure iron

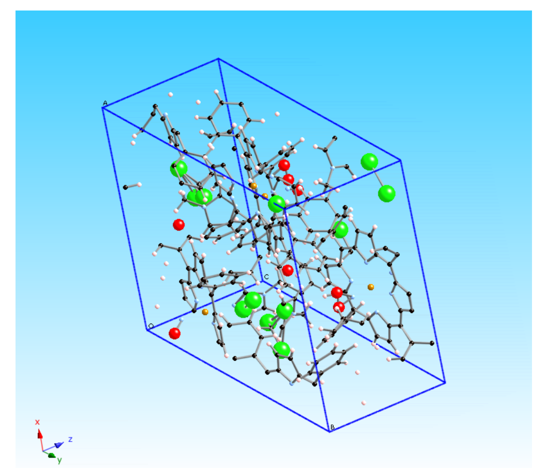


Fe-TPP-NO

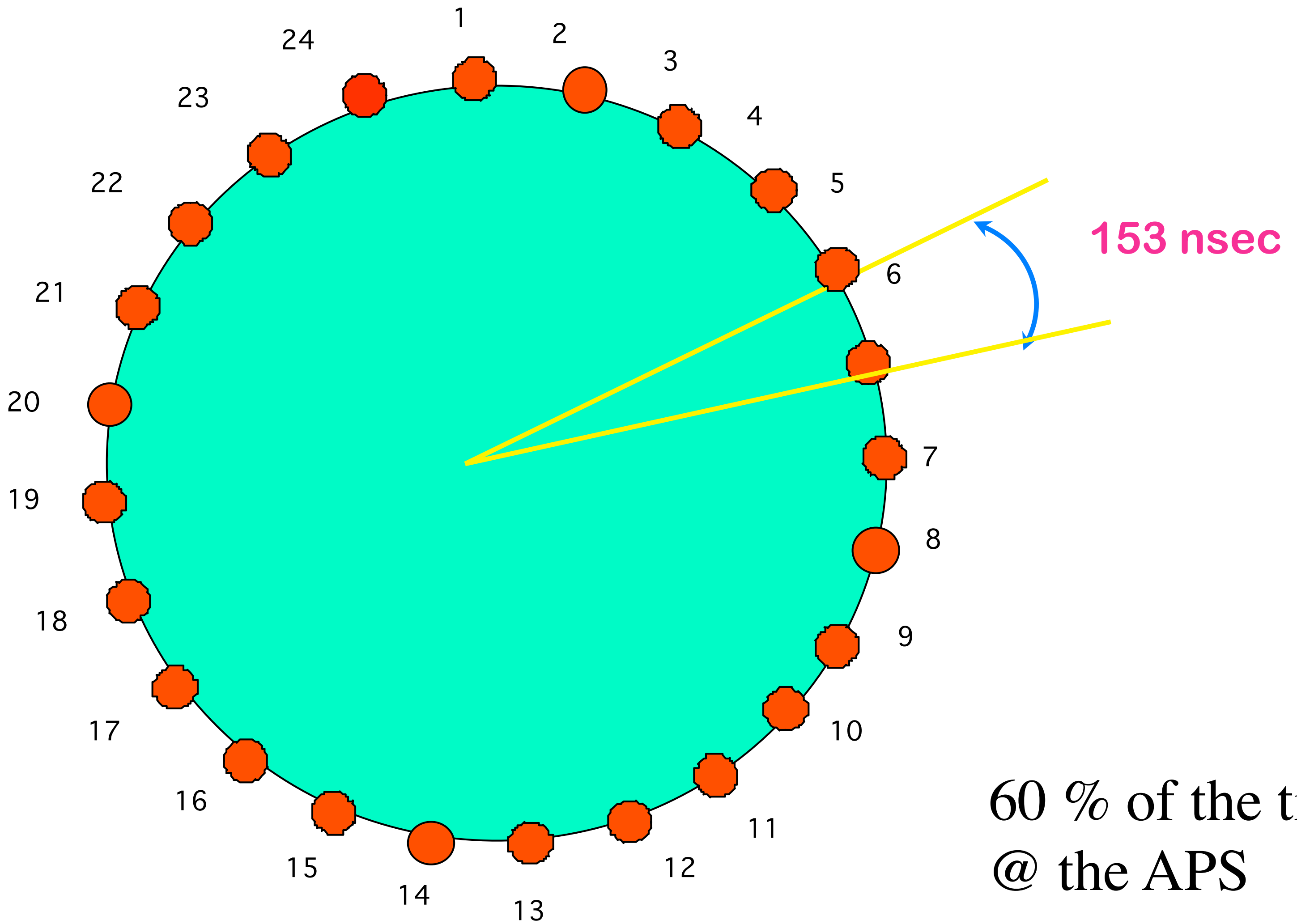


DyFe₃





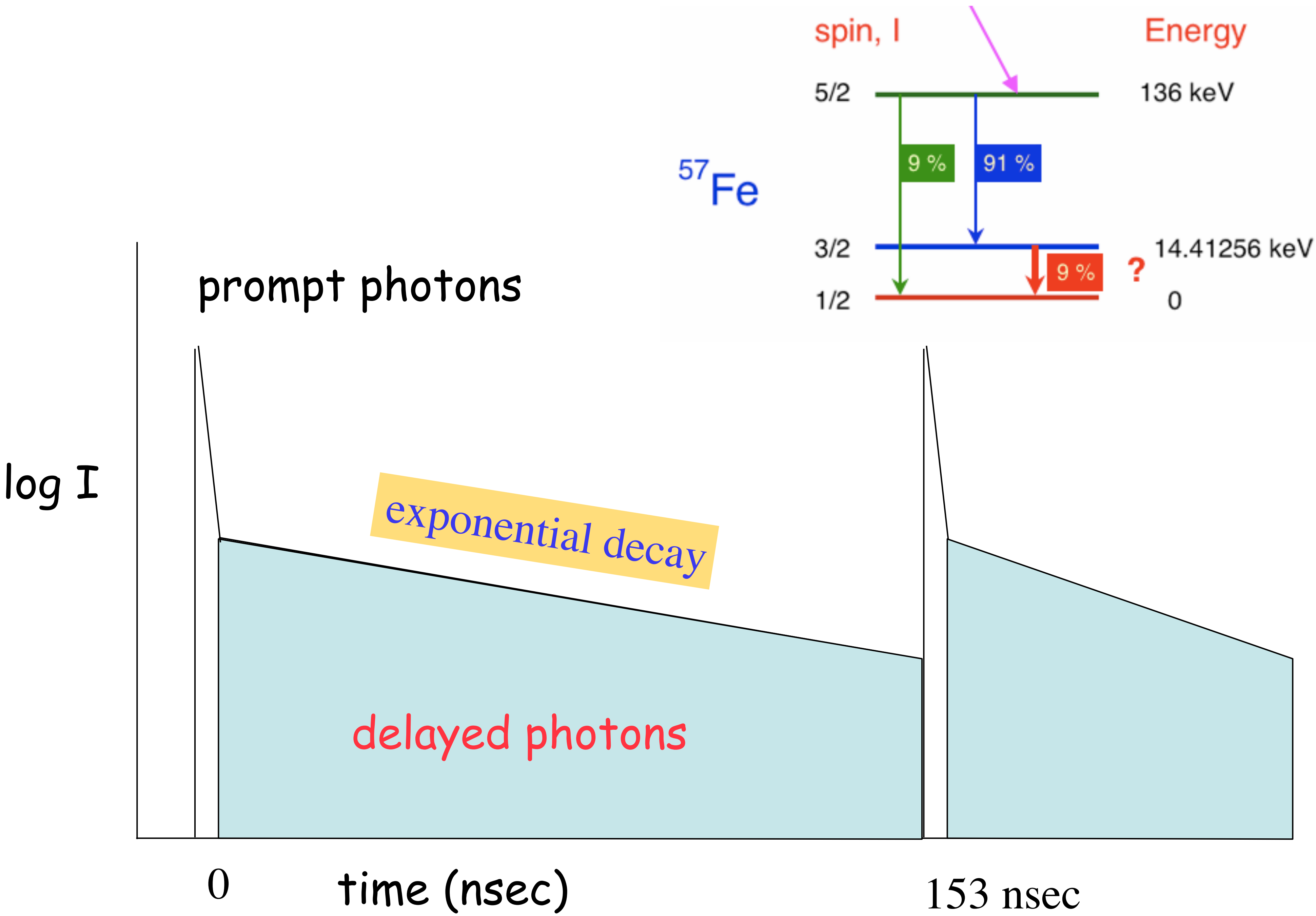
Standard Time structure @ APS



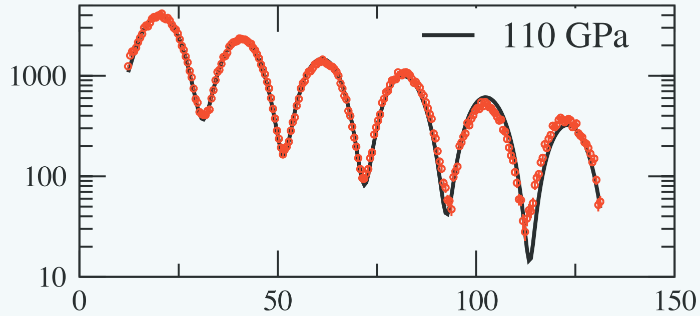
60 % of the time
@ the APS

1 revolution=3.68 μsec =>1296 buckets

Detection of nuclear decay

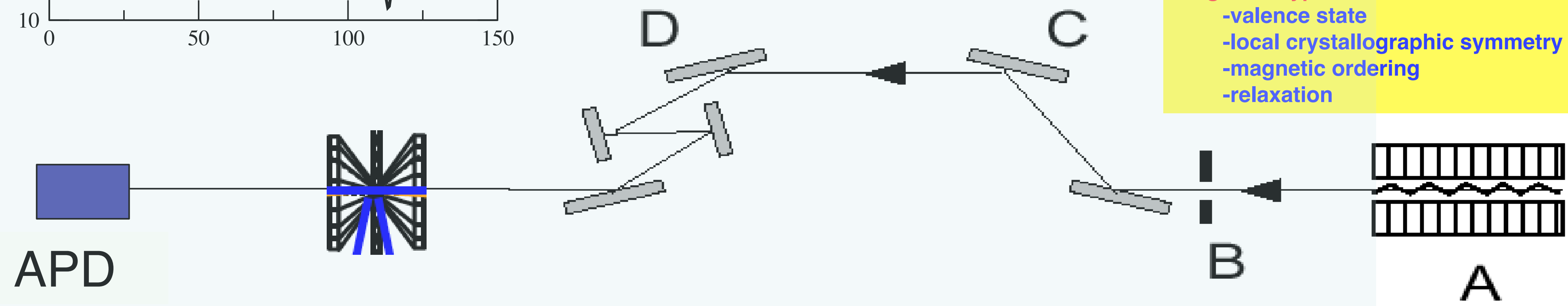


SMS: Synchrotron Mössbauer Spectroscopy
NFS : Nuclear Forward Scattering

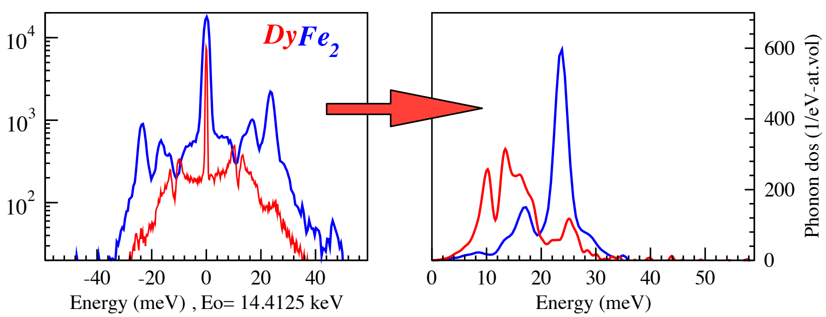


Isomer shift
Quadrupole splitting
Magnetic hyperfine field

- -valence state
- -local crystallographic symmetry
- -magnetic ordering
- -relaxation

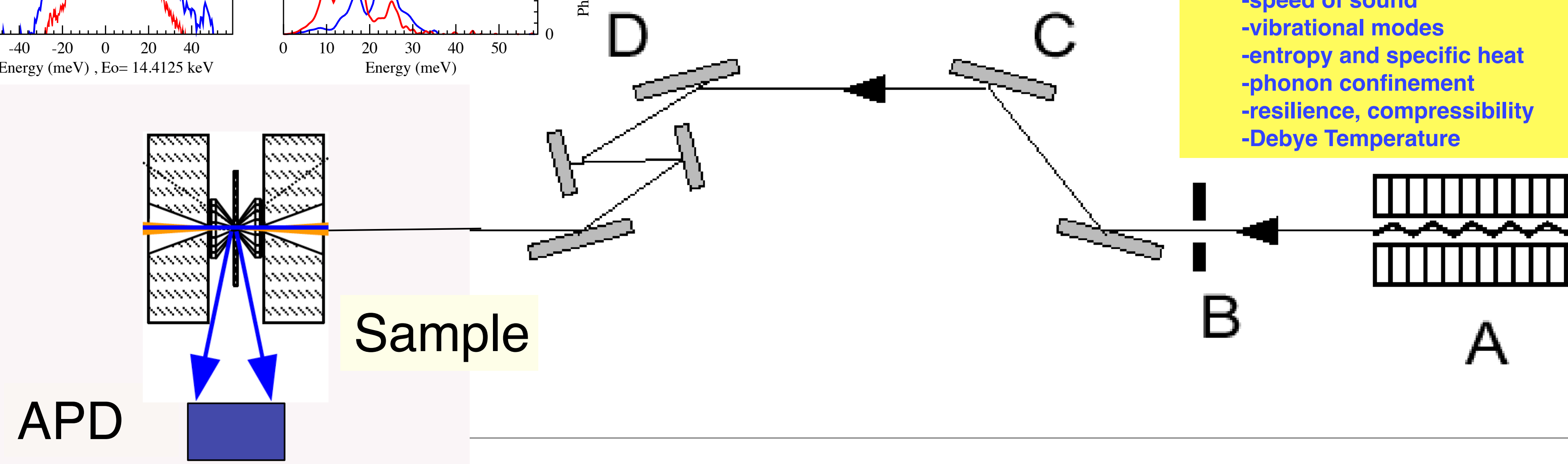


NRIXS: Nuclear Resonant Inelastic X-ray Scattering
NRVS: Nuclear Resonant Vibrational Spectroscopy

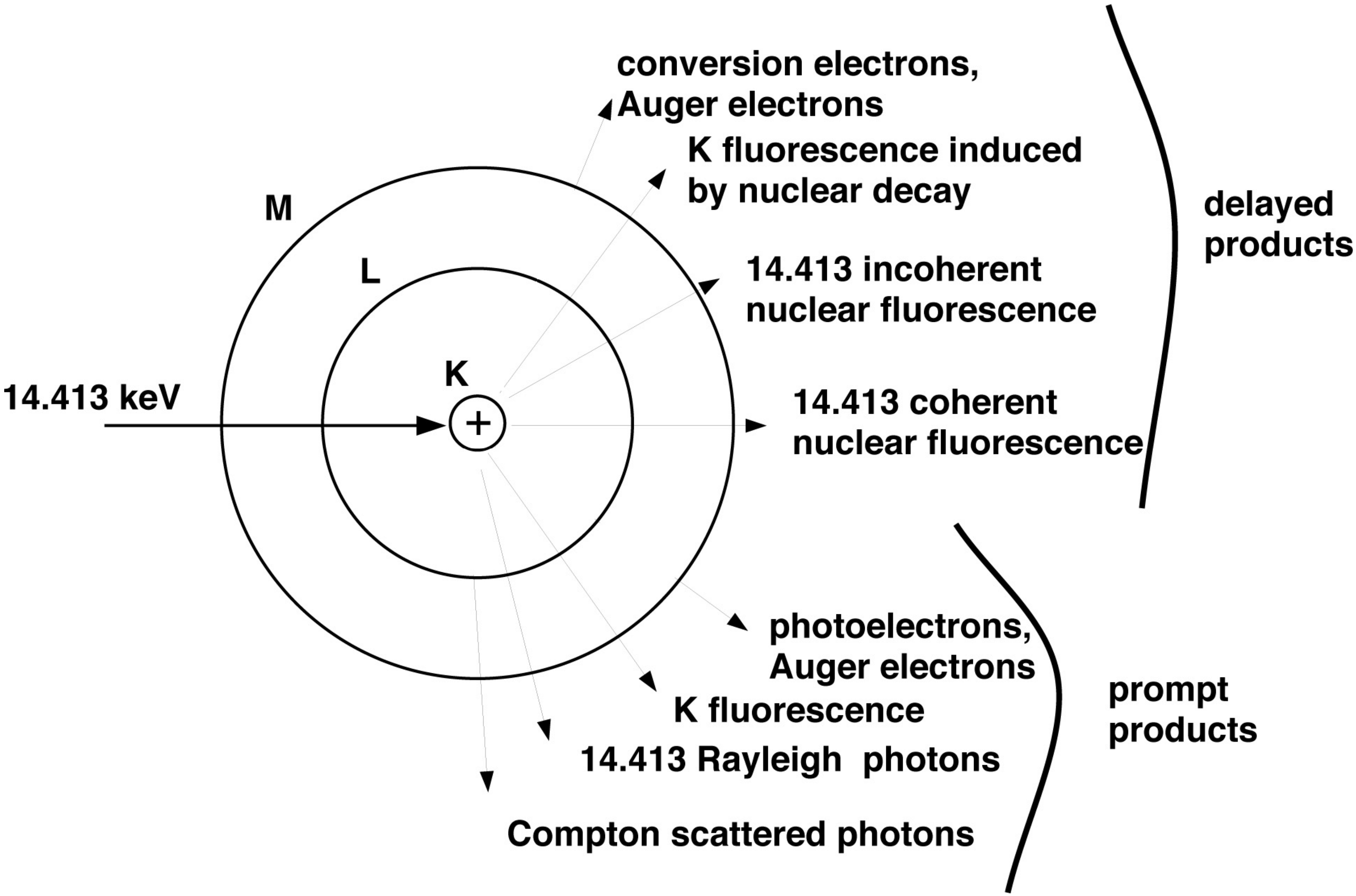


Partial phonon density of states
Recoil-free fraction

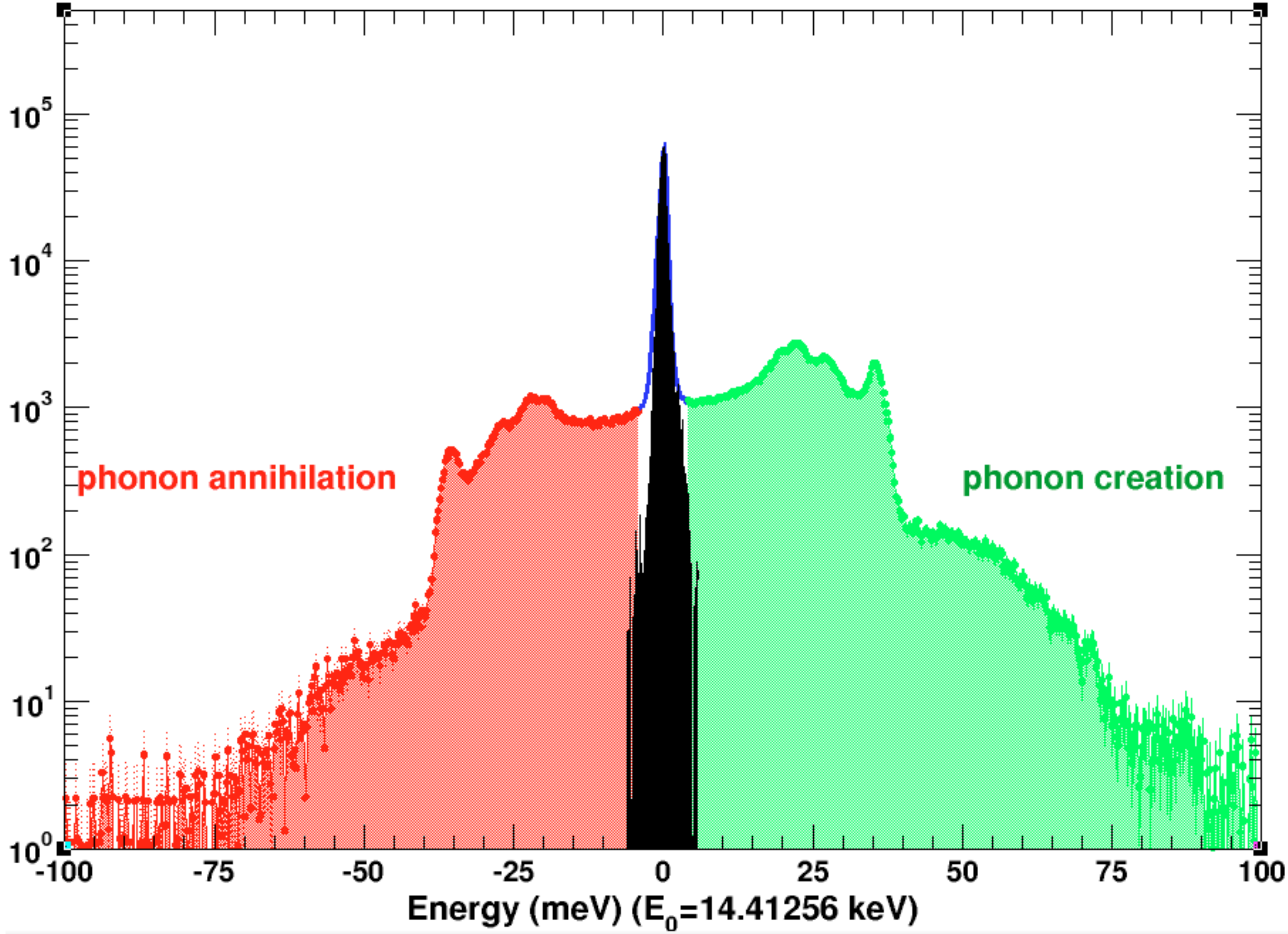
- -speed of sound
- -vibrational modes
- -entropy and specific heat
- -phonon confinement
- -resilience, compressibility
- -Debye Temperature



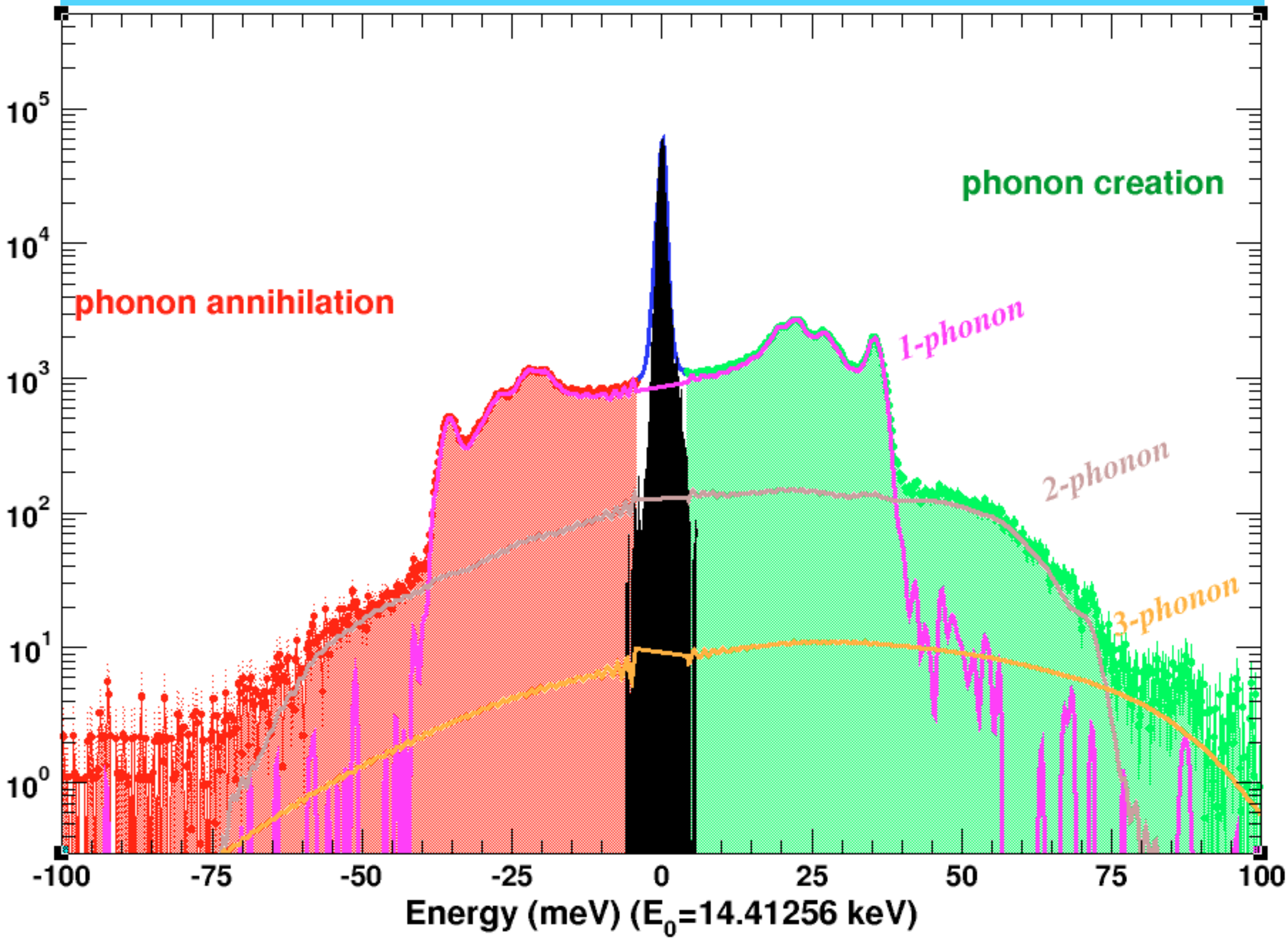
Nuclear Resonance and Fallout in ^{57}Fe-decay



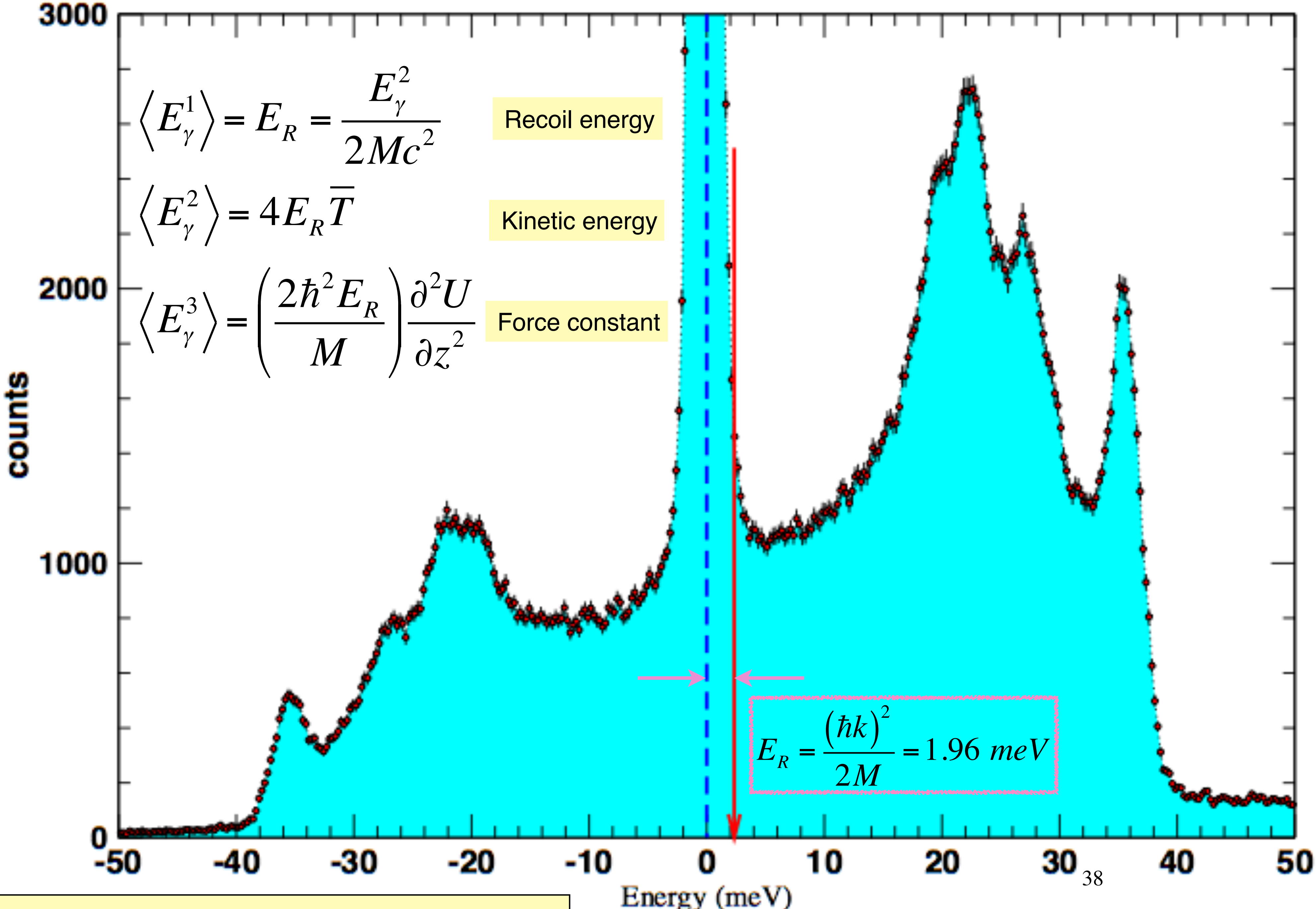
Phonon excitation probability



Multi-phonon decomposition



Lipkin's sum rules related to phonon excitation probability



$$\left\langle E_\gamma^1 \right\rangle = E_R = \frac{E_\gamma^2}{2Mc^2}$$

$$\left\langle E_\gamma^2 \right\rangle = 4E_R\overline{T}$$

$$\left\langle E_\gamma^3 \right\rangle = \left(\frac{2\hbar^2 E_R}{M}\right)\frac{\partial^2 U}{\partial z^2}$$

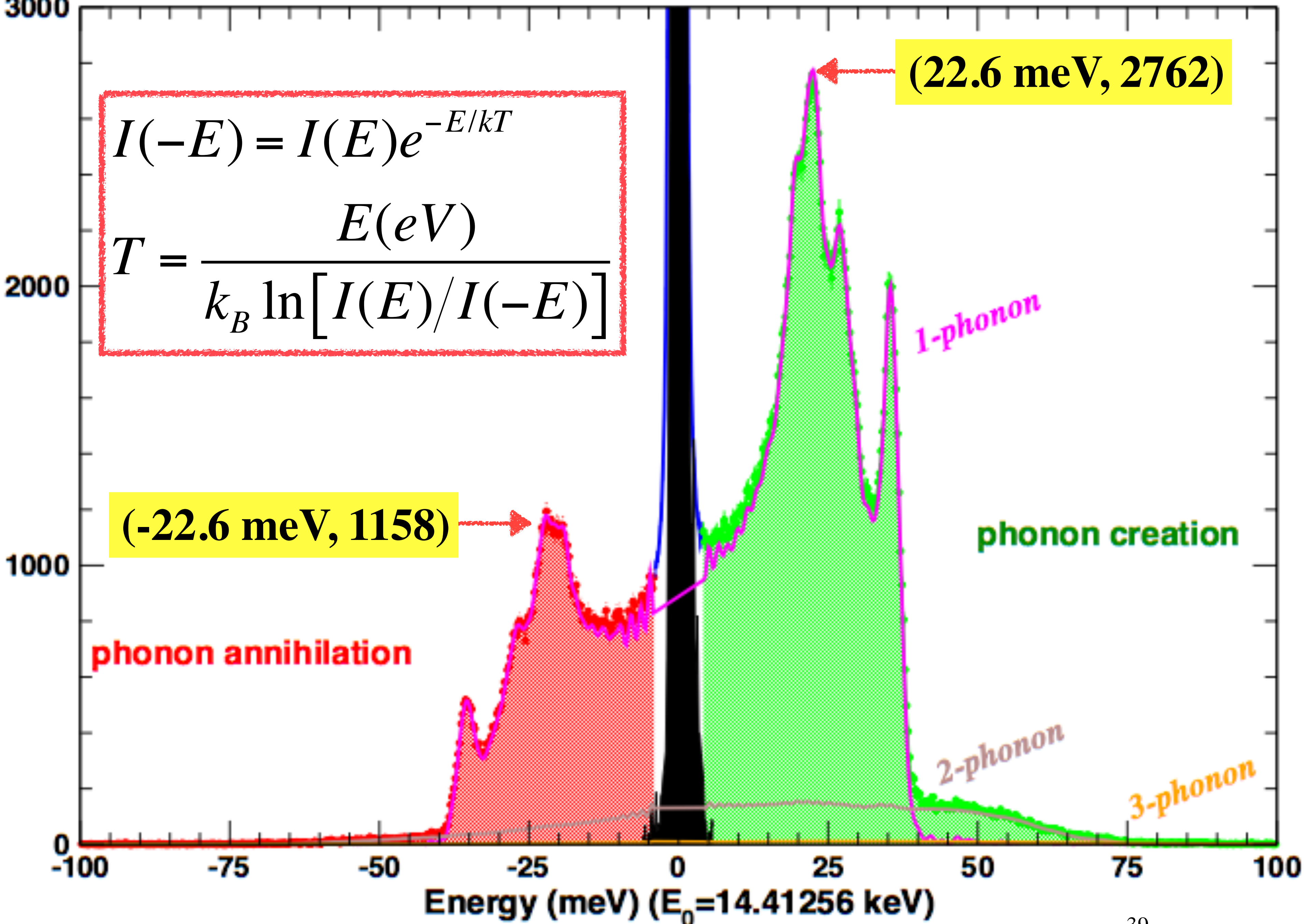
$$E_R = \frac{(\hbar k)^2}{2M} = 1.96\ meV$$

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

Detailed Balance

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

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



Detailed Balance

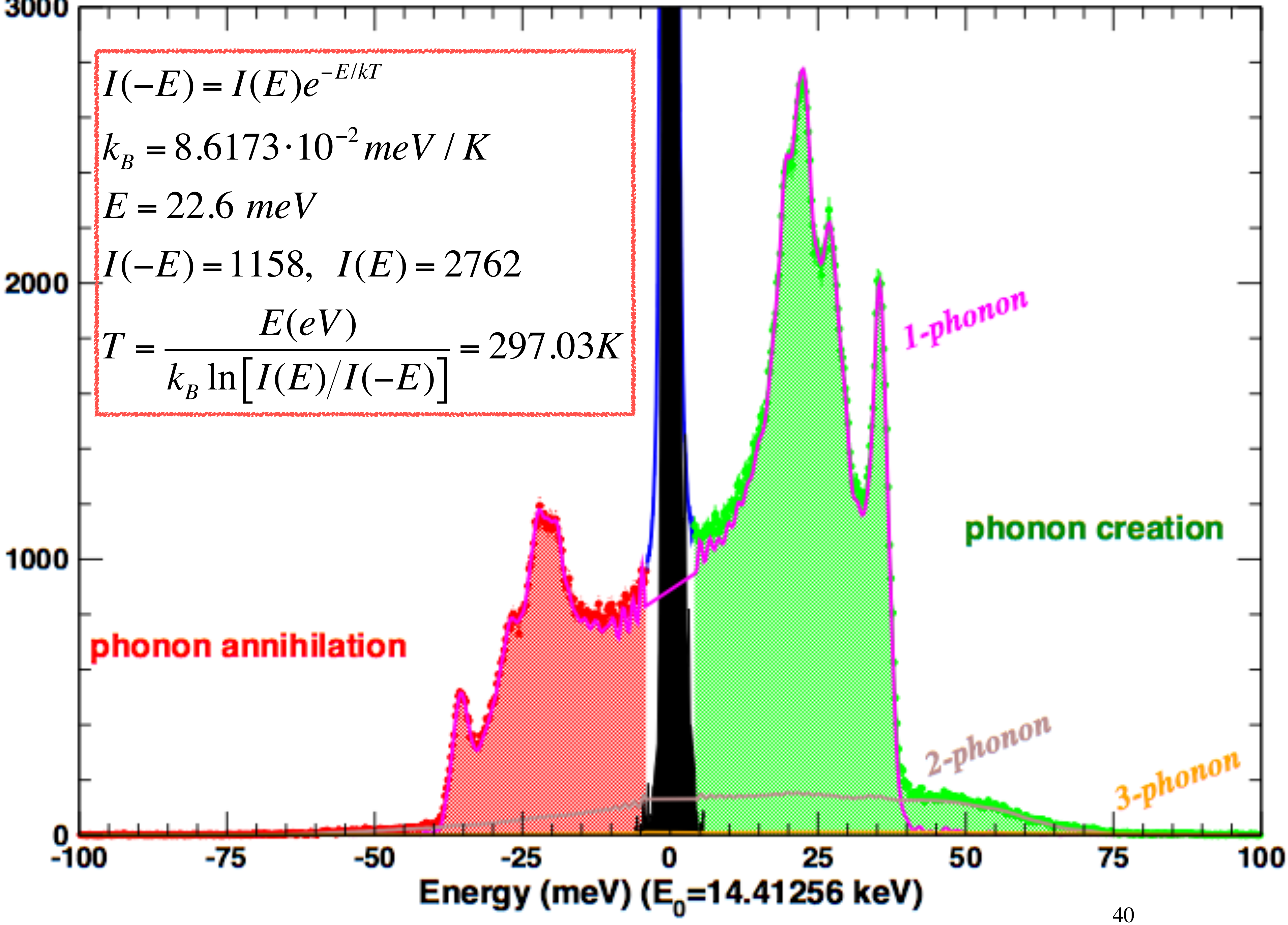
$$I(-E) = I(E)e^{-E/kT}$$

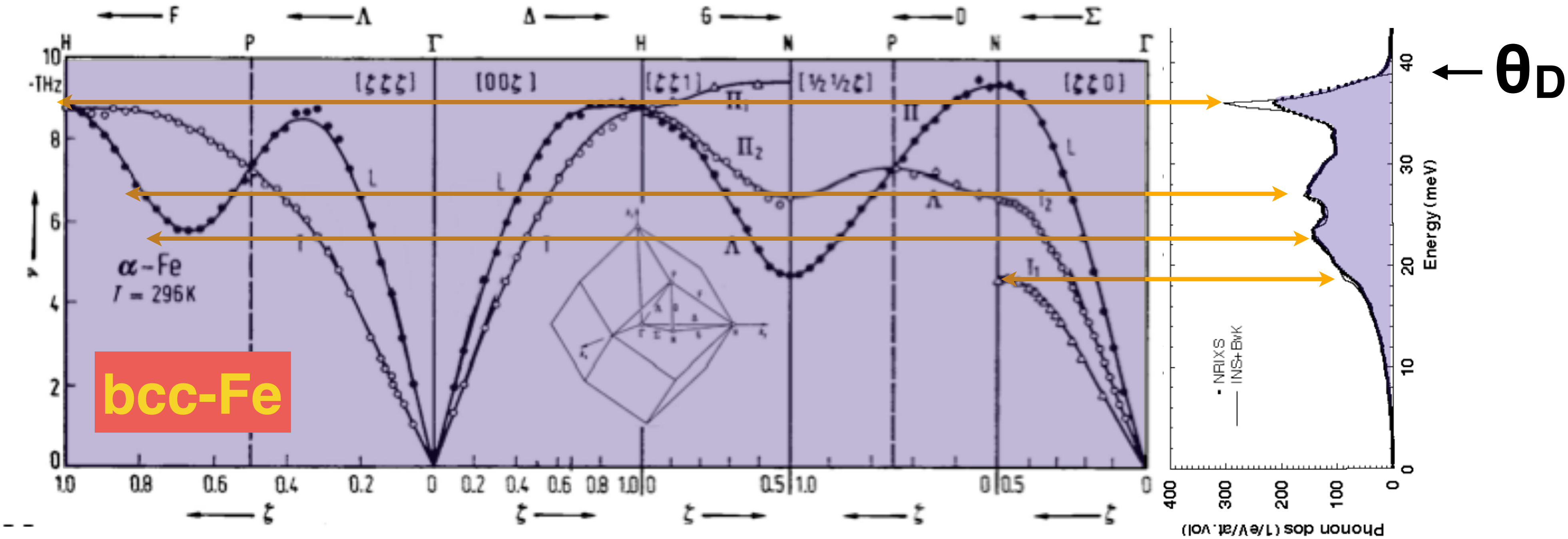
$$k_B = 8.6173 \cdot 10^{-2}\, meV/K$$

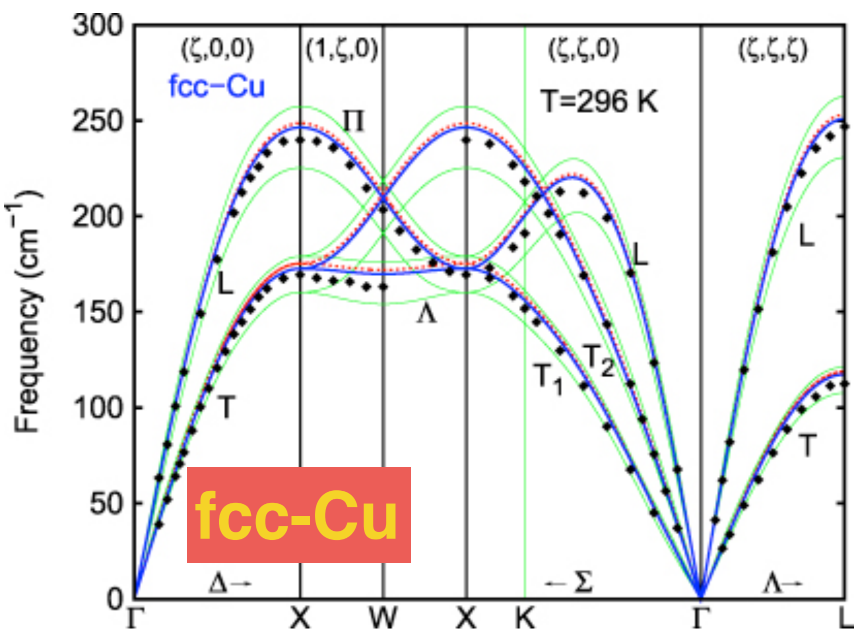
$$E = 22.6\ meV$$

$$I(-E) = 1158, \quad I(E) = 2762$$

$$T = \frac{E(eV)}{k_B \ln\left[I(E)/I(-E)\right]} = 297.03K$$







Let's assume that the acoustic modes have a linear relationship between frequency and wave vector:

$\omega = ck$, where ***c*** is average sound velocity

Maximum frequency cut off is at Debye energy: e.g. for Cu, this frequency is 240 cm^{-1} (~ 30 meV). Considering 1 meV = 11.605 K=8.065 cm^{-1}, this corresponds to 348 K, which is close to 344 K.
For Fe, the measured cut-off value is ~ 39.5 meV, which corresponds to 458 K, very close to reported 460 K.

Two examples why we need to know about phonons in new materials

1) Thermoelectrics : **clathrates** and **skutterudites**

2) Superconductors: **iron pnictides**

1. Thermoelectric materials: always something new !..

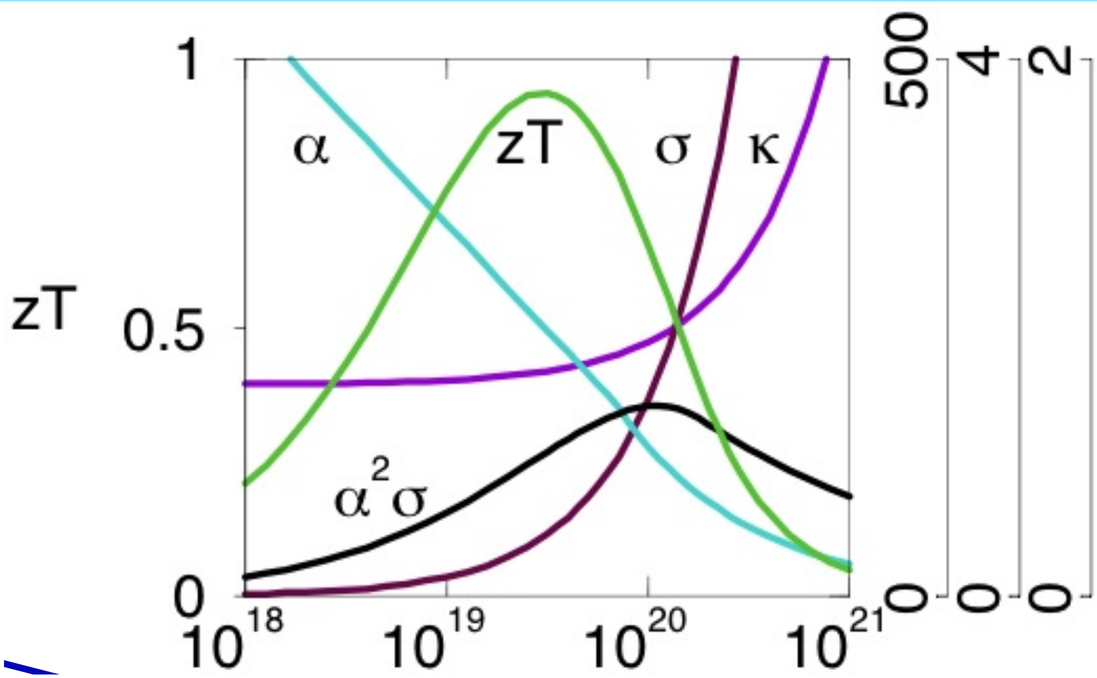
Thermoelectric materials converts heat to electrical energy.
They require high **figure of merit**, **zT > 1** at high temperatures ~ 1000 K or so.

$$zT = \frac{\alpha^2 \sigma}{\kappa} T$$

$$\kappa_{tot} = \kappa_{ph} + \kappa_{el}$$

Seebeck: 1822

Large **Seebeck coeff**. α requires small carrier concentration and large effective e-mass
Large **Electrical conductivity** σ requires the opposite
Small **Thermal conductivity** κ requires phonon glass or rattling atoms as in skutterudites or clathrates



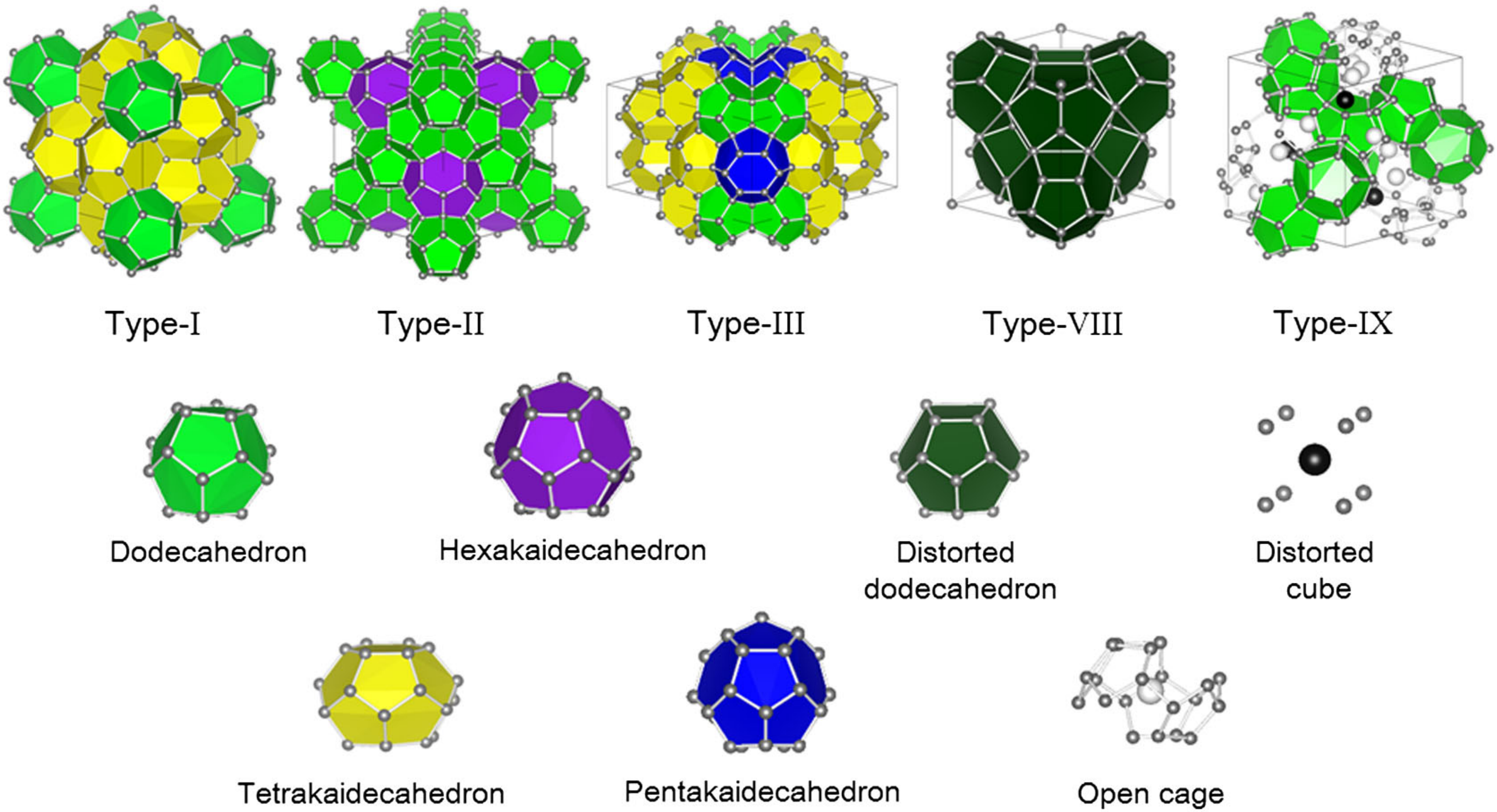
There seems to be a limit how much one can tune the carrier concentration. Thus, modifying κ seems to be another way to increase zT

1. Thermoelectric materials: always something new !..

Clathrates

Rev. Mod. Phys., Vol. 86, No. 2, April–June 2014

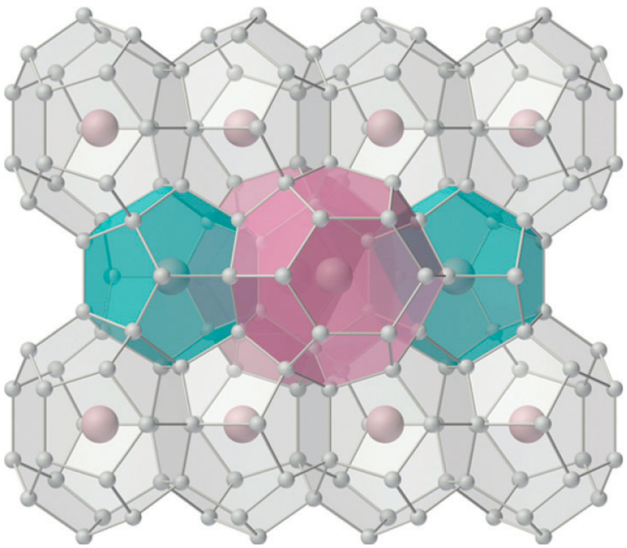
Takabatake *et al.*: Phonon-glass electron-crystal thermoelectric …

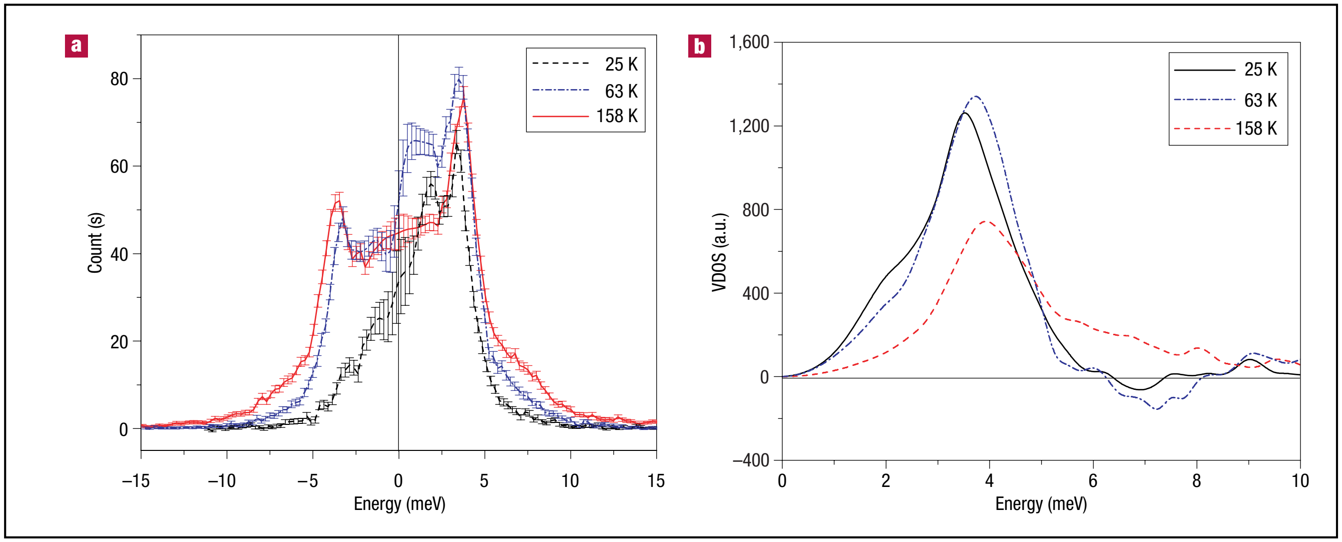


Anharmonic motions of Kr in the clathrate hydrate

Nature Materials, 2005

J. S. TSE[1,2*], D. D. KLUG[1], J. Y. ZHAO[3], W. STURHAHN[3], E. E. ALP[3], J. BAUMERT[4], C. GUTT[5], M. R. JOHNSON[6] AND W. PRESS[4,6]





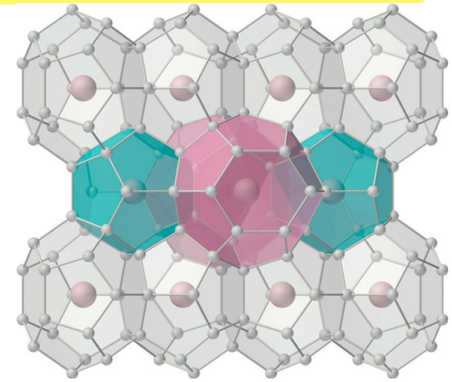
The anomalous glass-like thermal conductivity of crystalline clathrates is perhaps due to scattering of thermal phonons of the framework by 'rattling' motions of the guests in the clathrate cages.

Using the site-specific ^{83}Kr nuclear resonant inelastic scattering spectroscopy characterization of the effects on these guest–host interactions in a structure-II Kr clathrate hydrate are possible.

The resonant scattering of phonons leads to large anharmonic motions of the guest atoms. The anharmonic interaction underlies the anomalous thermal transport in this system.

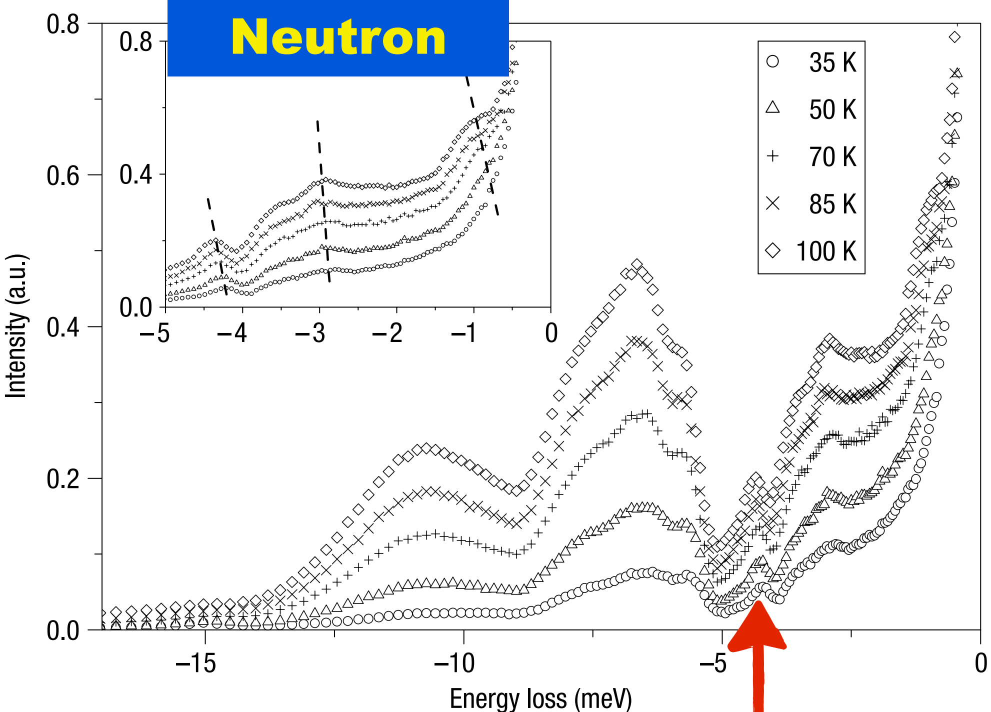
Clathrates are prototypical models for a class of crystalline framework materials with glass-like thermal conductivity. The explanation of the unusual dynamics has a wide implication for the understanding of the thermal properties of disordered solids and structural glasses.

The observable in a NRIXS experiment is S(ω), the dynamic structure factor, which is related to the **Fourier transform of the self-intermediate scattering function**, L(ko,t). For systems with large anharmonicity, calculation of L(k0,t) from molecular-dynamics simulations is necessary.



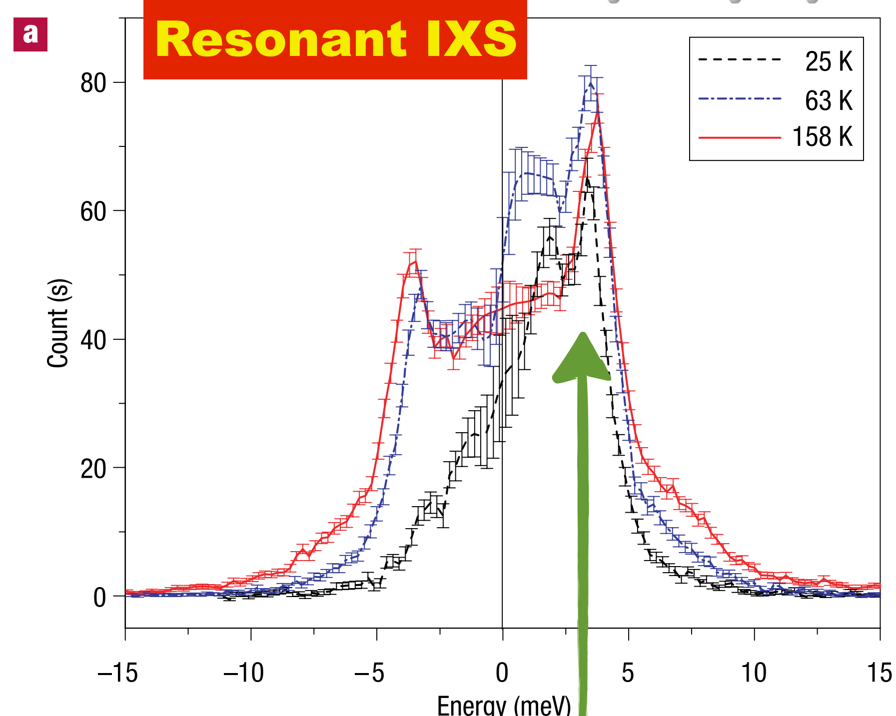
$$L(\mathbf{k}_0, t) = \frac{1}{N}\left\langle \sum_i e^{i\mathbf{k}\cdot(\mathbf{r}_i(t)-\mathbf{r}_i(0))} \right\rangle = \langle e^{i\mathbf{k}_0\cdot\mathbf{r}_i(t)} e^{-i\mathbf{k}_0\cdot\mathbf{r}_i(0)} \rangle$$

Inelastic Neutron



Low peak due to small incoherent scattering length of Kr

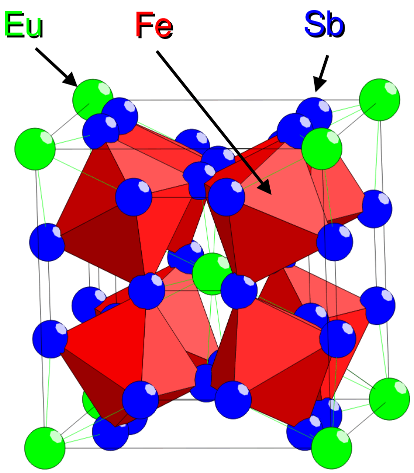
^{83}Kr-Nuclear Resonant IXS

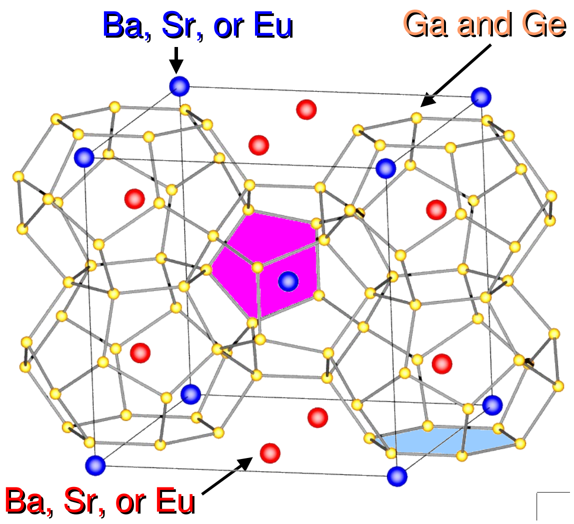


Localized vibrations of Kr in smaller water cages

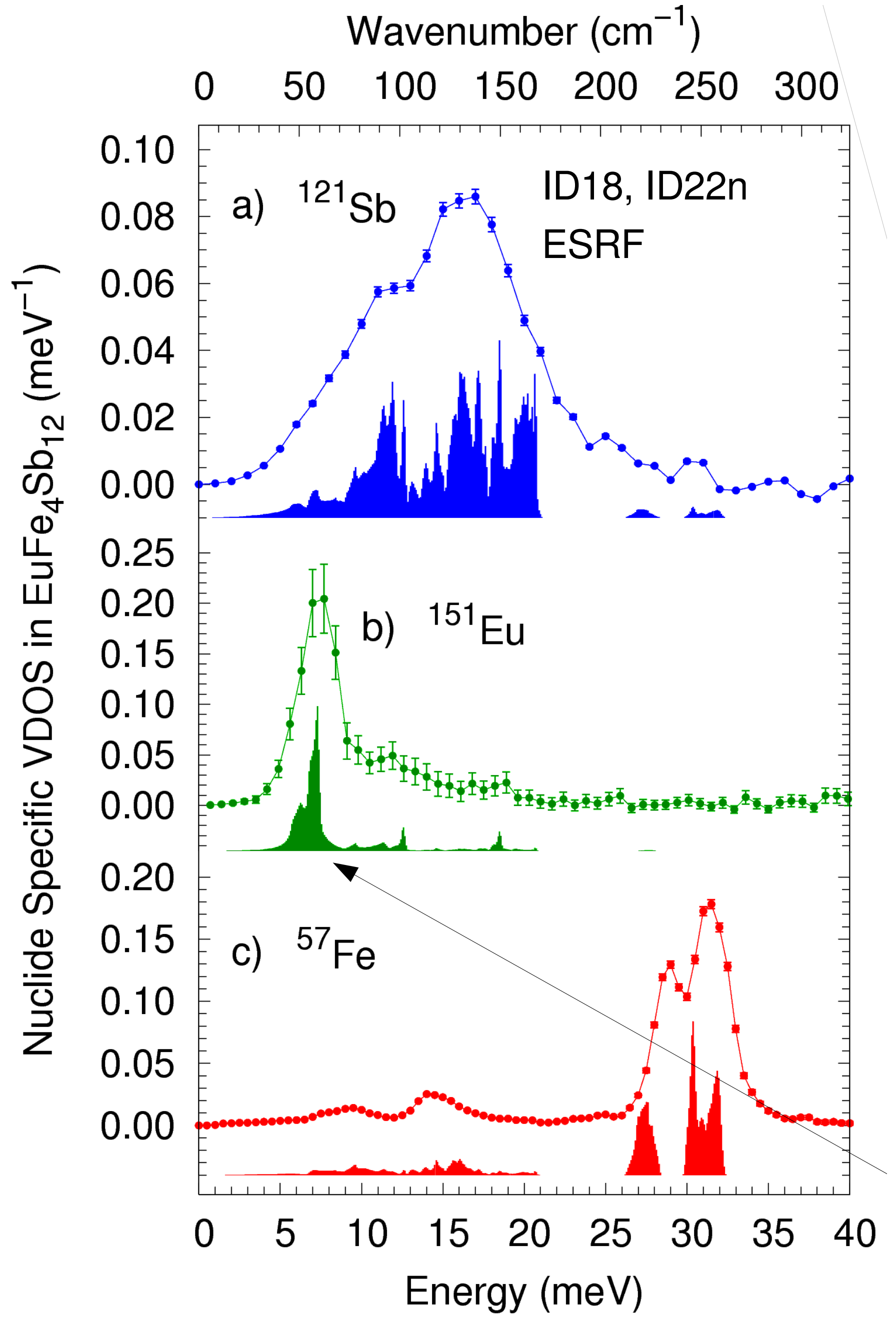
1. Thermoelectric materials: always something new !..

Skutterudites





$EuFe_4Sb_{12}$



The loosely bound guests affect the characteristics of the vibrations, and change the thermal conductivity

Many elements in modern thermolelectric materials include Fe, rare-earth atoms like Eu, Sm, Dy, as well as Sb, and Te. These are all proper Mössbauer resonances we can exploit, and we do..

Courtesy: Raphael Hermann, Jülich

PHYSICAL REVIEW B **90**, 104304 (2014)

Vibrational dynamics of the host framework in Sn clathrates

Bogdan M. Leu,[1,*] Mihai Sturza,[2] Michael Y. Hu,[1] David Gosztola,[3] Volodymyr Baran,[4] Thomas F. Fässler,[4] and E. Ercan Alp[1]

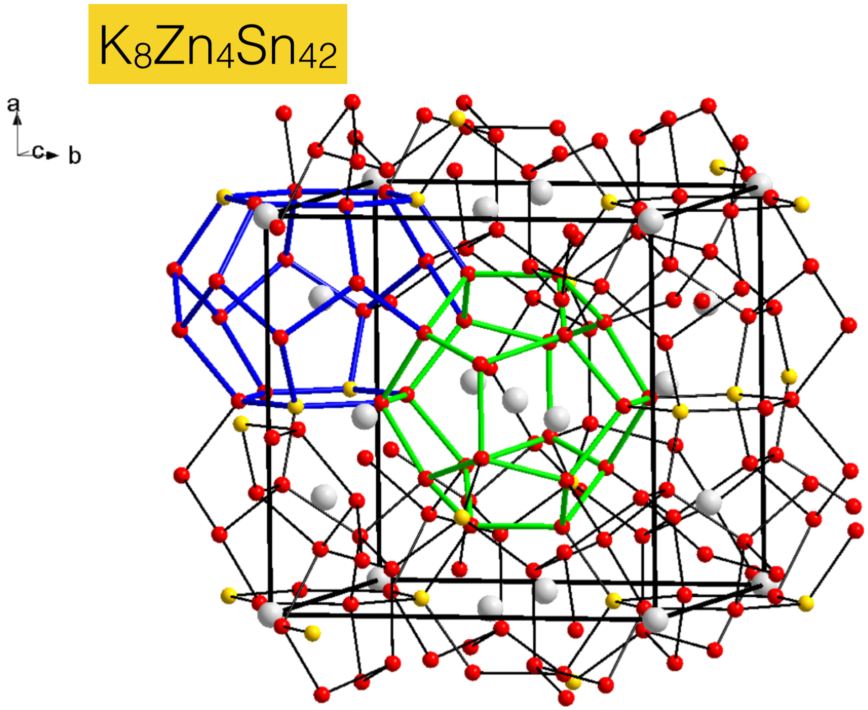


FIG. 1. (Color online) Structure of type-I clathrate $K_8Zn_4Sn_{42}$. Color scheme: gray = K, yellow = Zn/Sn, red = Sn. One small (pentagonal dodecahedron) and large (tetrakaidecahedron) host framework cage are highlighted in green and blue, respectively.

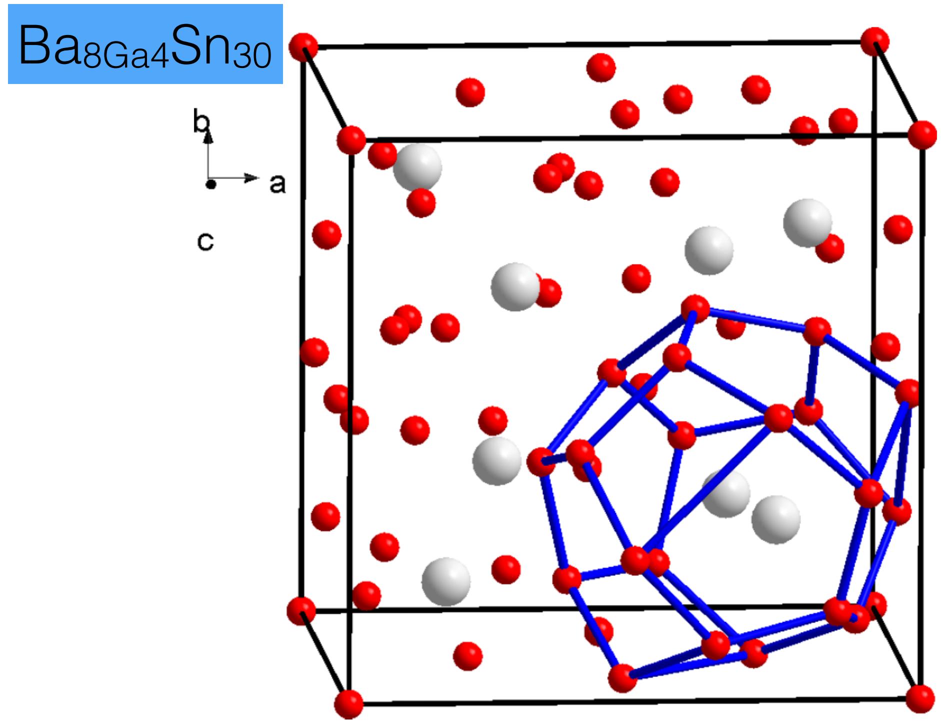
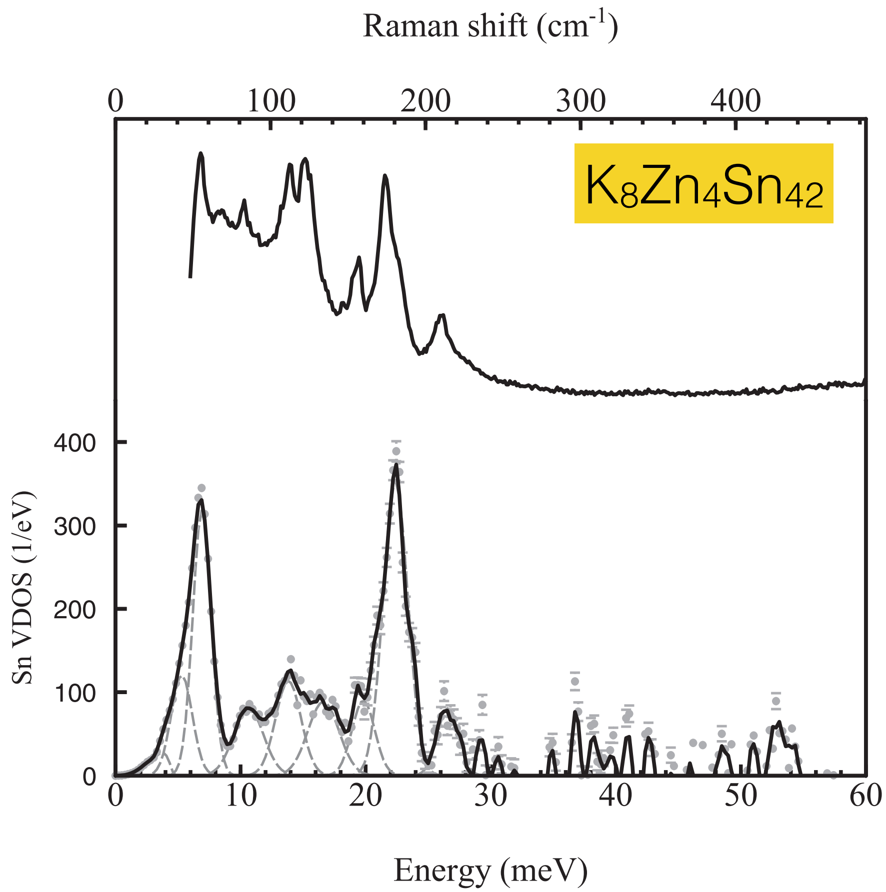
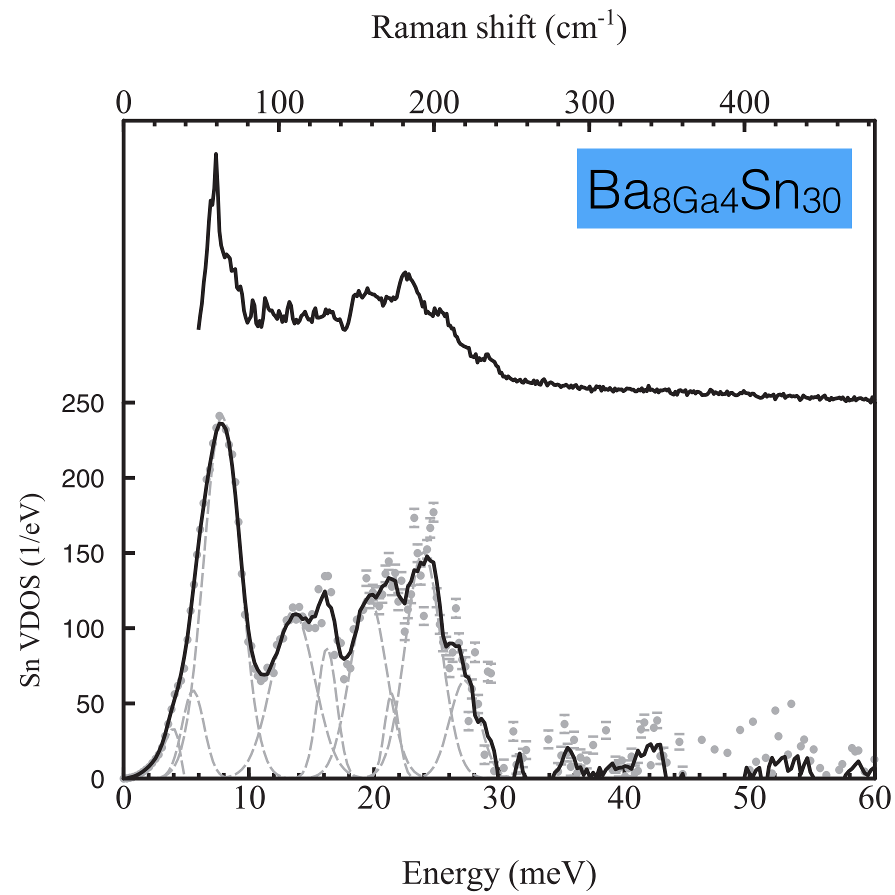


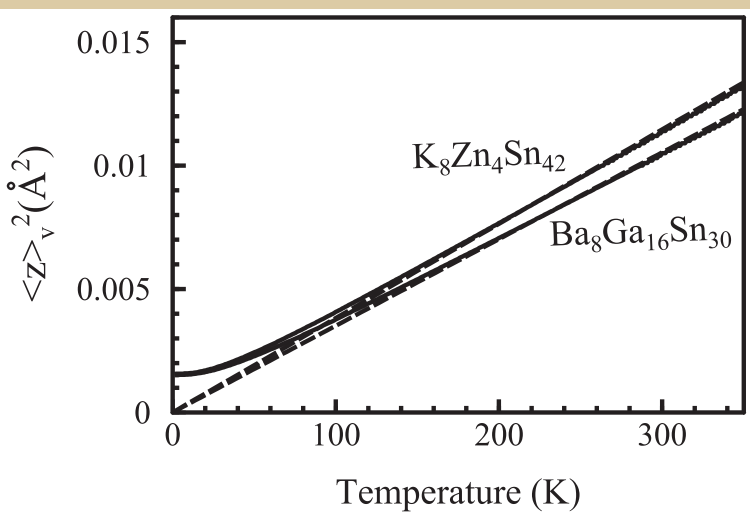
FIG. 2. (Color online) Structure of type-VIII clathrate $Ba_8Ga_{16}Sn_{30}$. Color scheme: gray = Ba, red = Sn/Ga. One host framework cage (pentagonal dodecahedron) is highlighted in blue.

type-I clathrate: pentagonal dodecahedra and tetrakaidecahedra alternating in a 1:3 ratio

type VIII : pentagonal dodecahedra; however, BGS adopts the type-I clathrate structure at high-temperature





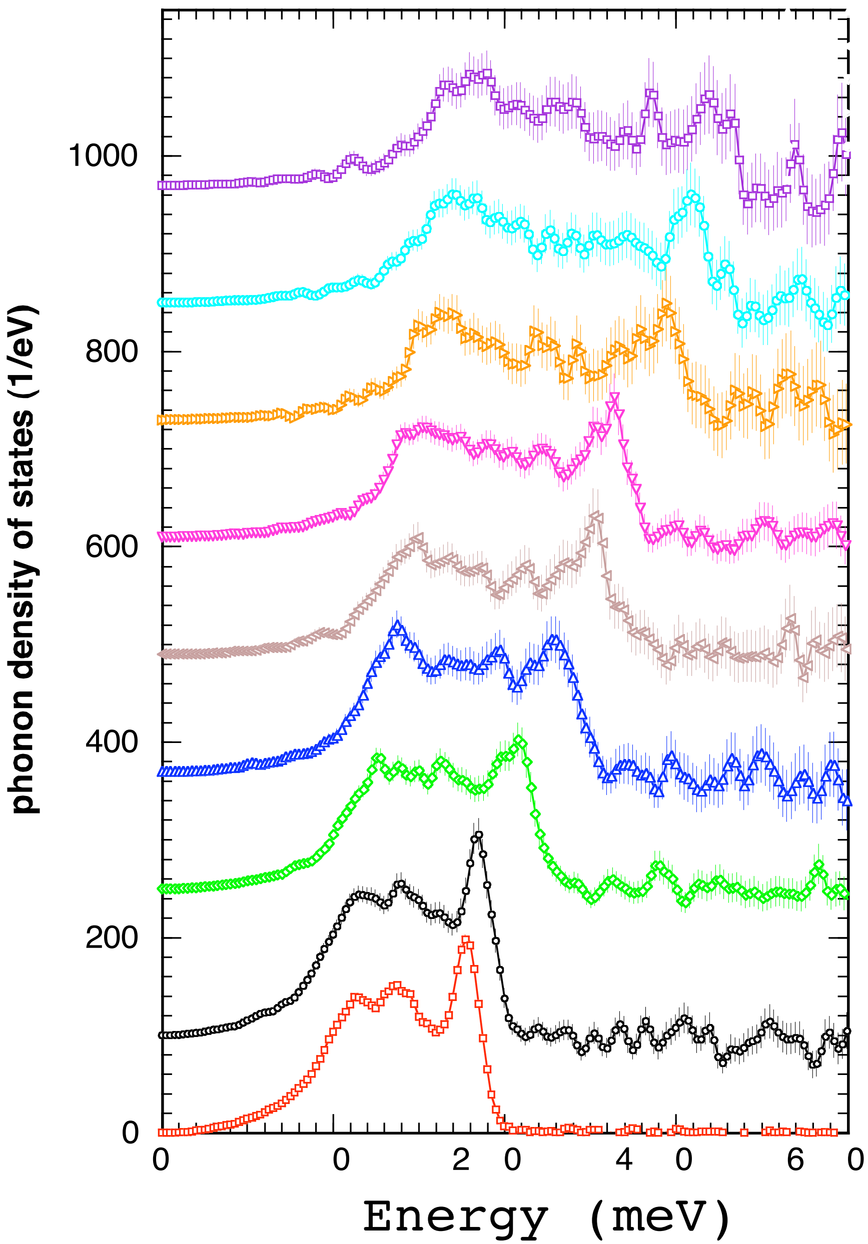


mean square displacement via phonon dos

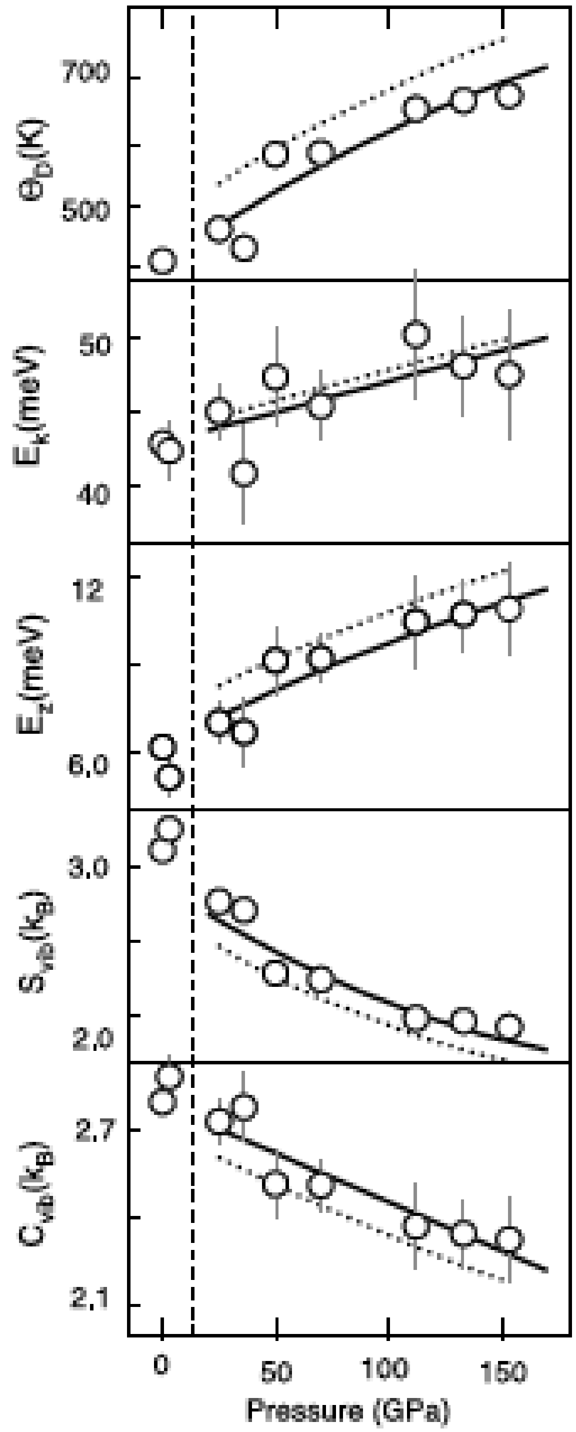
$$\langle z^2 \rangle_v = \frac{1}{3k^2} \int \left[2\bar{n}(\bar{\nu}) + 1\right] \frac{\bar{\nu}_R}{\bar{\nu}} D(\bar{\nu}) d\bar{\nu},$$

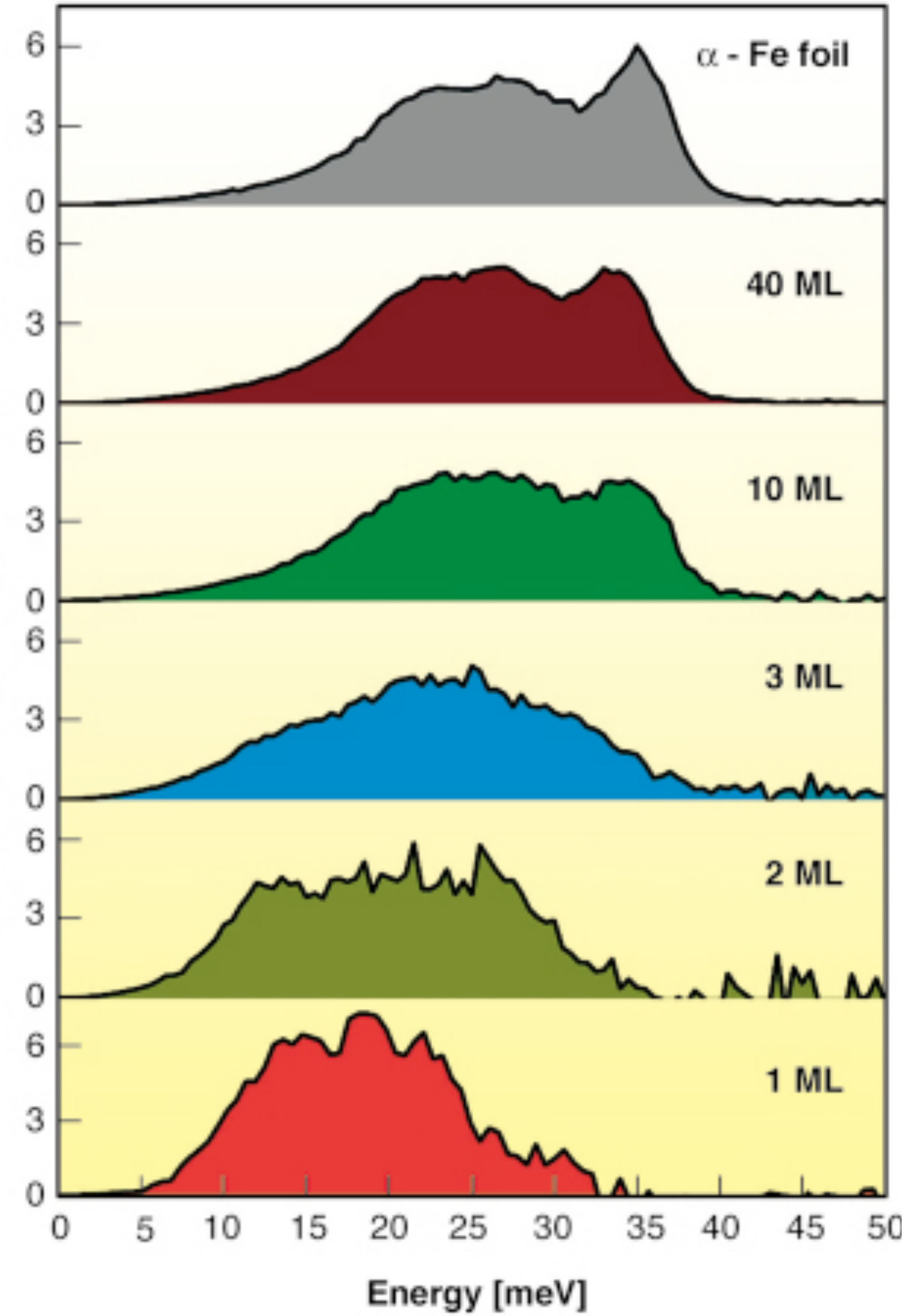
3.8×10^{-5} Å^2/K for KZS and 3.5×10^{-5} Å^2/K for BGS.

Phonon density of states of iron under high pressure



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



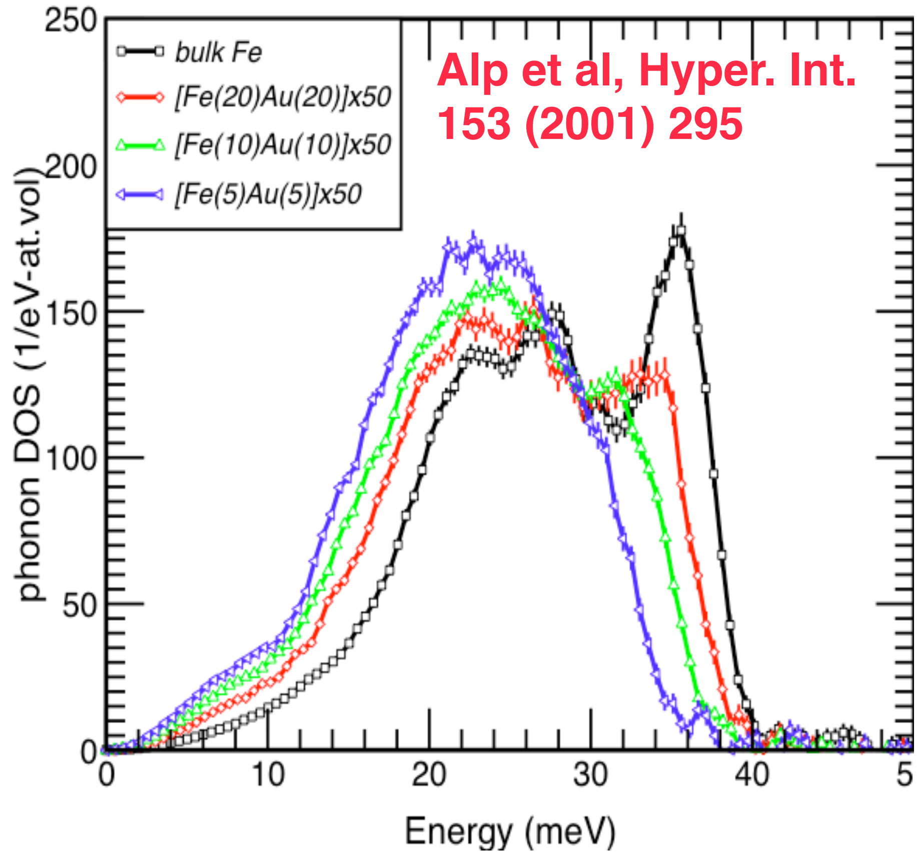


Fe films deposited on W(110)

Transition from the bulk to a single iron monolayer

S. Stankov, R. Röhlsberger, T. Slezak, M. Sladecek, B. Sepiol, G. Vogl, A. I. Chumakov, R. Rüffer, N. Spiridis, J. Lazewski, K. Parlinski, and J. Korecki,

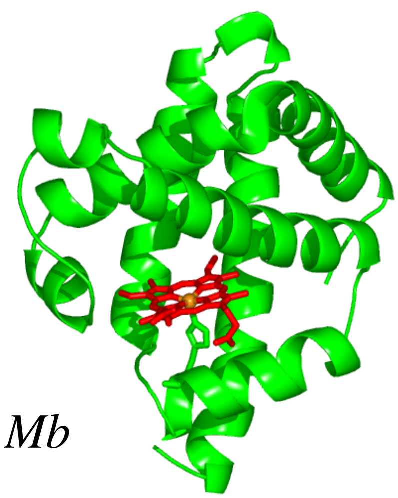
ESRF Highlights 2006



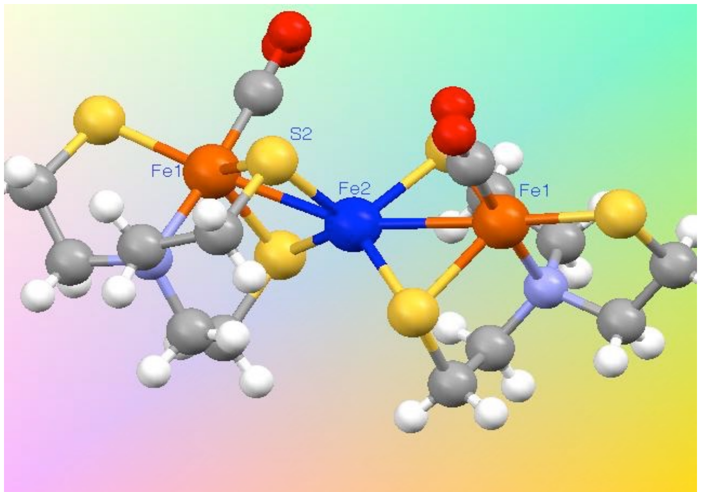
Alp et al, Hyper. Int. 153 (2001) 295

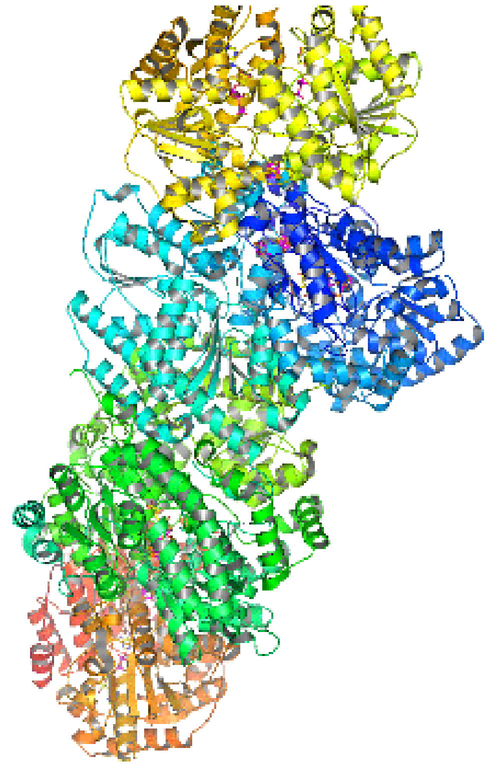
Biology & bio-inorganic chemistry

S. Cramer	University of California-Davis
E. Solomon	Stanford University
T. Sage	Northeastern University
E. Munck	University of Pittsburg
DeBeer George	Cornell University
Nicolai Lehnert	University of Michigan
R. Scheidt	University of Notre Dame

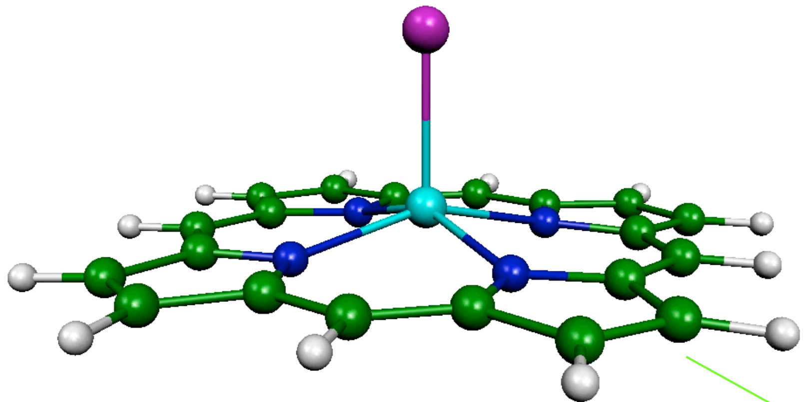


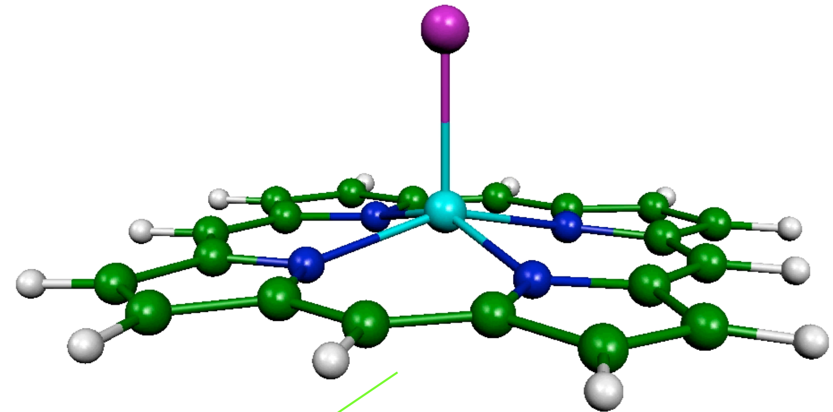
Mb

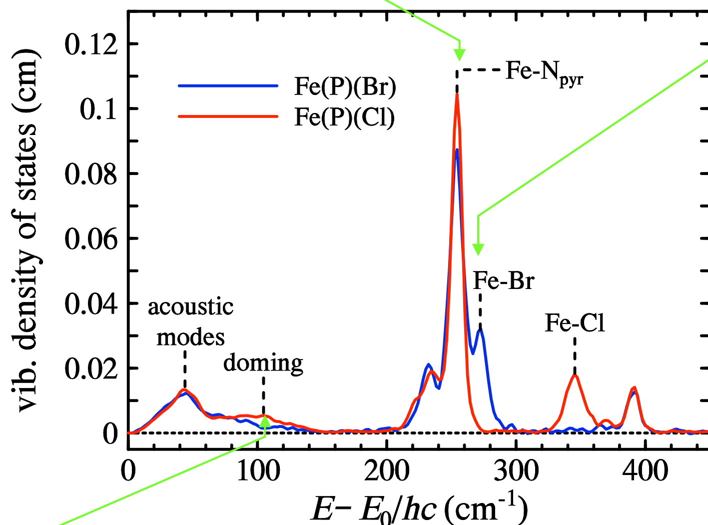




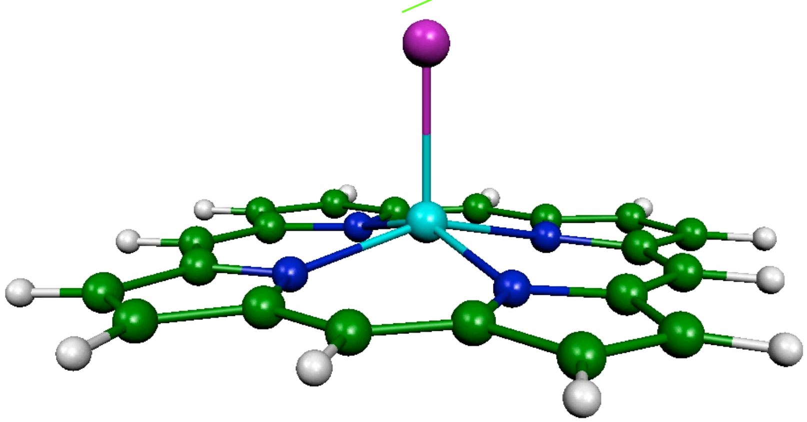
Vibrational spectroscopy of proteins, enzymes and biomimic model porphyrins and cubanes

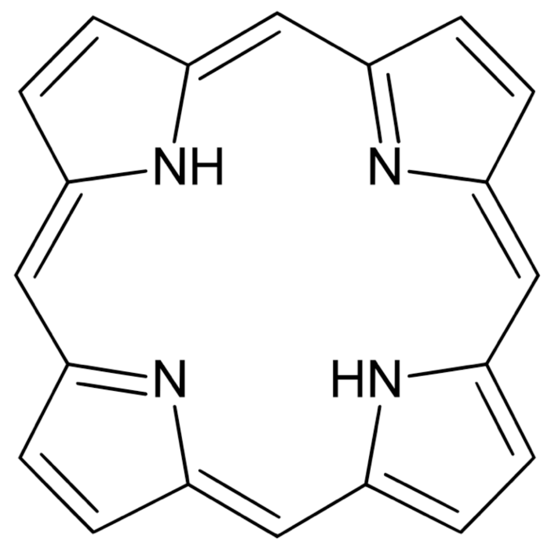






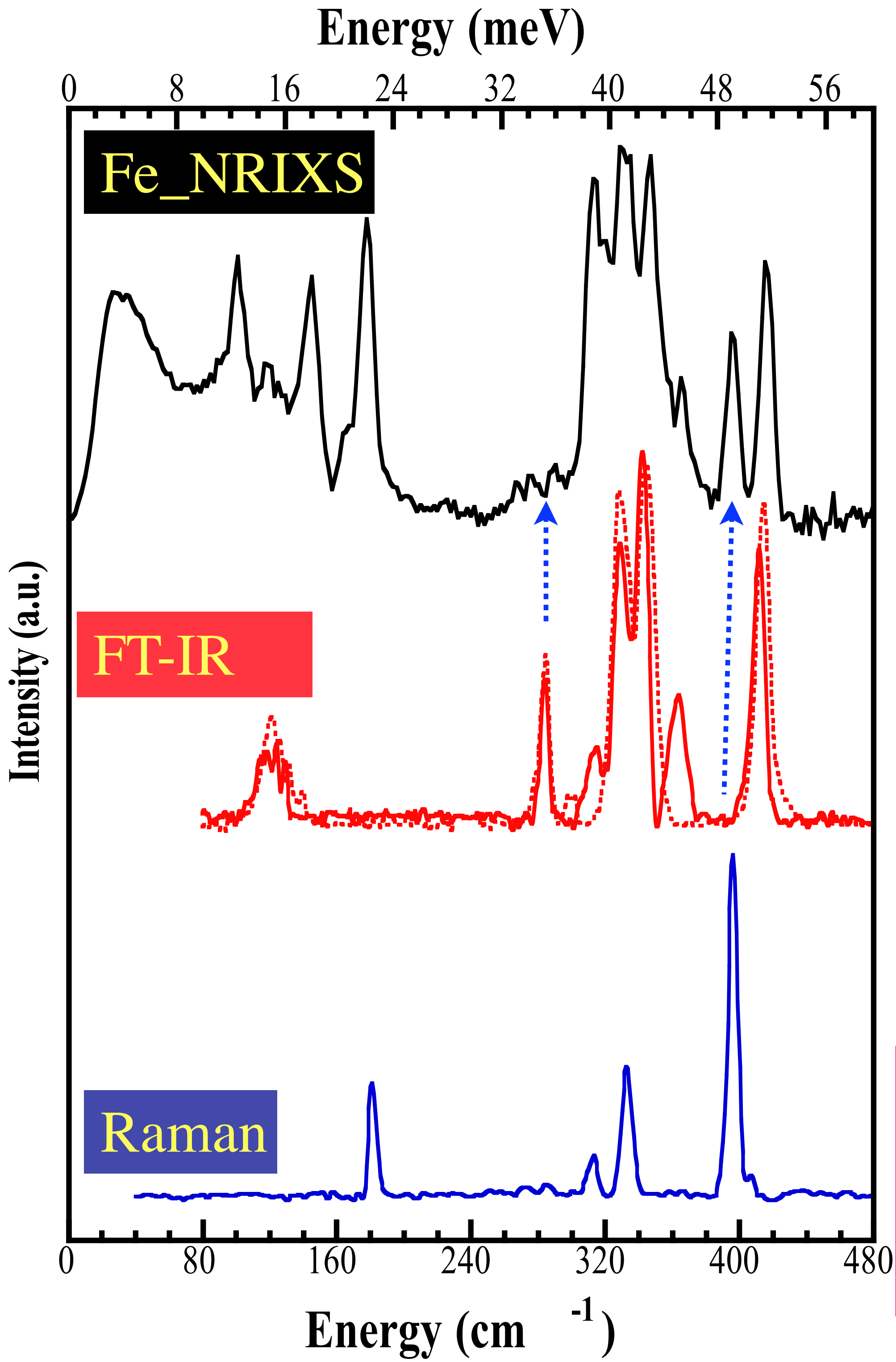
vib. density of states (cm)
0.12
0.1
0.08
0.06
0.04
0.02
0
Fe(P)(Br)
Fe(P)(Cl)
Fe-N$_{pyr}$
Fe-Br
Fe-Cl
acoustic modes
doming
0
100
200
300
400
$E - E_0/hc$ (cm^{-1})

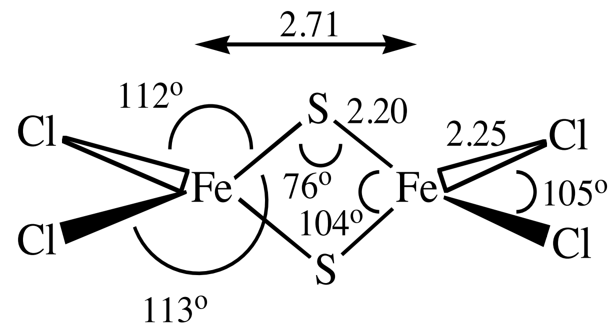




NH
N
N
HN

$[NEt_4]_2[Fe_2S_2Cl_4]$.



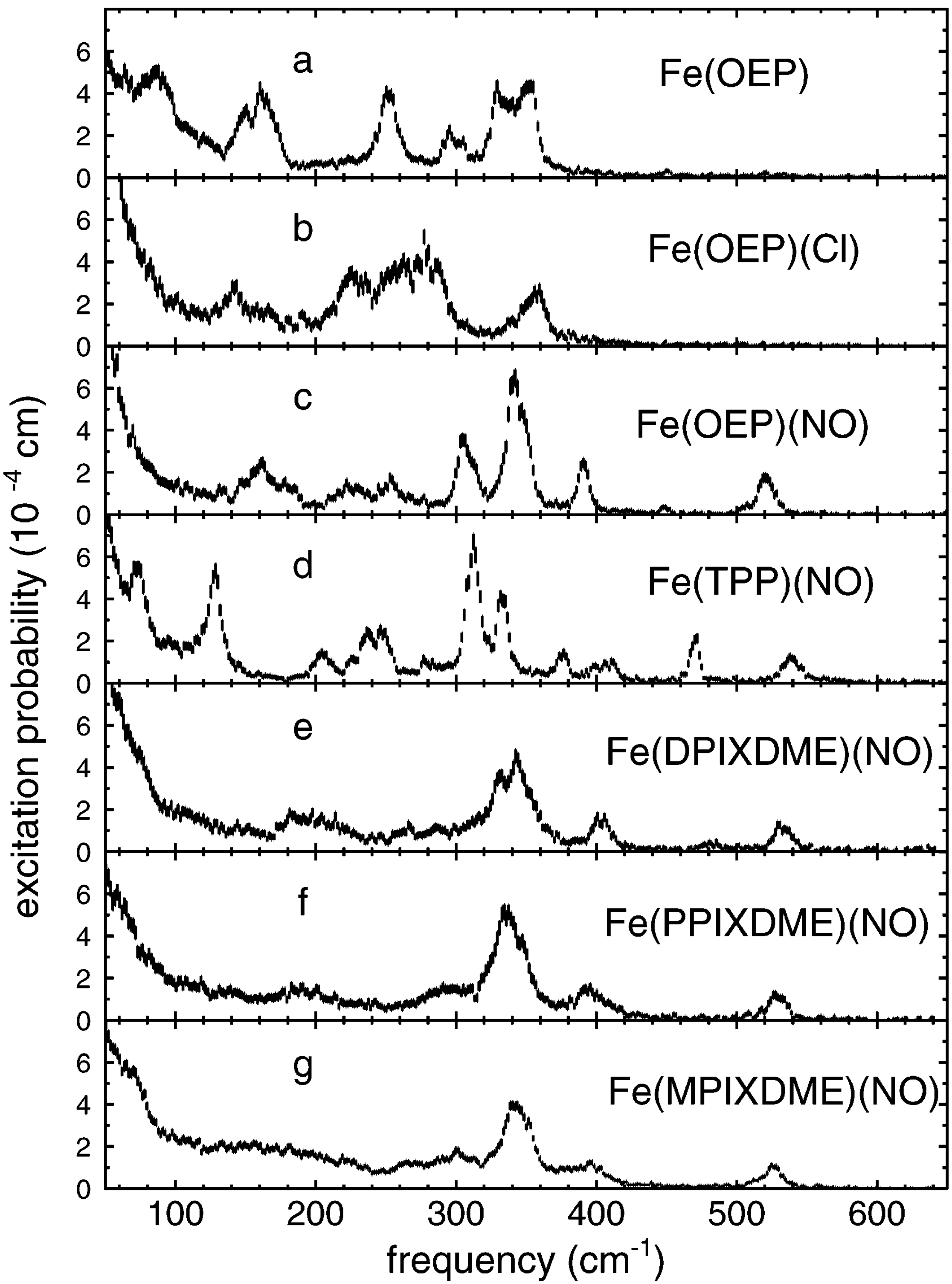


Some unique advantages of NRIXS

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

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

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



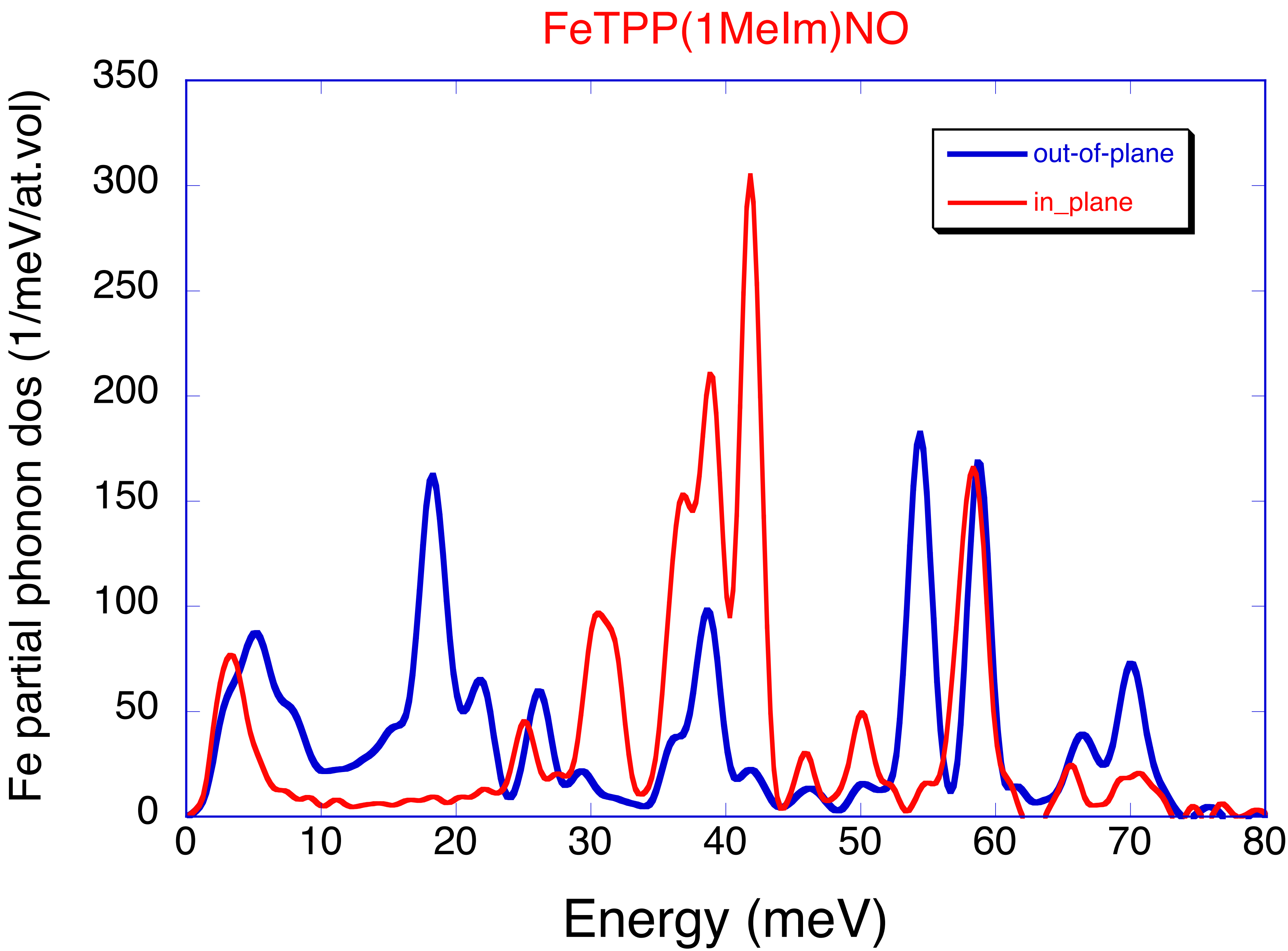
OEP: octaethylporphyrin;

TPP: Tetraphenylporphyrin

DPIXDME, deuteroporphyrin IX dimethyl ester

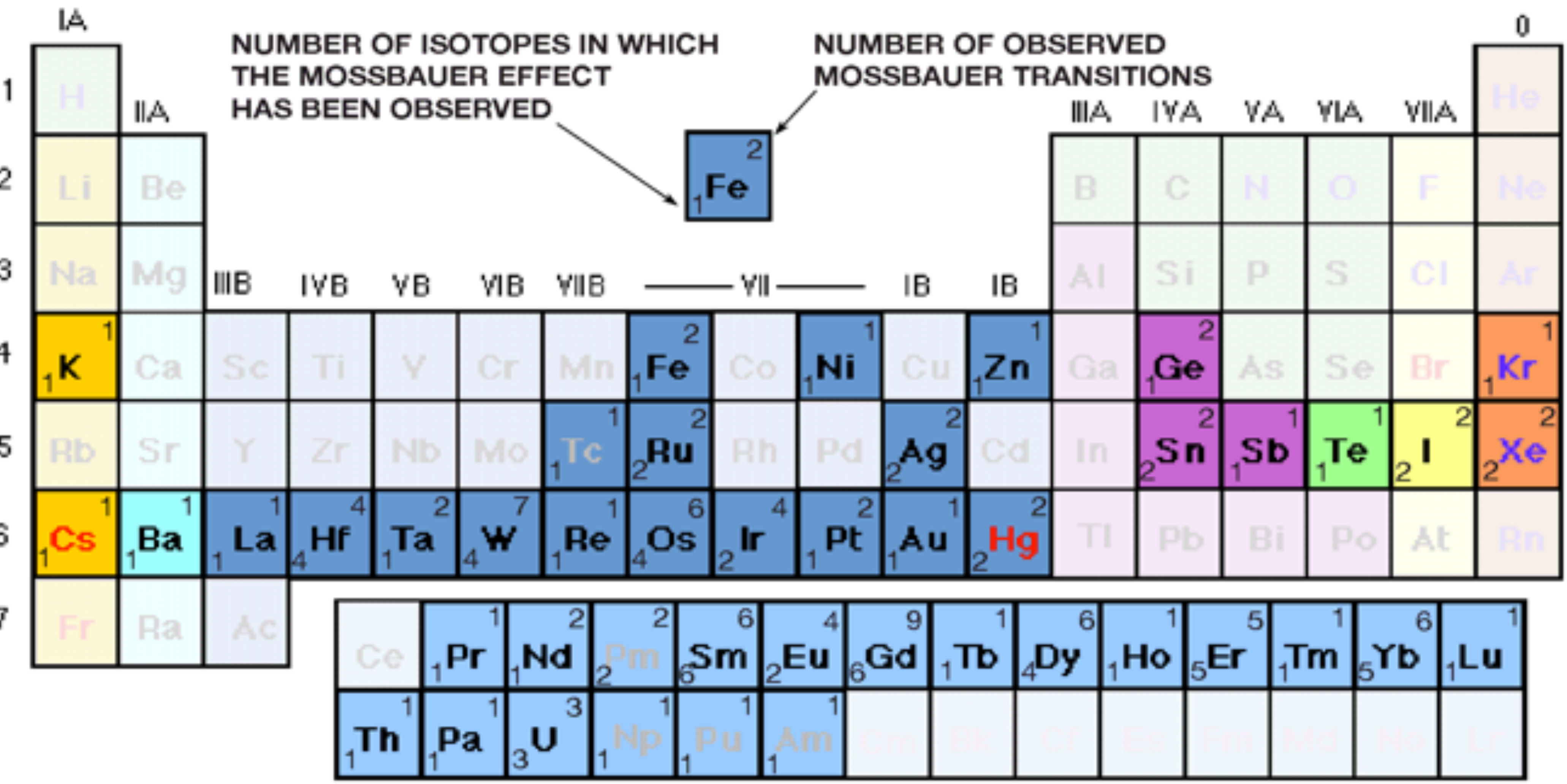
PPIXDME, protoporphyrin IX dimethyl ester

MPIXDME, mesoporphyrin IX dimethyl ester


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

Mössbauer Effect Data Center

http://www.medc.dicp.ac.cn/Resources.php



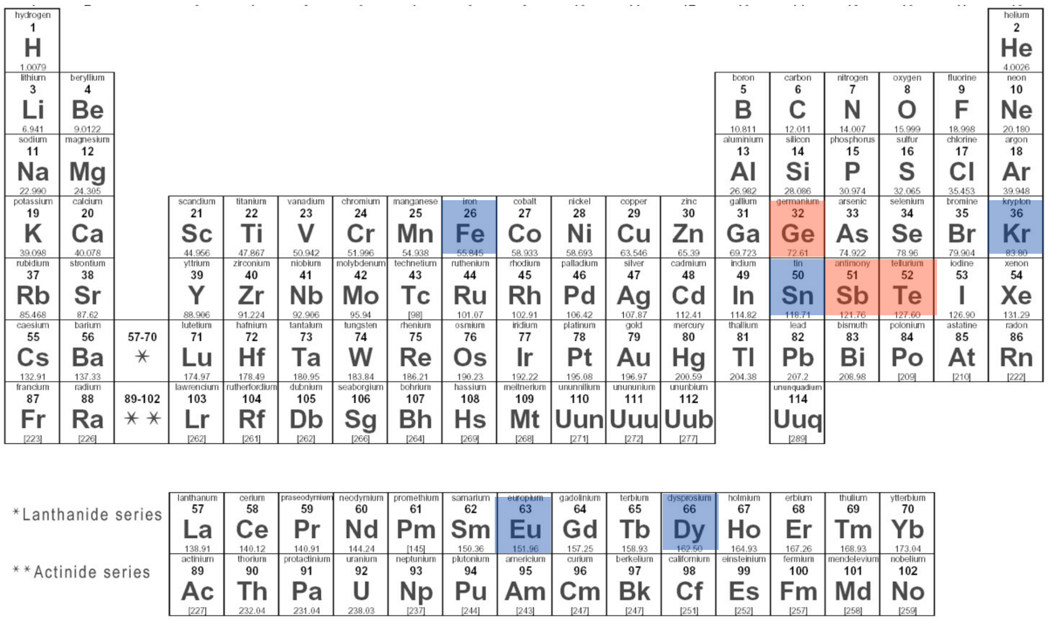
46 elements have Mössbauer transitions. Why do we use only a few?

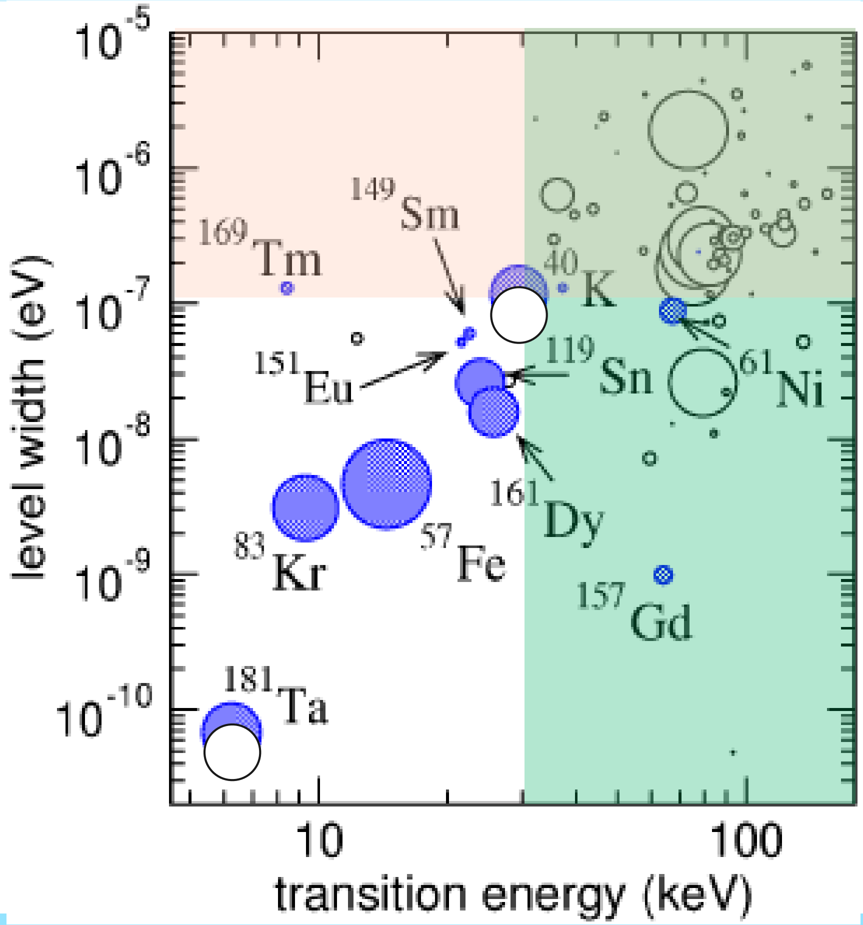
The Mössbauer isotopes observed with synchrotron radiation (1985-2014)

Isotope	Energy (eV)	Half-life (ns)	ΔE (neV)	Tabulated E (eV)
^{181}Ta	6215.5	9800.	0.067	6238
^{169}Tm	8401.3	4.	114.0	8409.9
^{83}Kr	9403.5	147.	3.1	9400
^{57}Fe	14412.5	97.8	4.67	14413
^{151}Eu	21541.4	9.7	47.0	21532
^{149}Sm	22496.	7.1	64.1	22490
^{119}Sn	23879.4	17.8	25.7	23870
^{161}Dy	25651.4	28.2	16.2	25655
^{129}I	27770.	16.8	27.2	27800
^{40}K	29834.	4.25	107.0	29560
^{125}Te	35460	1.48	308.0	35491.9
^{121}Sb	37129.	4.53	100.0	37133.
^{129}Xe	39581.3	1.465	311.2	39578.
^{61}Ni	67419.	5.1	89.0	67400
^{73}Ge	68752	1.86	245.	68752
^{176}Hf	88349.	1.43	319.4	83000
^{176}Hf	88349.	1.43	319.4	83000
^{99}Ru	89571.	28.8	15.8	89651.8
^{67}Zn	93300.	9200.	0.049	

Why limited number of isotopes ?

Absorption **cross-section**, nuclear **life time**, and **resonance energy** must be suitable for a General User program with wide applicability





- With **Fe** (3d-element), **Sn,** (semi-metal), **Eu** and **Dy** (Rare earth), and **Kr** (Noble element) a diverse scientific program has already been created.

- Sb, Te, and Ge can be added in the future, if new resources, and undulators become available..

Thank you ….