Lattice dynamics for beginners

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Nuclear Resonant Scattering Workshop,
November 7-9, 2014, Argonne

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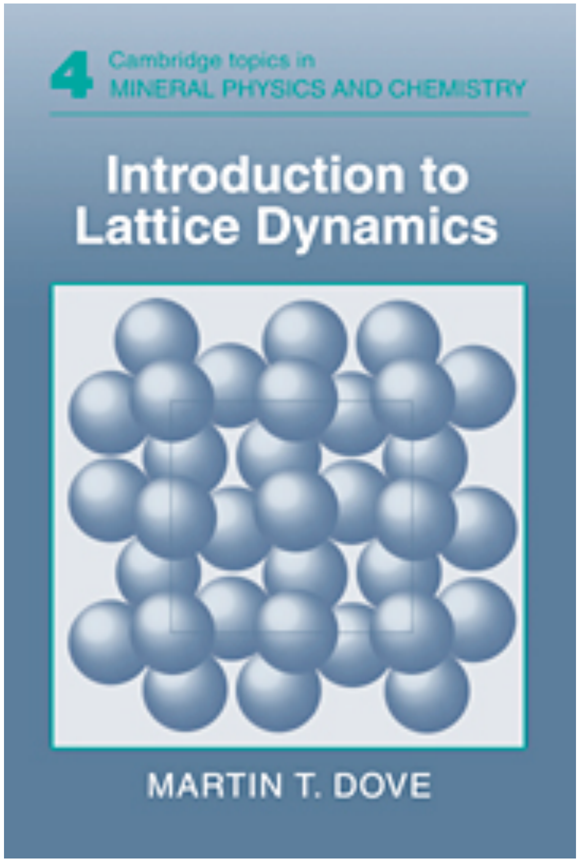
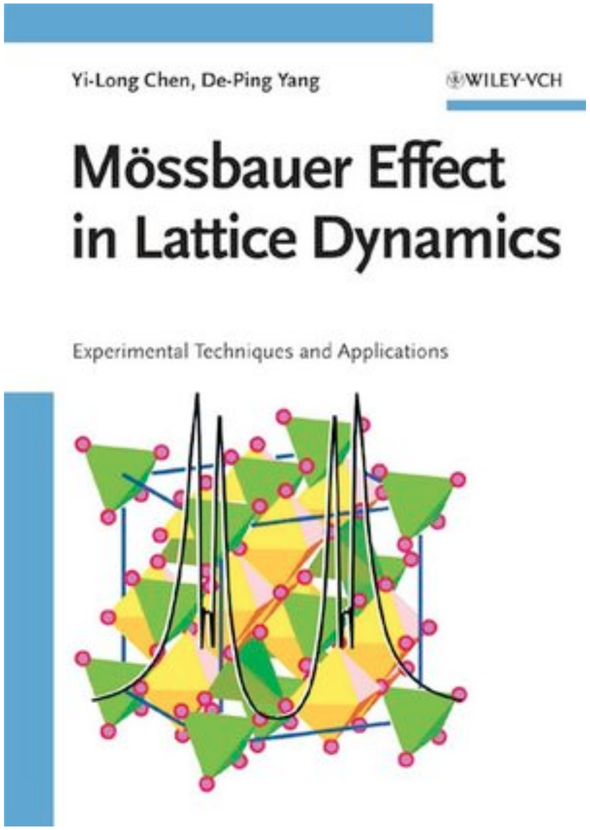
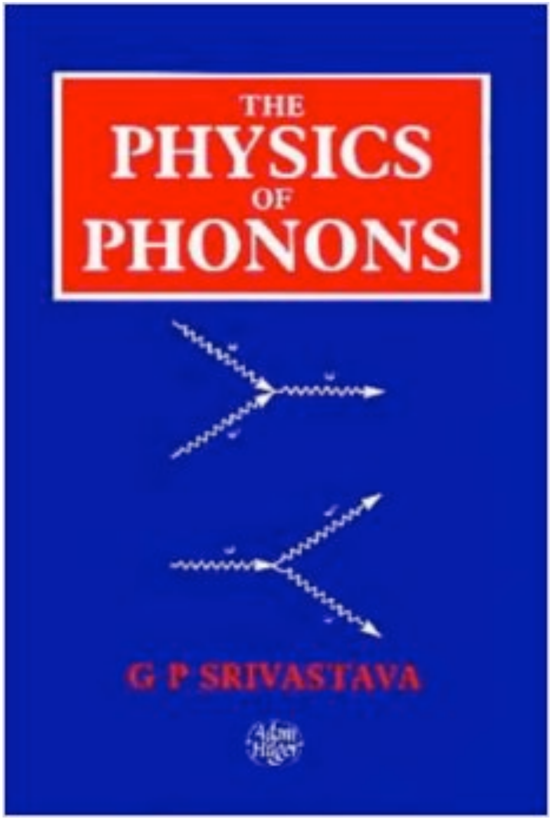






Lattice dynamics for beginners

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

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, $\vec{k} = \dfrac{\lambda}{2\pi}$

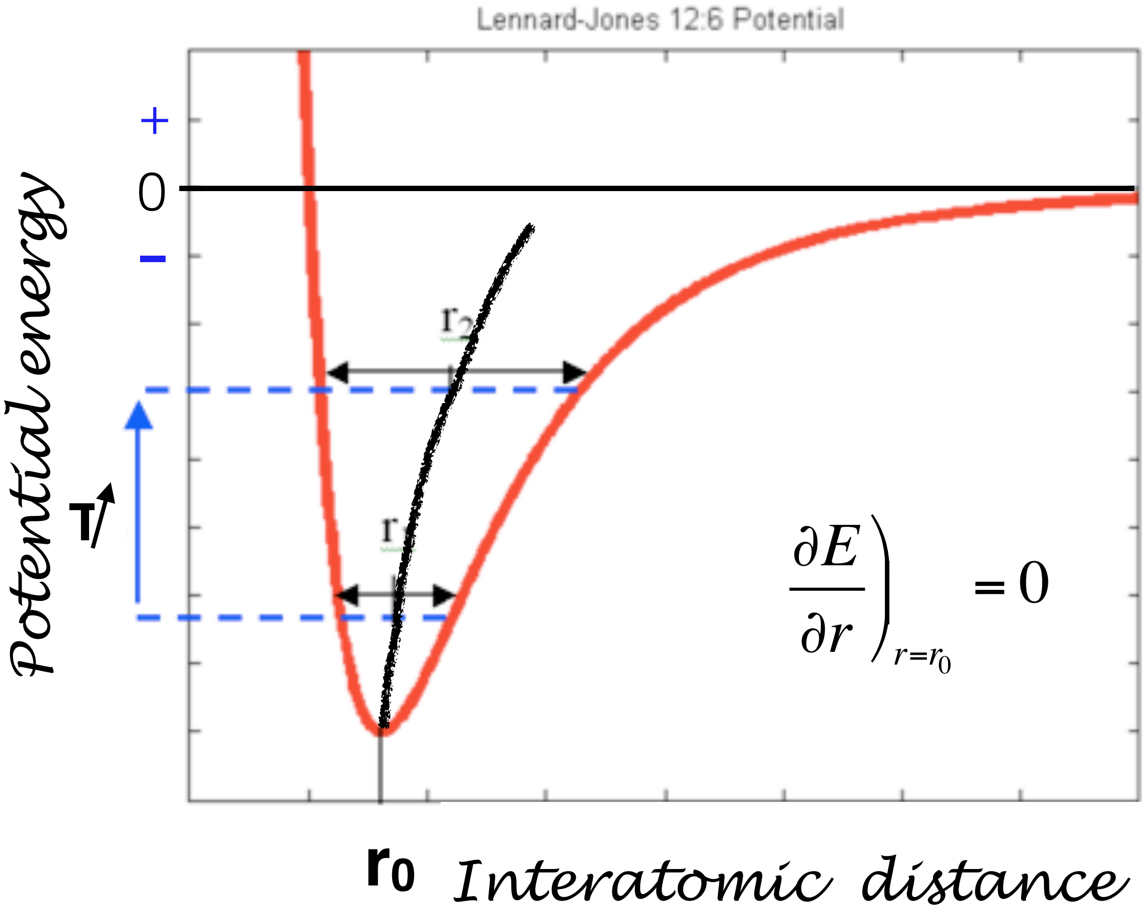
Two main approximations should be noticed:

- **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.



$$\left.\frac{\partial E}{\partial r}\right)_{r=r_0} = 0$$

There should be no thermal expansion in the harmonic model.

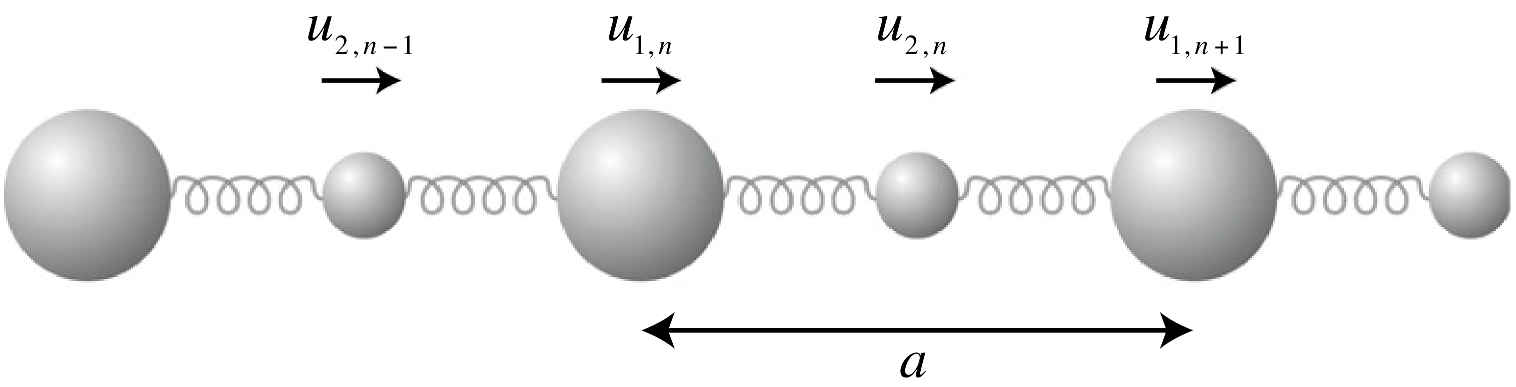
The fact that there is thermal expansion is an indication that the potential under which the atoms move is not harmonic.

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)

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

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

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

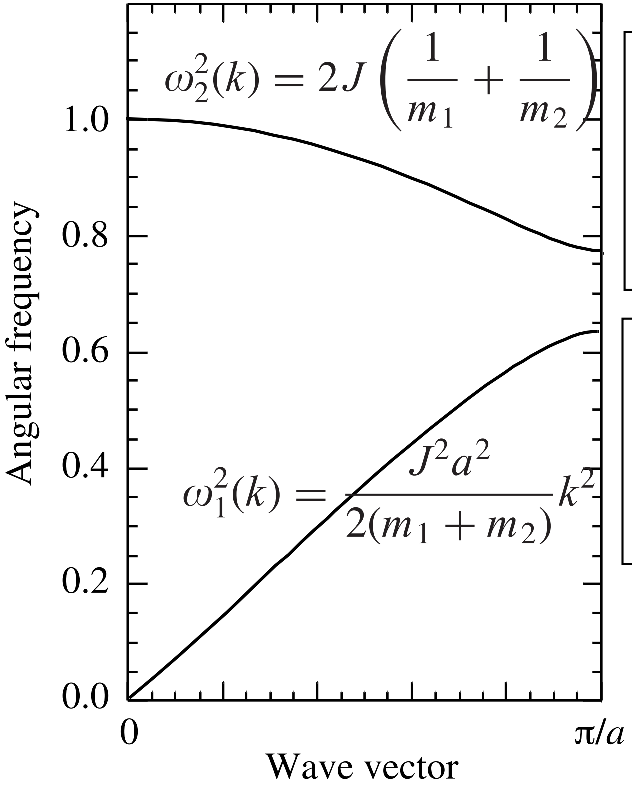
Mass normalized displacements (real)

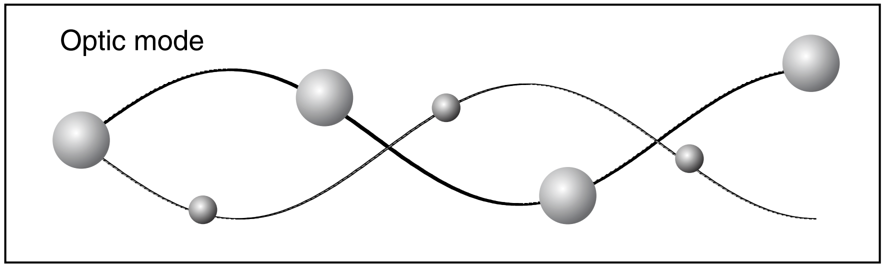
$$\omega^2 \begin{pmatrix} e_1 \\ e_2 \end{pmatrix} = \mathbf{D}(k) \cdot \begin{pmatrix} e_1 \\ e_2 \end{pmatrix}$$

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

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

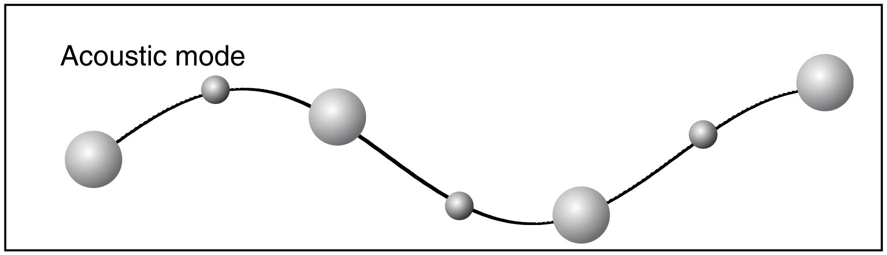
Eigen solutions





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

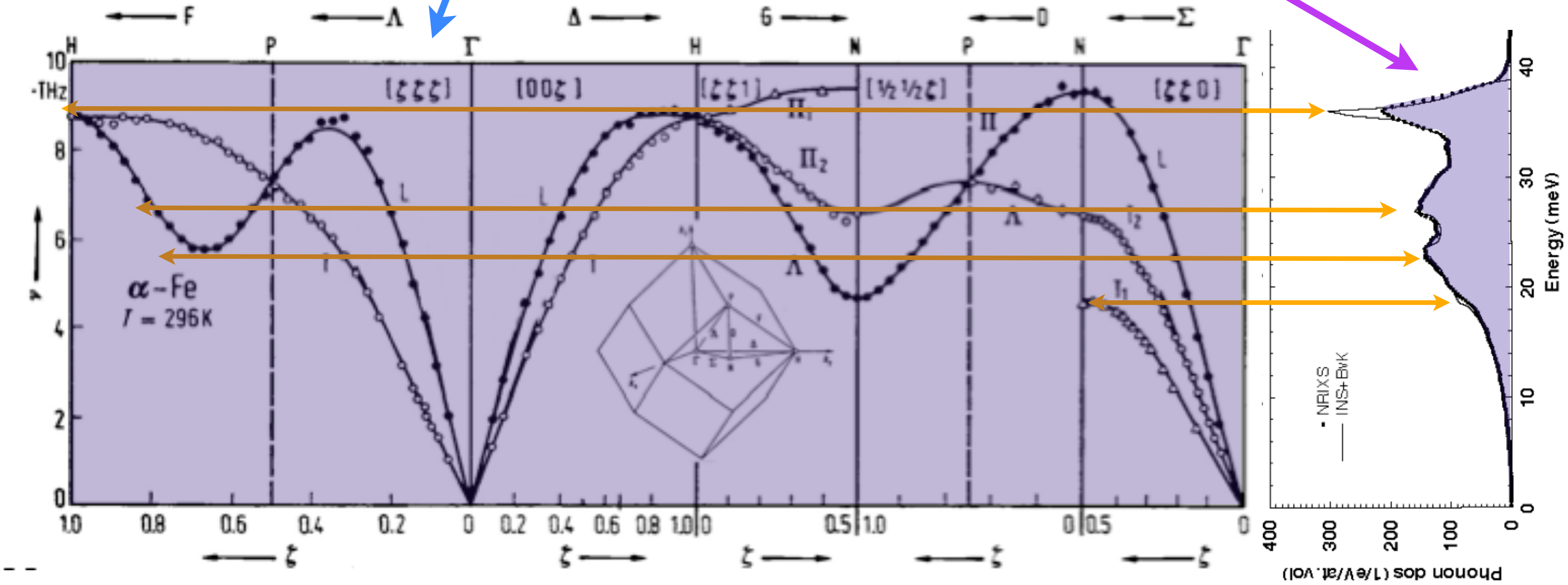
IXS

Non-Resonant

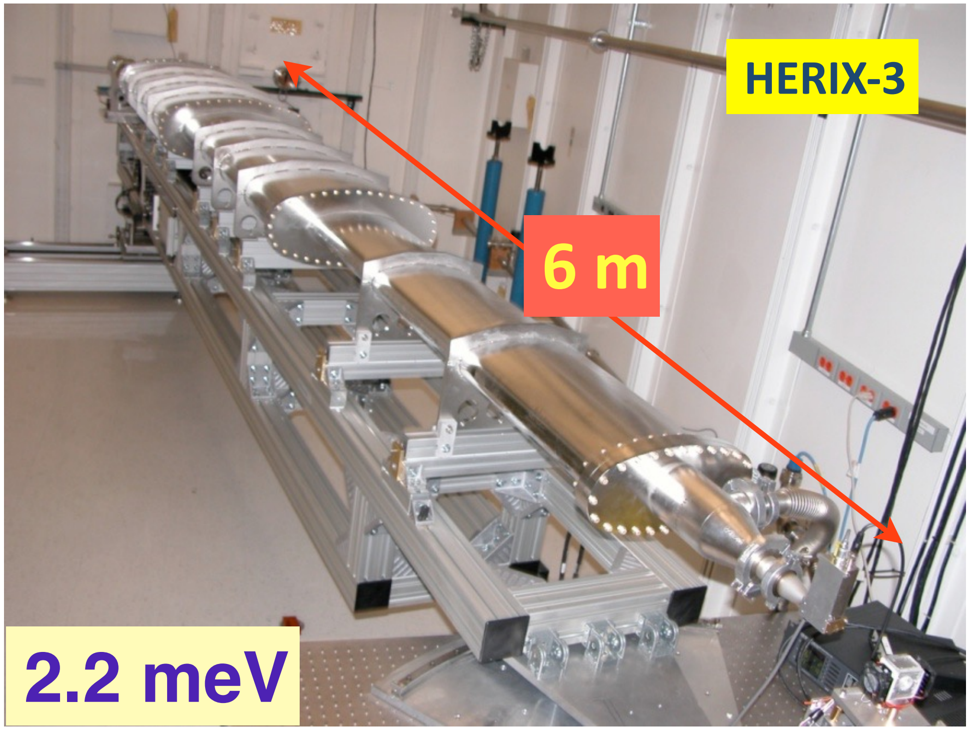
Resonant

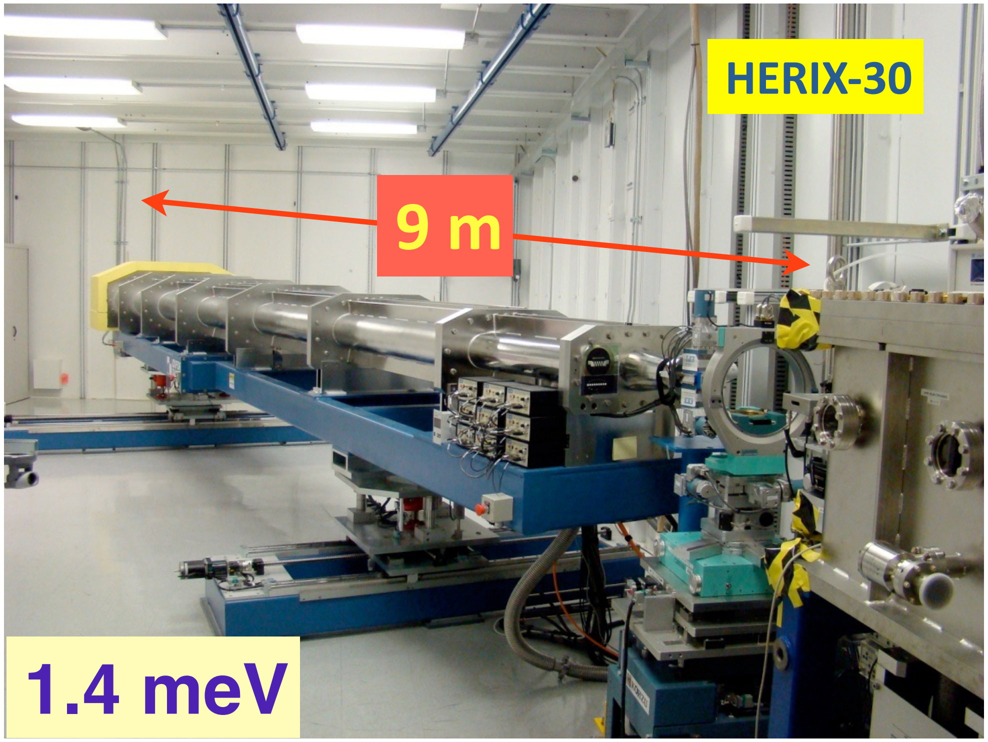
ΔE ~ meV
IXS

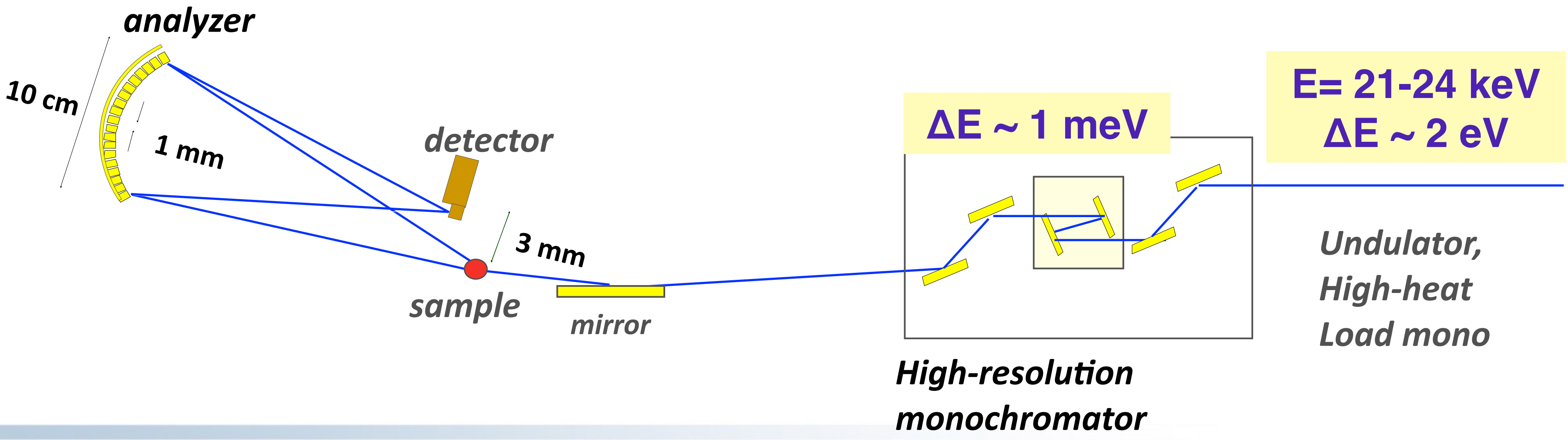
ΔE ~ 1 meV
Nuclear resonant

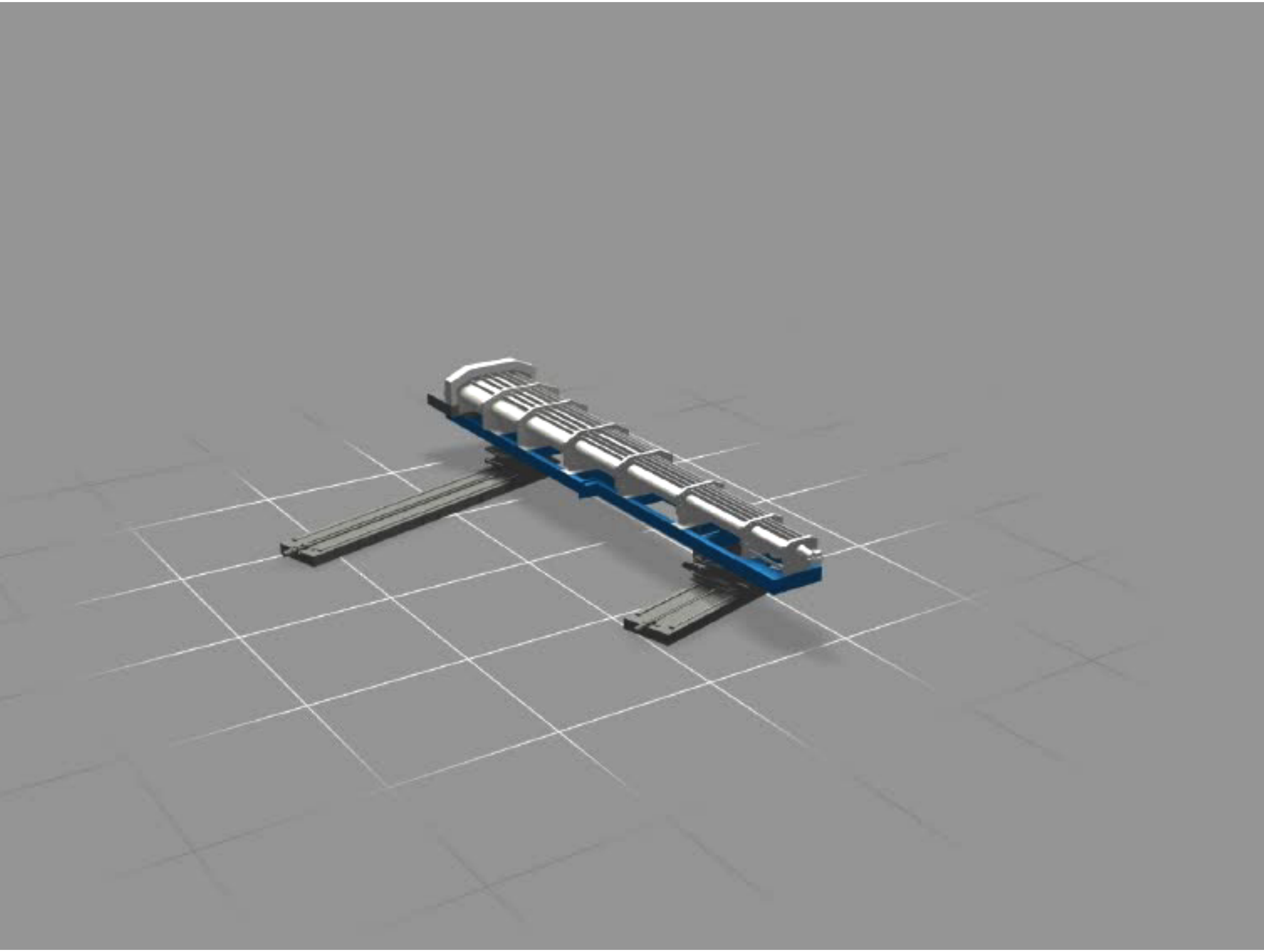


HERIX-3 and HERIX-30









What is being measured ?

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

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

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

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

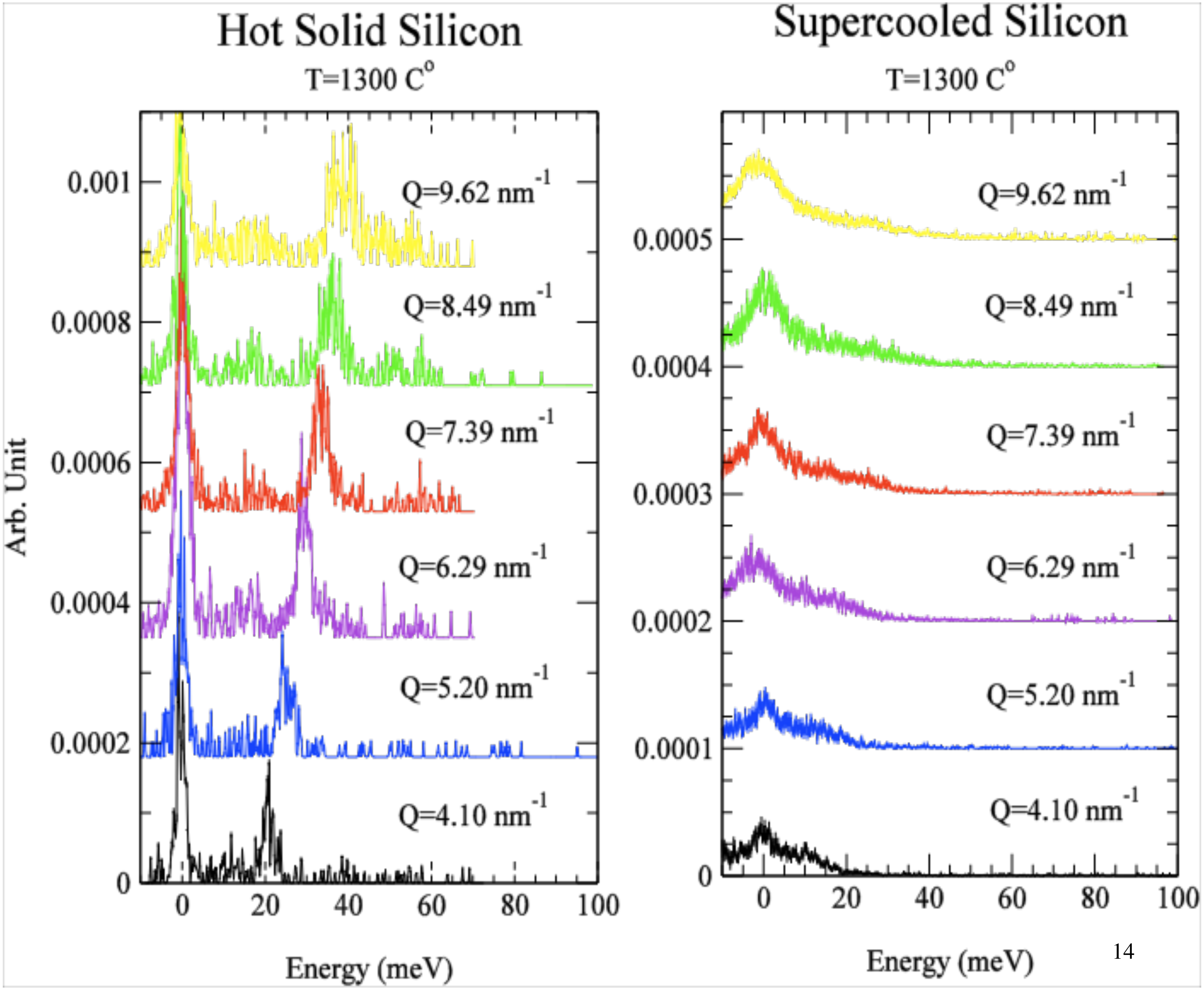
$$S(Q,\omega)=\sum_{q,j}\left|\sum_{s} f_s(Q)\frac{\hbar}{\sqrt{2m_s}}e^{-W_s}e^{i\vec{Q}\bullet\vec{R}_s}\left[\vec{Q}\cdot\vec{e}(q,s,j)\right]\right|^2\frac{\left(\frac{1}{e^{\hbar\omega/kT}-1}+\frac{1}{2}\pm\frac{1}{2}\right)}{\omega_{q,j}}\delta\left(\omega\pm\omega_{q,j}\right)$$

Phase of the scattering amplitude

phonon frequency

Polarization factor between momentum transfer and photon’s electric field

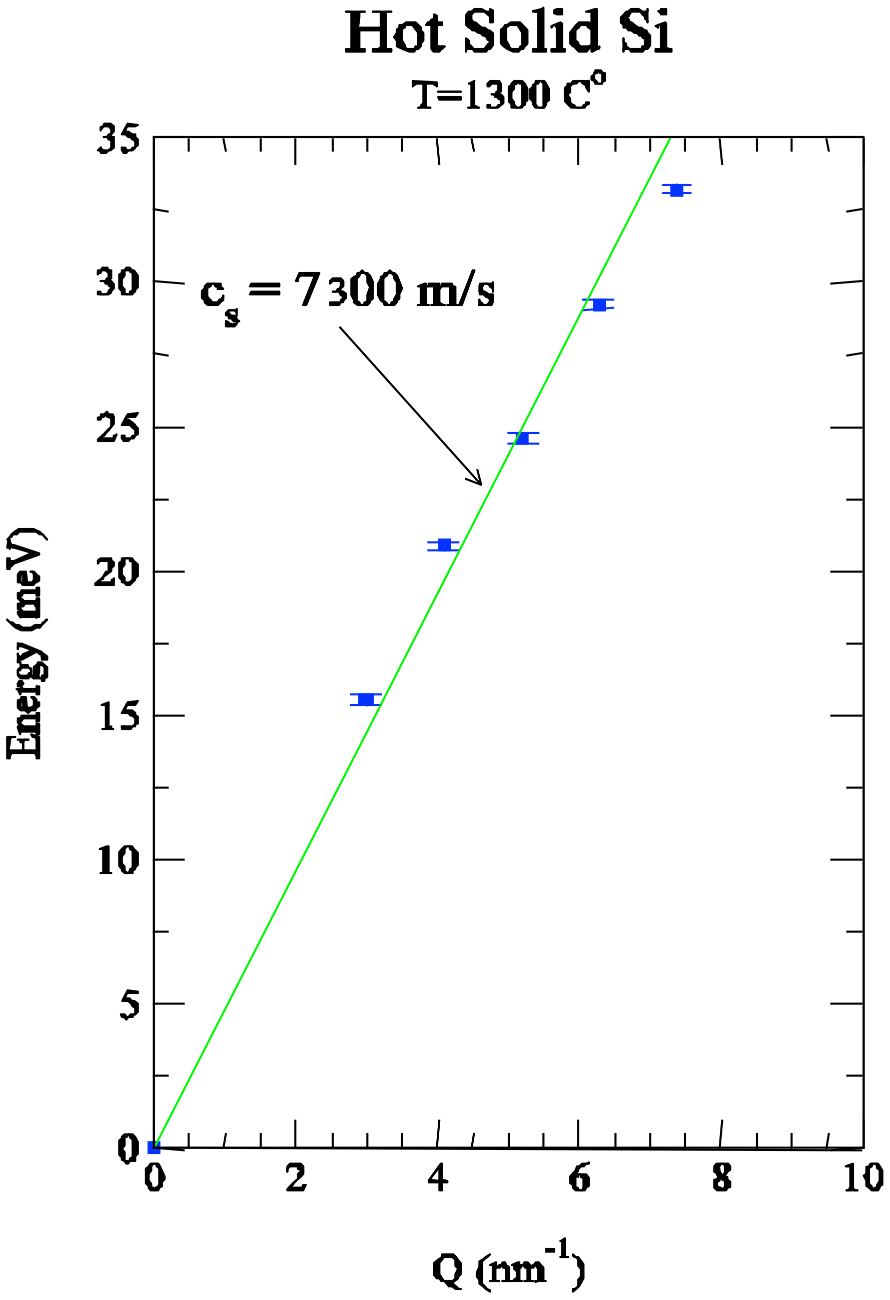
delta-function in ω


Hot Solid Silicon

T=1300 C°

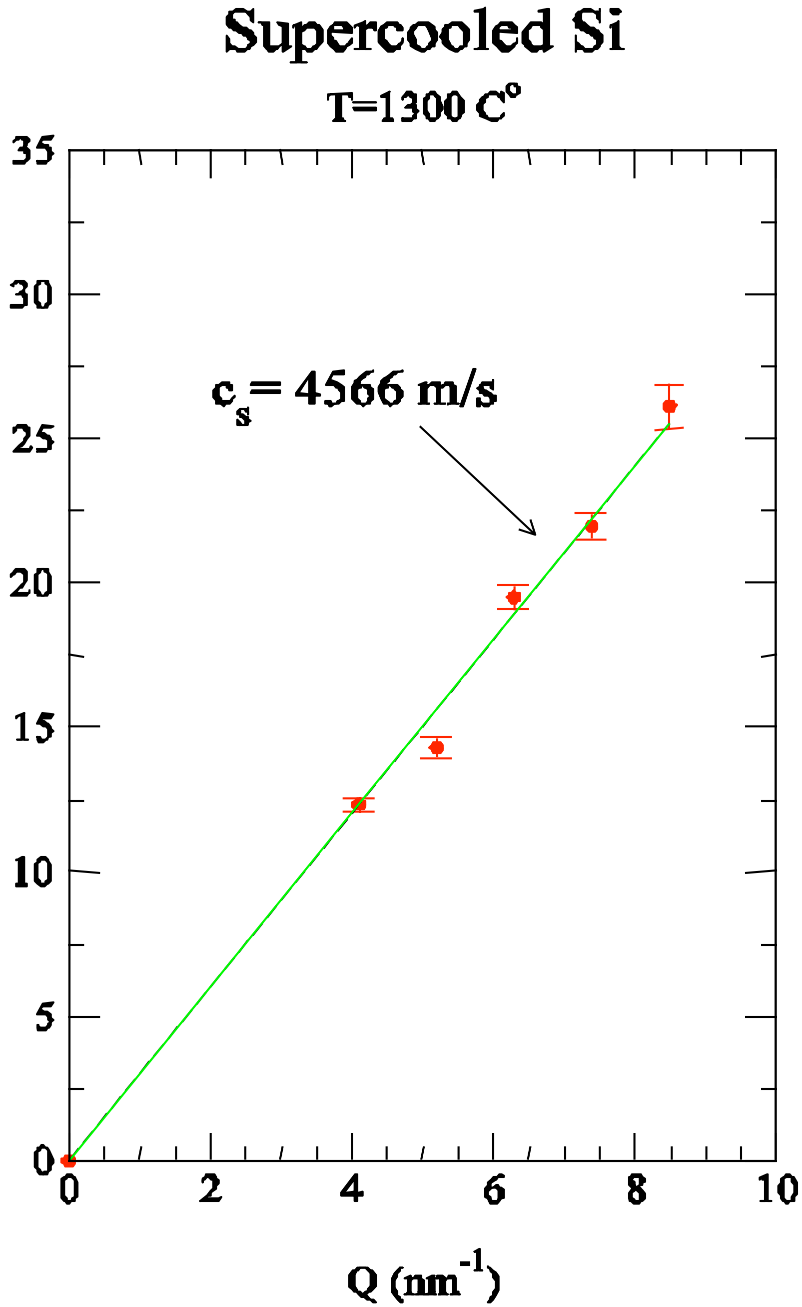
Supercooled Silicon

T=1300 C°



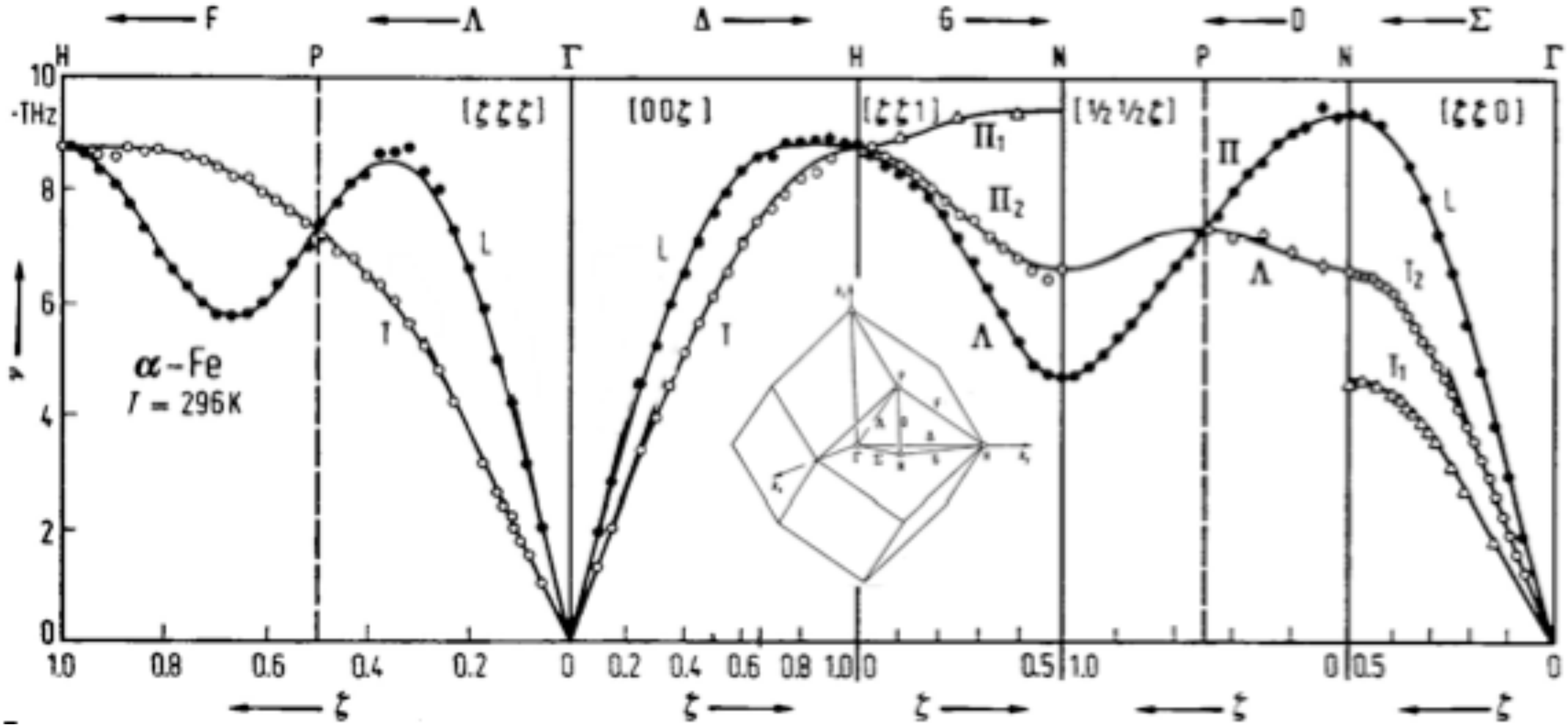
Hot Solid Si

T=1300 C°



Supercooled Si

T=1300 C°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Π₁
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Λ
T₂
T₁
L
α-Fe
T = 296K
1.0
0.8
0.6
0.4
0.2
0
0
0.2
0.4
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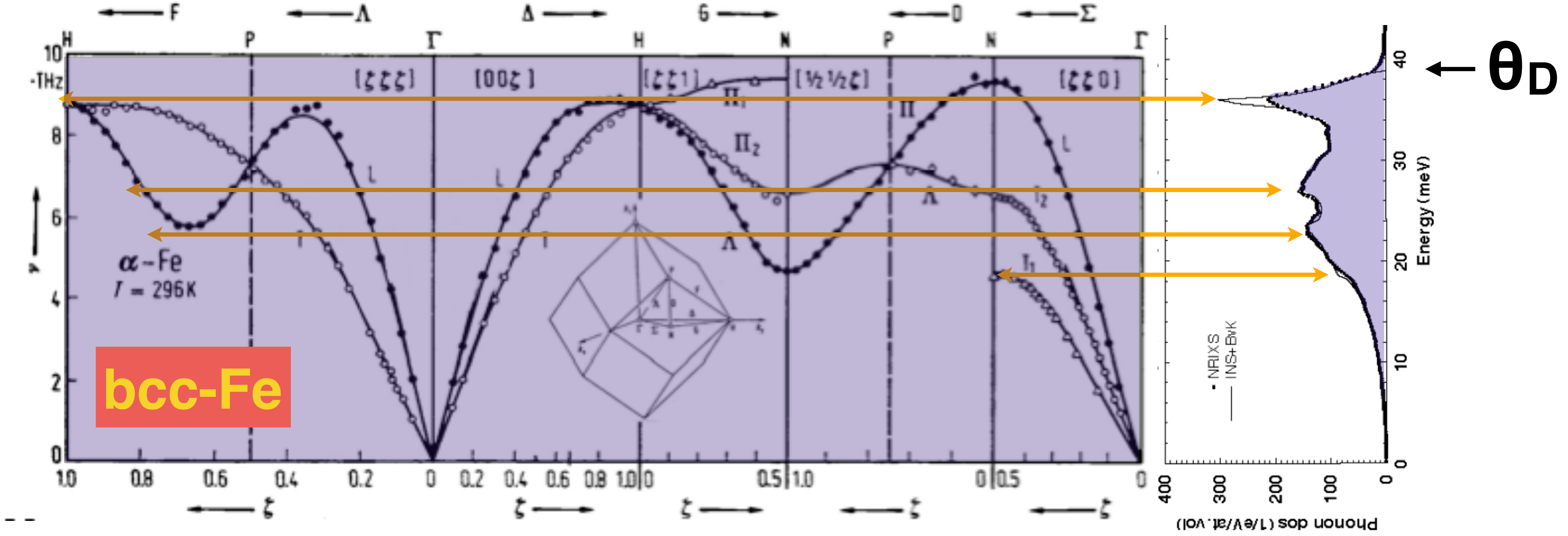
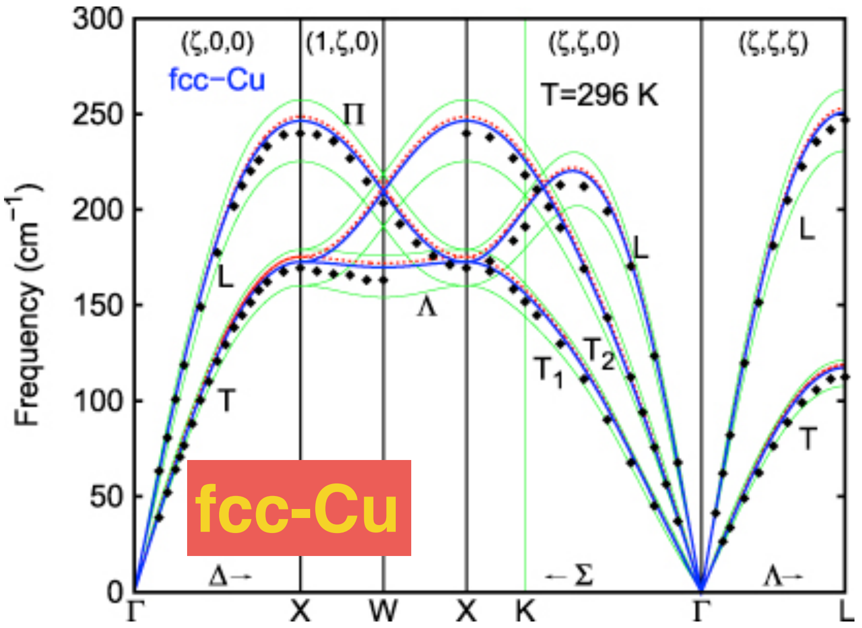




Let's assume that the acoustic modes have a linear relationship between frequency and wave vector:

$\omega = ck$, 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.

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

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

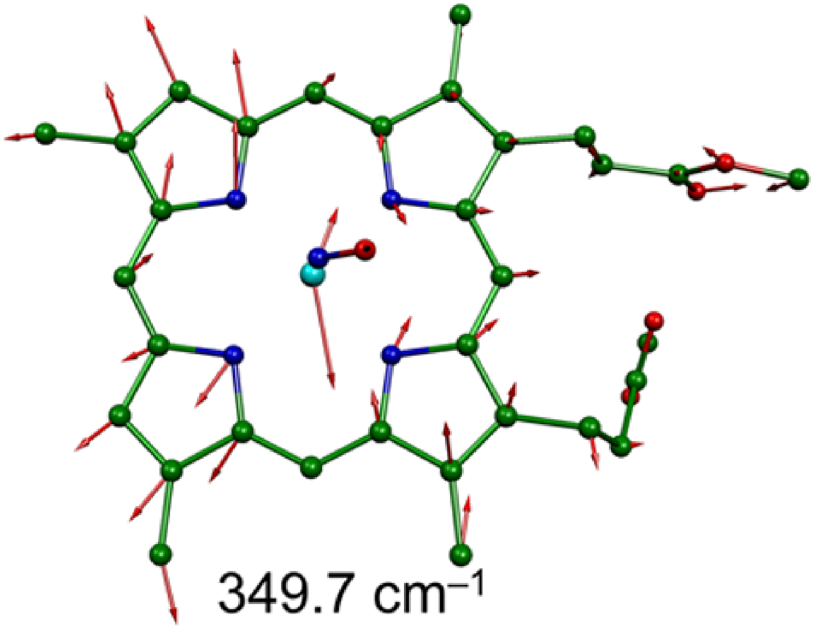
Eigenvalue eq^{n}.

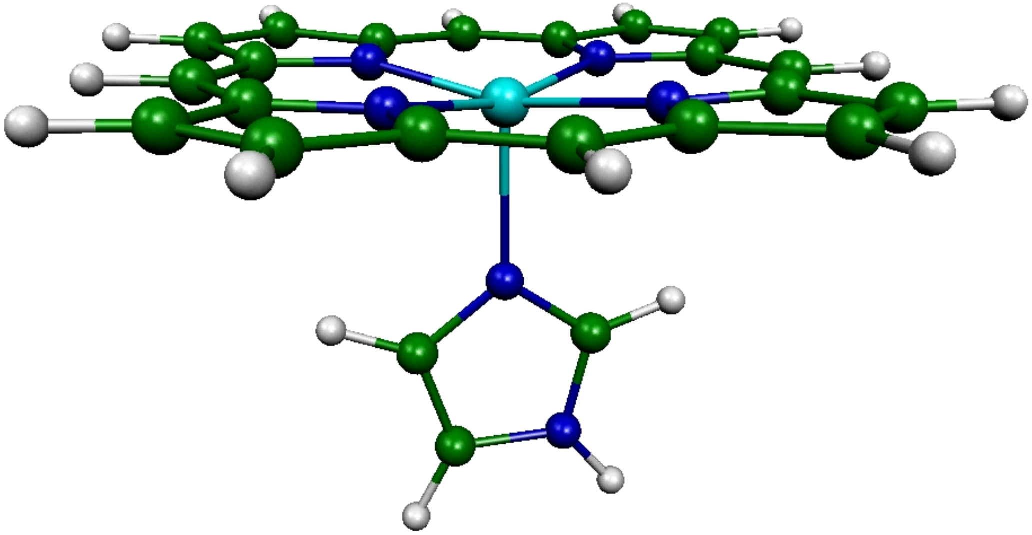
$$\boxed{D_{j,j'}(\mathbf{k}) = \frac{1}{\sqrt{m_j m_{j'}}} \sum_{n'} \Phi_{0,n'}^{j,j'} \exp\left(i\mathbf{k} \cdot (\mathbf{r}_{j,0} - \mathbf{r}_{j',n'})\right)}$$

Dynamical matrix

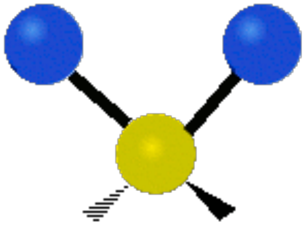
$$\boxed{\mathbf{e}_{\lambda}^{\mathrm{T}} \cdot \mathbf{e}_{\lambda} = 1; \quad \mathbf{e}_{\lambda'}^{\mathrm{T}} \cdot \mathbf{e}_{\lambda} = \delta_{\lambda',\lambda}}$$

Eigenvalues are orthonormal..

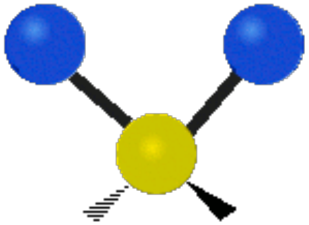




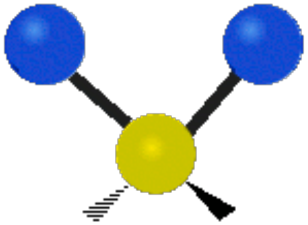
symmetrical stretching



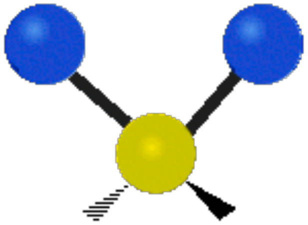
asymmetrical stretching



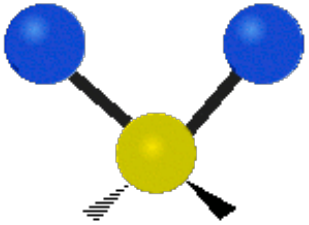
scissoring



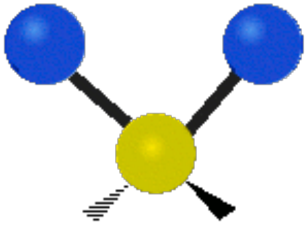
rocking



wagging



twisting



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 ħω as quanta of excitation of the lattice vibration mode of angular frequency ω. Since momentum, ħk, 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.

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.

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

Total energy, in terms of normal mode coordinates

$$\left\langle n(\omega_{\mathbf{k},\lambda})\right\rangle = \frac{1}{\exp(\hbar\omega_{\mathbf{k},\lambda}/k_{\mathrm{B}}T) - 1}$$

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

And, some thermodynamics

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

Partition function

$$F = -k_{\mathrm{B}} T \ln \mathcal{Z}$$

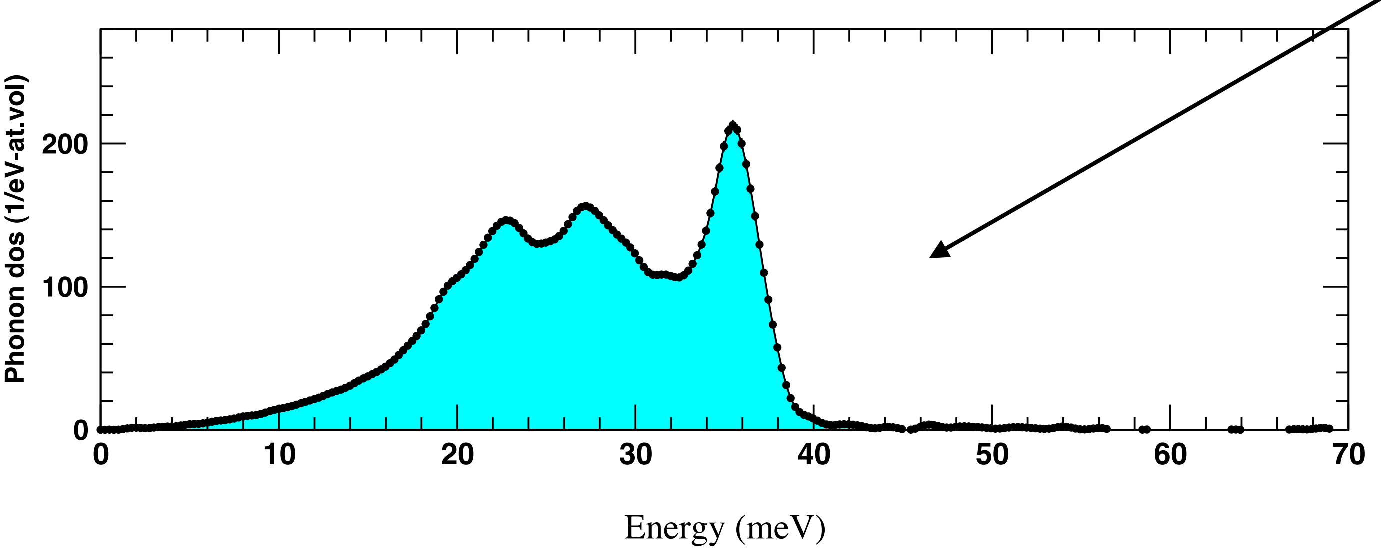
Free energy

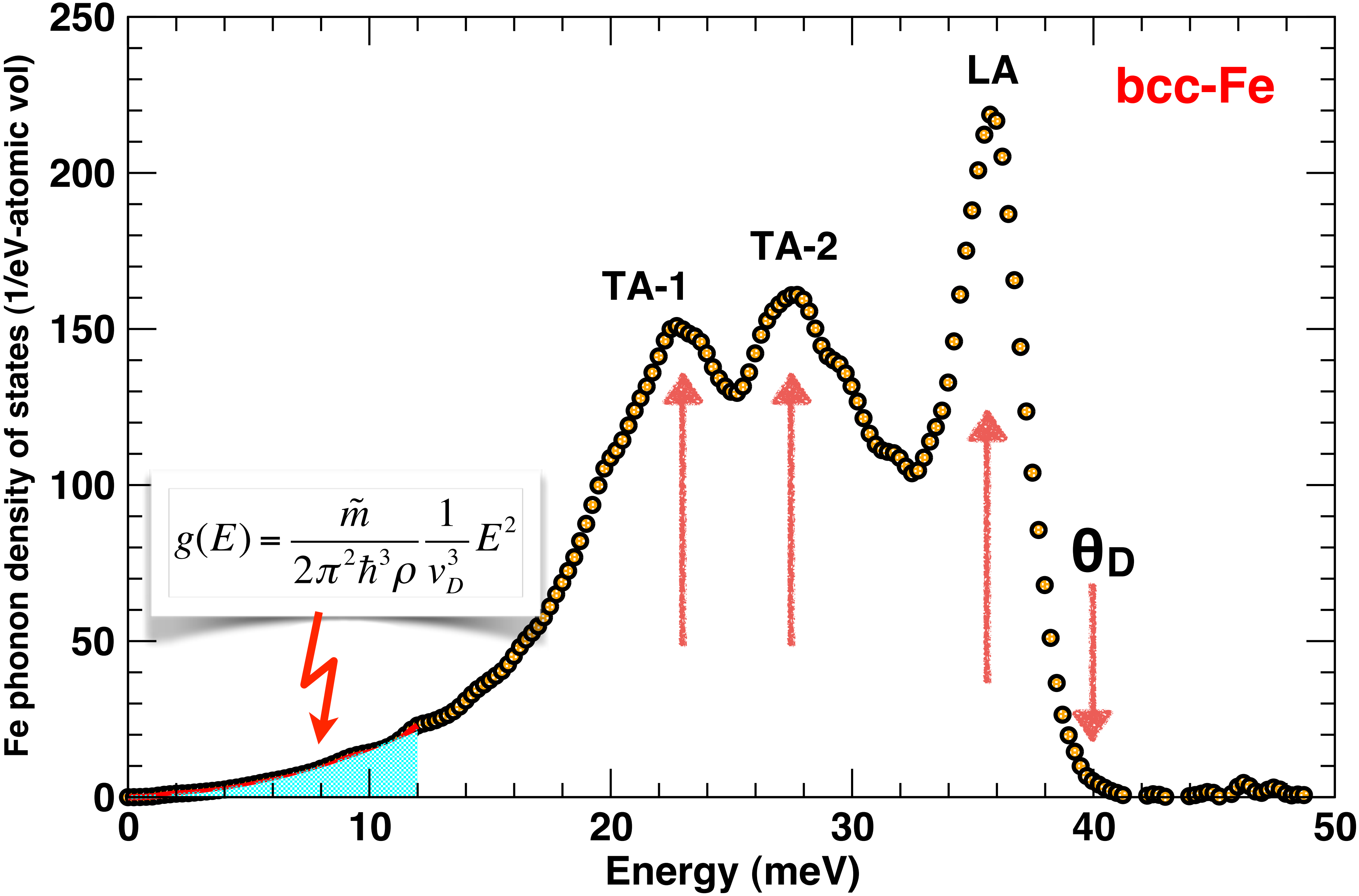
$$C = -T \frac{\partial^2 F}{\partial T^2}$$

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***





$$g(E) = \frac{\tilde{m}}{2\pi^2\hbar^3\rho}\frac{1}{v_D^3}E^2$$

Phonon density of states

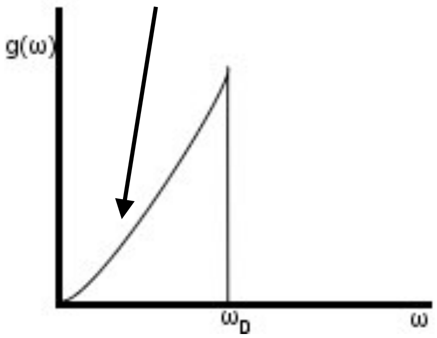
$$g(k)\,\mathrm{d}k = \frac{V}{(2\pi)^3}\,4\pi k^2\,\mathrm{d}k.$$

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

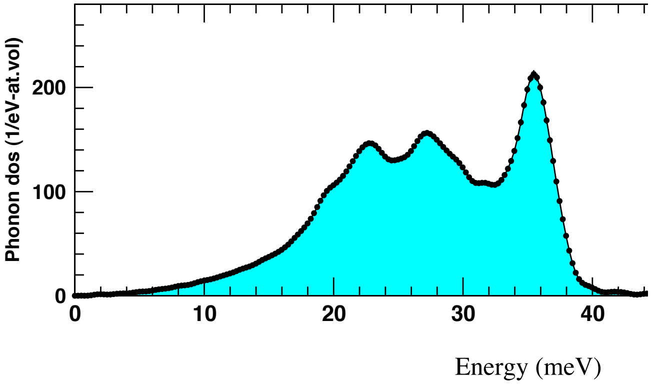
$$g(\omega) = \frac{3V}{2\pi^2 c^3}\omega^2$$

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

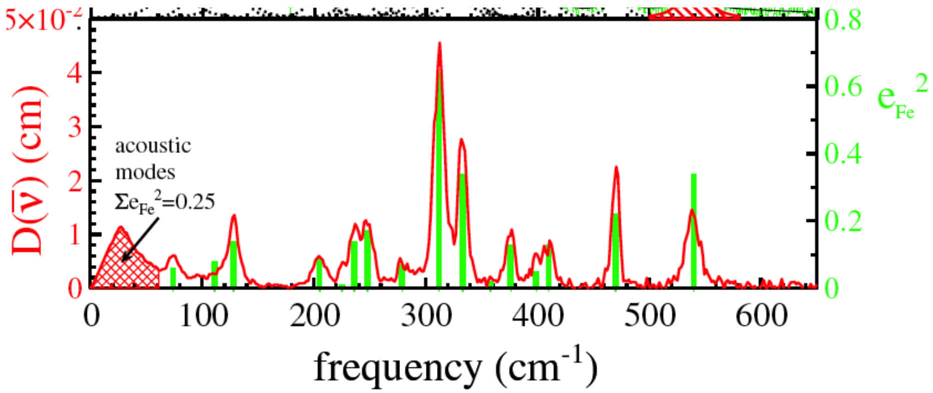
Debye model

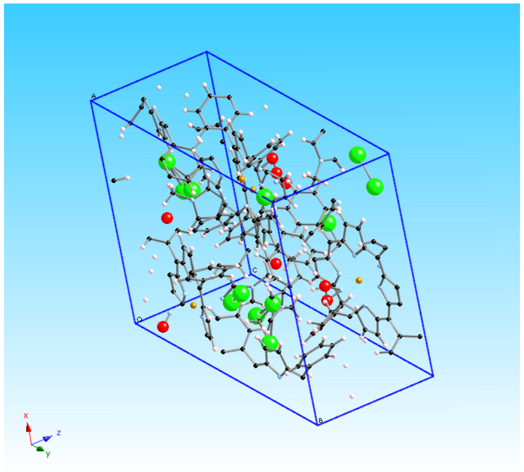


pure iron

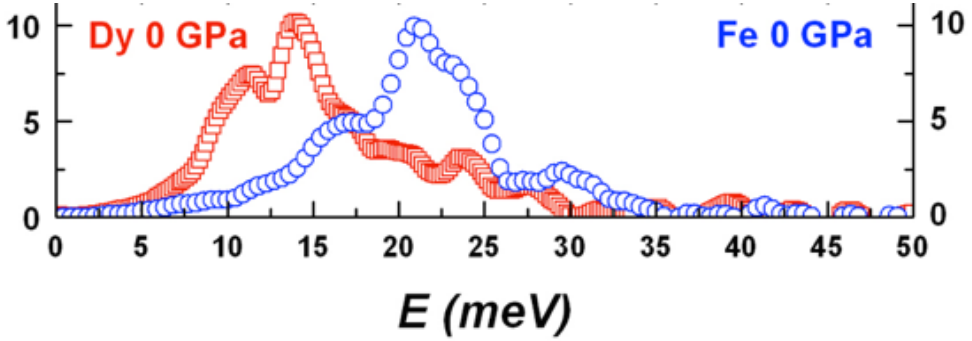


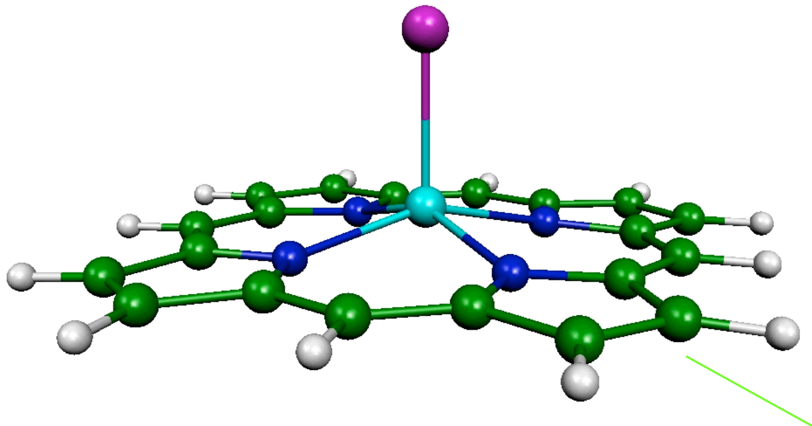
Fe-TPP-NO

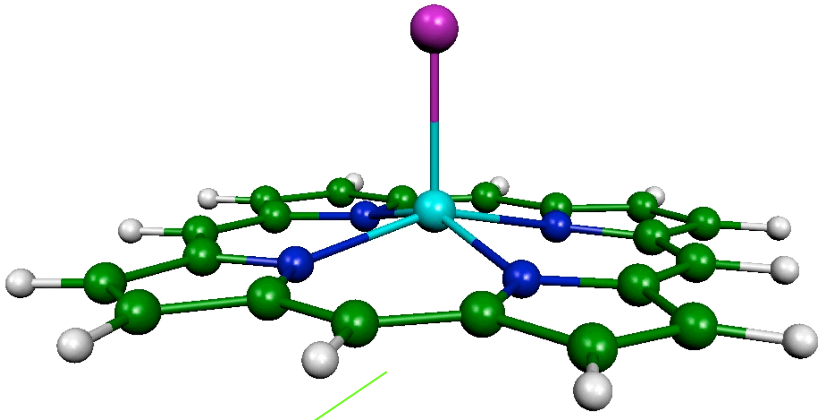


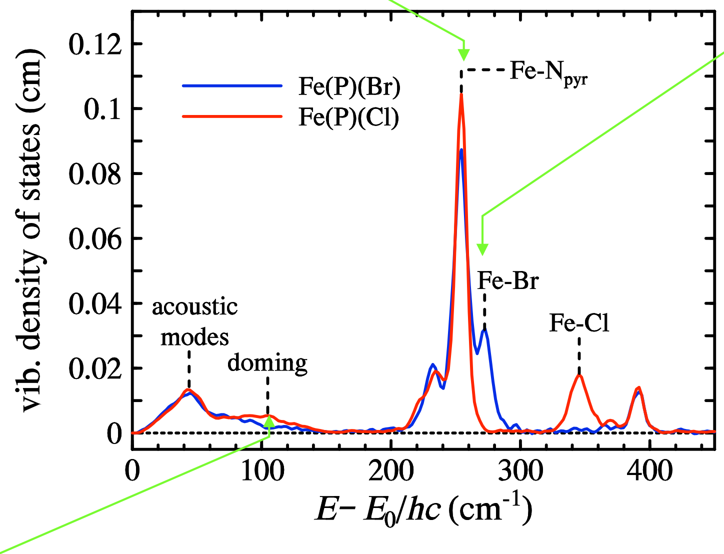


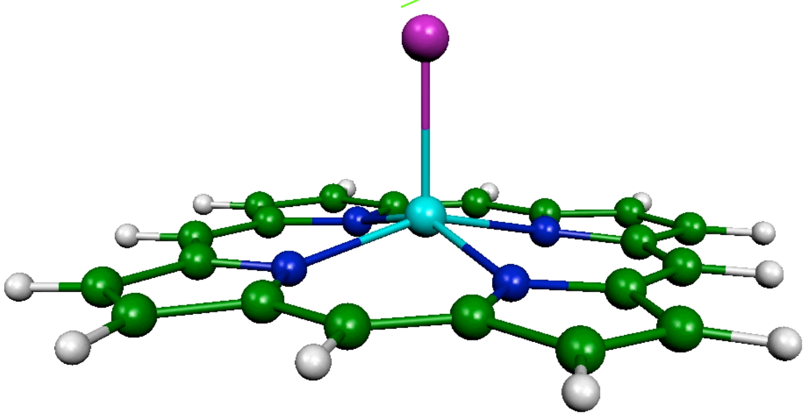
DyFe₃

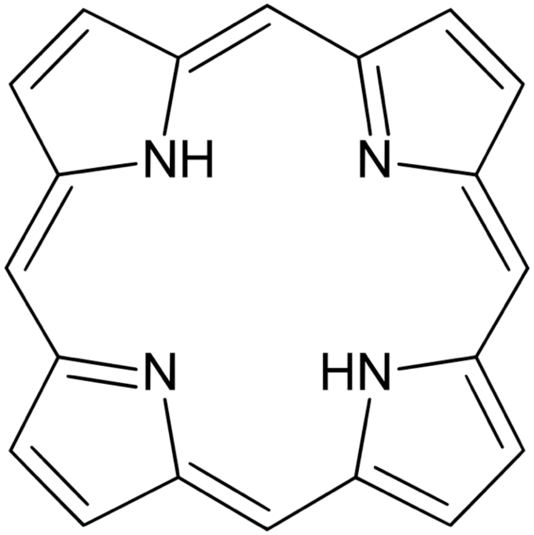







vib. density of states (cm)
0.12
0.1
0.08
0.06
0.04
0.02
0
Fe(P)(Br)
Fe(P)(Cl)
Fe-N_{pyr}
Fe-Br
Fe-Cl
acoustic modes
doming
0
100
200
300
400
$E - E_0/hc$ (cm^{-1})




NH
N
N
HN

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.

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

Vibrational specific heat

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

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

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

Vibrational specific heat

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

Vibrational entropy

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

Lamb-Mössbauer factor

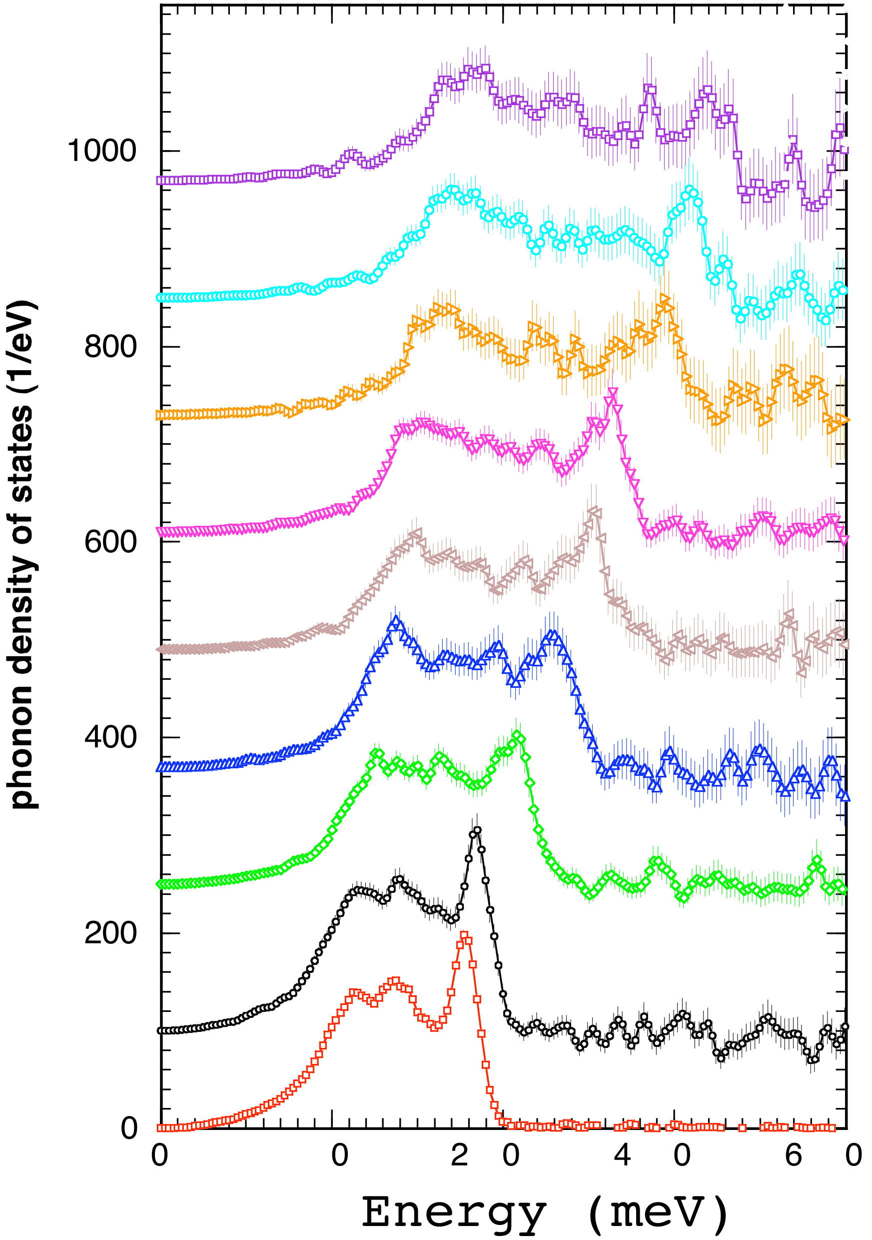
$$\boxed{g(E) = \frac{3m}{2\pi^2 \hbar^3 \rho v_D^3} E^2}$$

Debye Sound velocity

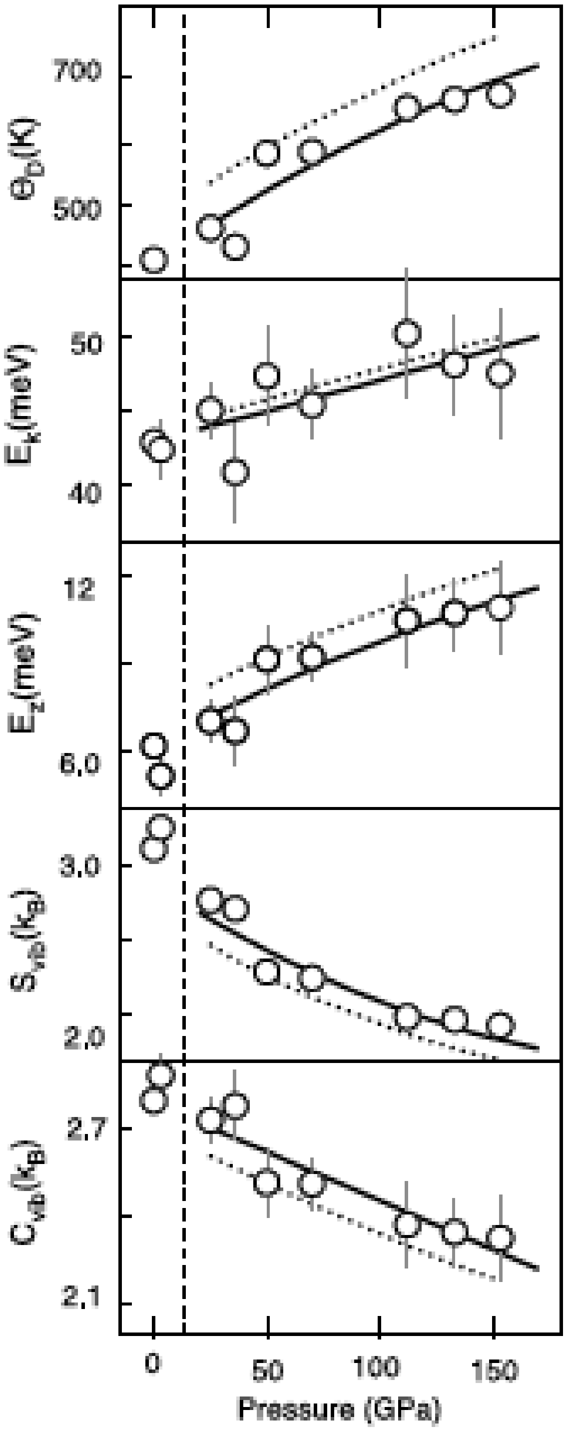
$$\boxed{\langle F \rangle = \frac{M}{\hbar^2} \int_0^\infty E^2 g(E) dE}$$

Average restoring force constant

Phonon density of states of iron under high pressure



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

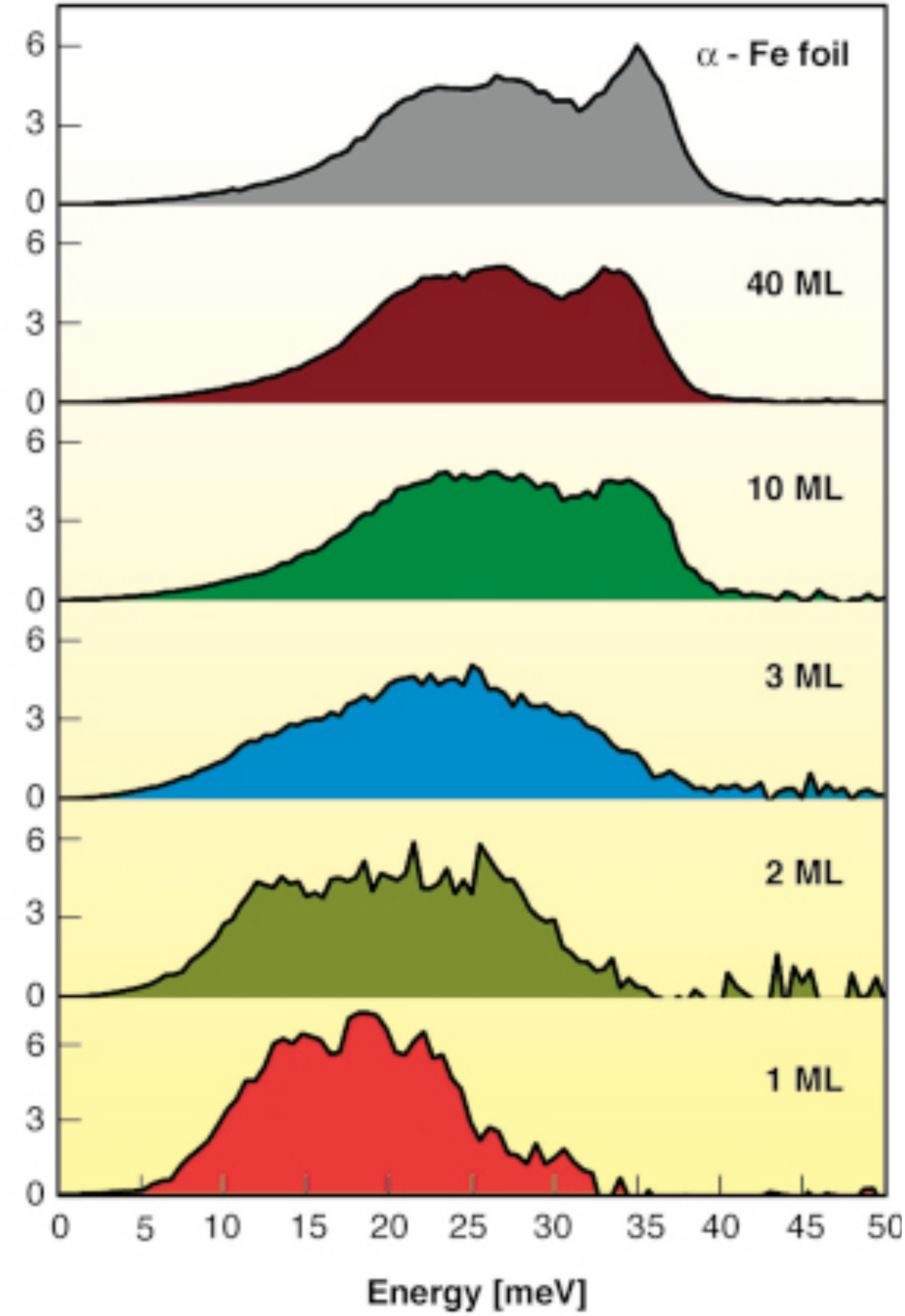


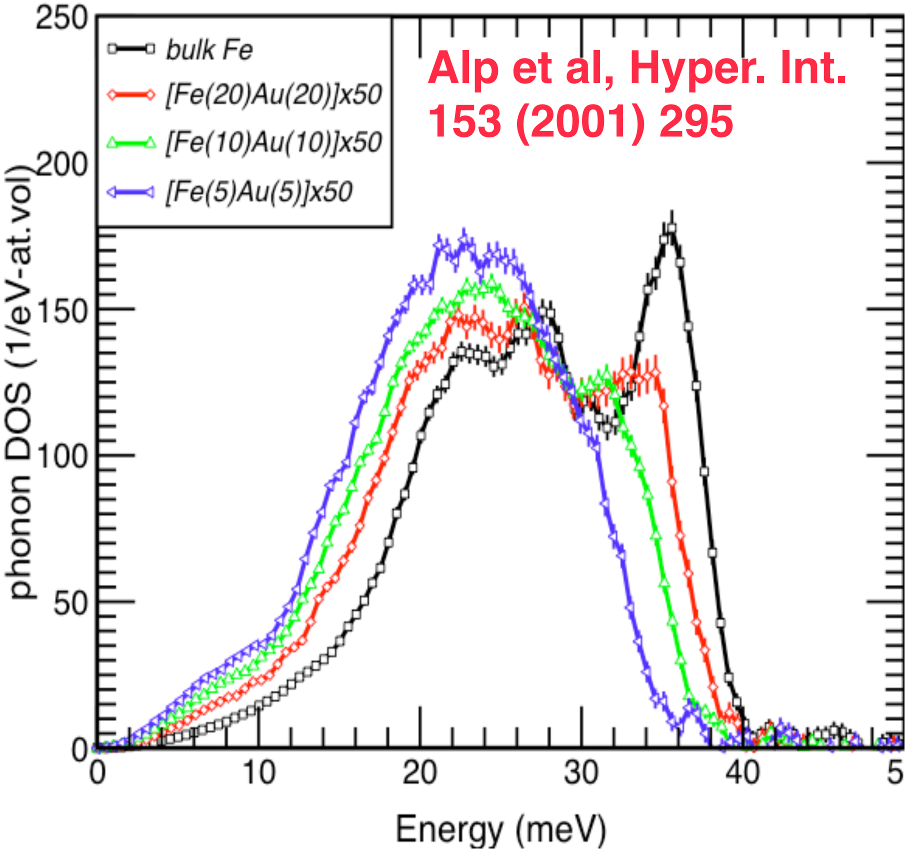
Fe films deposited on W(110)

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

Determining the phonon density of states from specific heat measurements via maximum entropy methods

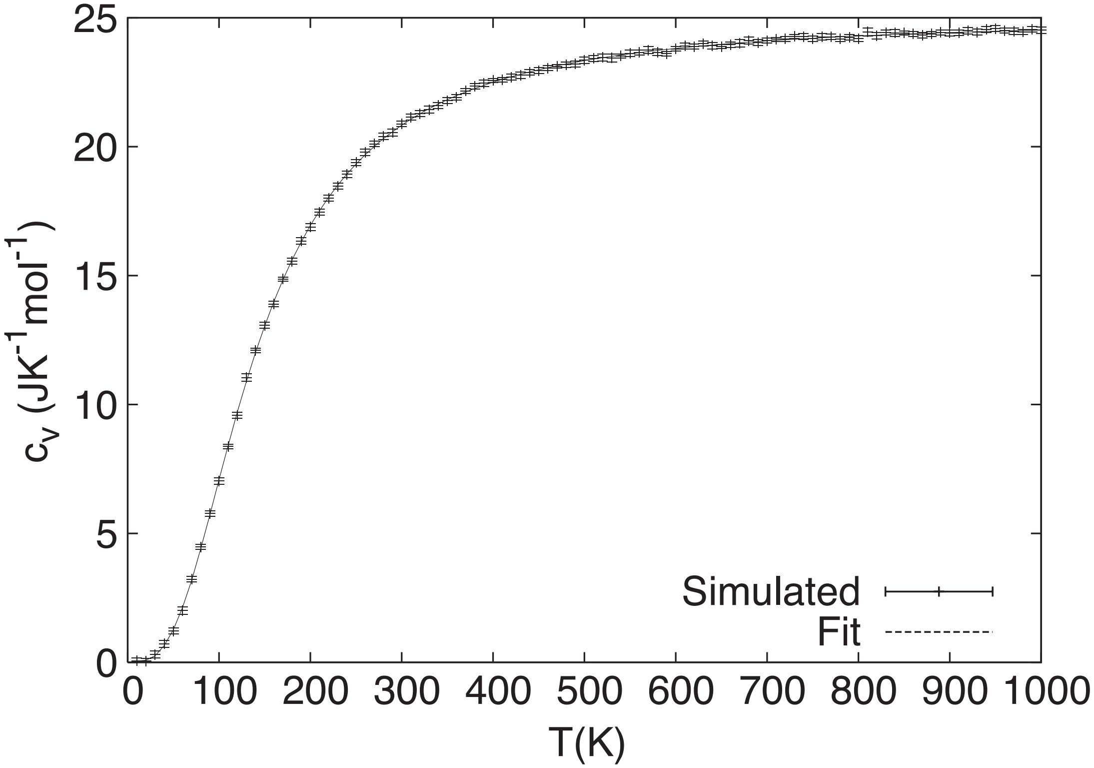
J. Phys.: Condens. Matter **17** (2005) 2397–2405

$$c_v(T) = 3R\int_0^\infty d\omega\, D(\omega)\frac{\hbar^2\omega^2 e^{\hbar\omega/kT}}{(kT)^2(1-e^{\hbar\omega/kT})^2}$$

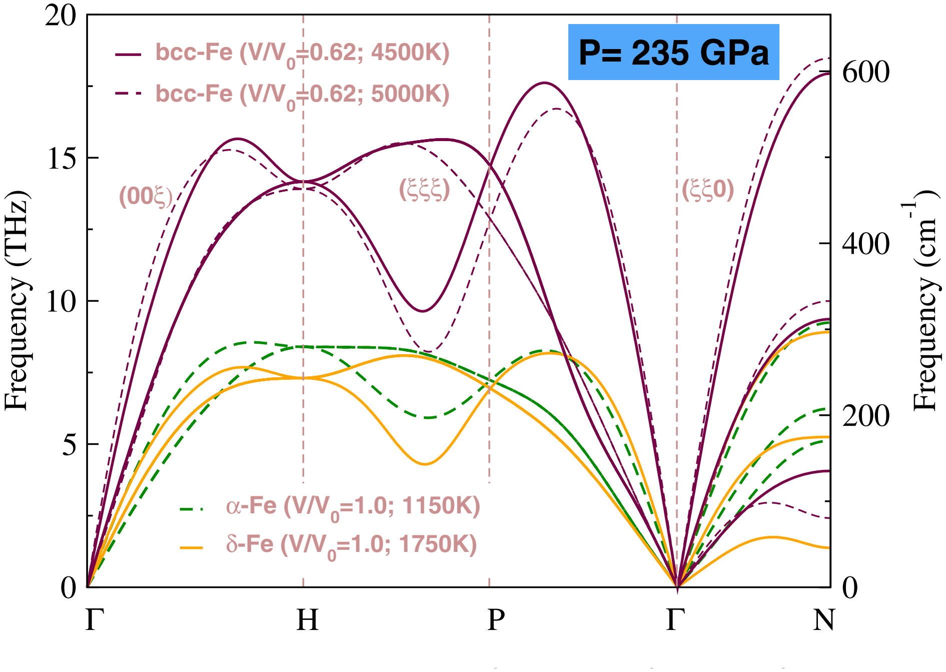
$$\mathcal{F} = \chi^2\{s_i\} + \alpha S\{s_i\}$$

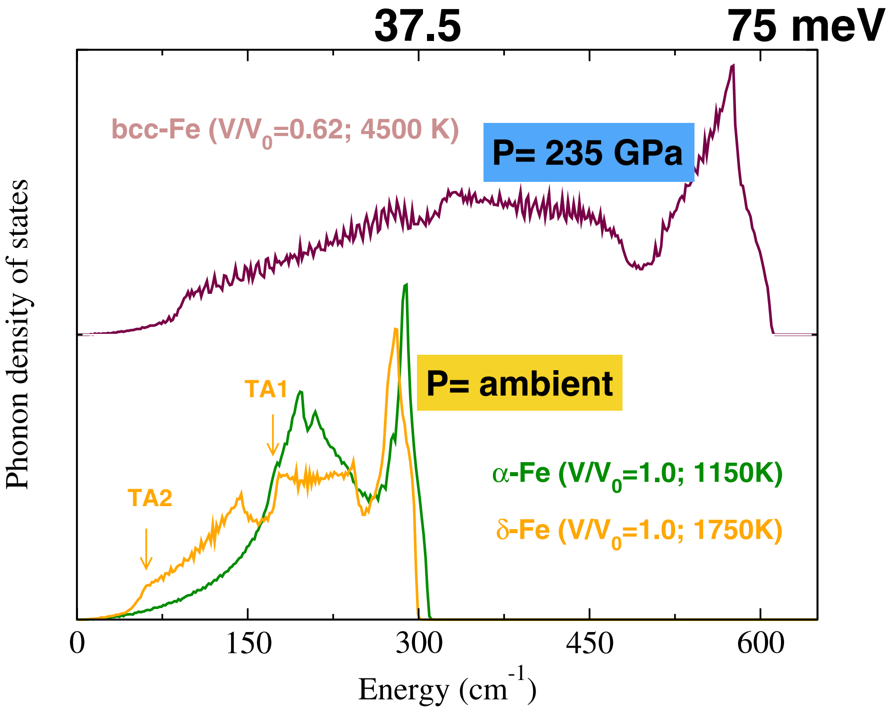
$$\chi^2 = \sum_{i=1}^{N_d}\frac{c_{\mathrm{obs}}(T_i) - c_{\mathrm{calc}}(T_i)}{\sigma_i^2}$$

$$S = \sum_{i=1}^{N_s}\left[m_i - s_i + s_i \ln\left(\frac{s_i}{m_i}\right)\right]$$



Thank you ….





9962–9964 | PNAS | **June 1, 2010** | vol. 107 | no. 22