Lattice Dynamics

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Outline

Day 1

- Interatomic interaction and vibrations
- Lattice vibrations and phonons
- Vibrational spectrum and properties

Day 2

- Mossbauer effect
- Vibrational density of states
- Isomer shift, Quadrupole splitting and Hyperfine interaction
- Applications

?


?
Perturb
Observe


?
Perturb
Observe

?

Perturb

Observe

- Knock
- Burn
- Smash

- Sound
- Heat
- Inside

?

Perturb (Pump)

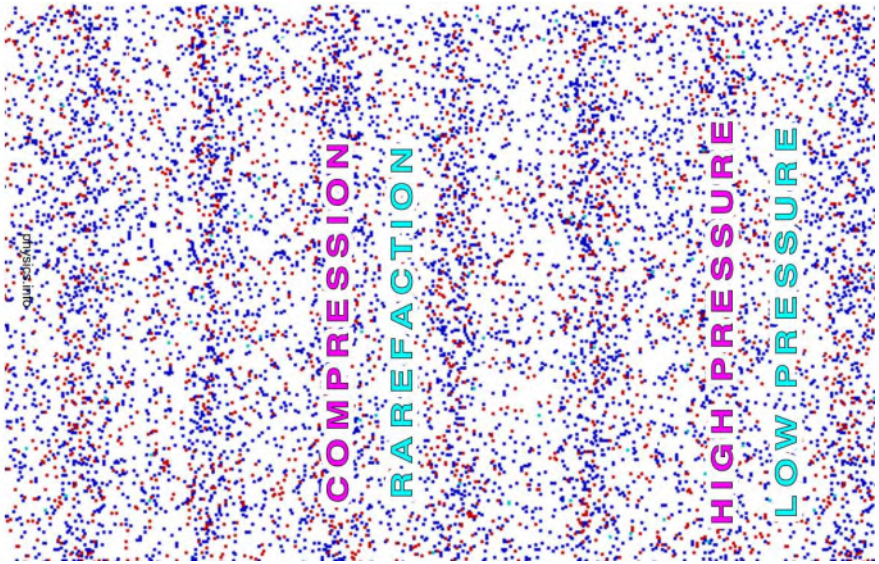
- Knock
- Burn
- Smash

Observe (Probe)

- Sound
- Heat
- Inside

Inelastic Scattering !!!!

The **pitch** of a note **depends** on the frequency of the source of the **sound**.



solids	v (m/s)	liquids	v (m/s)
aluminum	6420	alcohol, ethyl	1207
glass, pyrex	5640	argon	319
wood, maple	4110	water, distilled	1497

The acoustic velocity is related to the change in pressure and density of the substance

$$v_s = \sqrt{\frac{dP}{d\rho}} = \sqrt{\frac{E}{\rho}}$$ (Hooke's law)

Heat capacity is a measure of the amount of heat a material can **store** when the temperature is changed

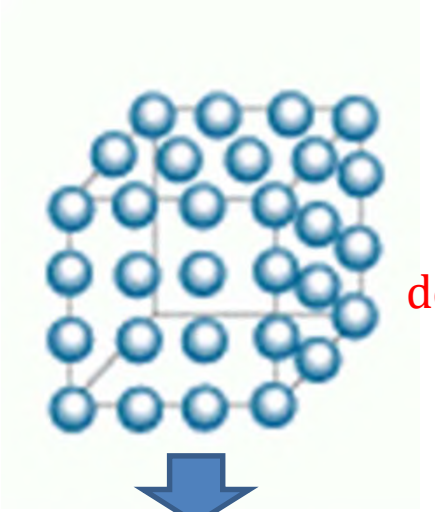
	C_p (J/mol.K)
Al	24.3
Fe	25.7
Ni	26.8
Cu	24.4
Pb	26.9
Ag	25.5
C	10.9
Water	75.3

$$C_p = \frac{dU}{dT}$$

Dulong–Petit law (1819) states that the gram-atomic heat capacity (specific heat times atomic weight) of an element is a constant; that is, it is the same for all solid elements.

Dynamics →

related to movement of atoms
about their equilibrium positions



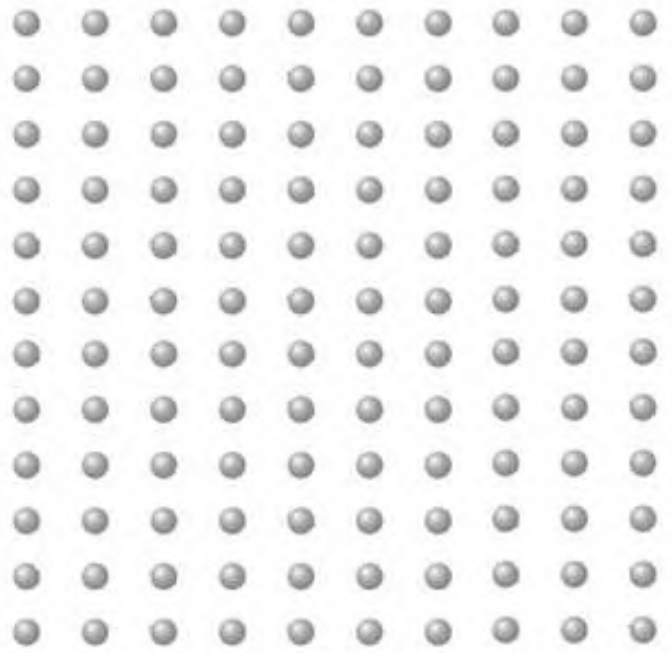
← **Structure**

determined by electronic structure

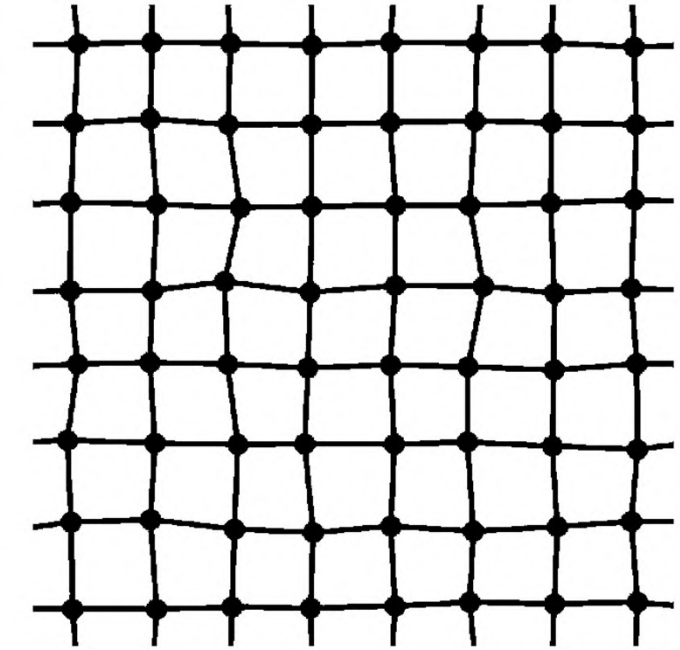
Electronic and Physical properties

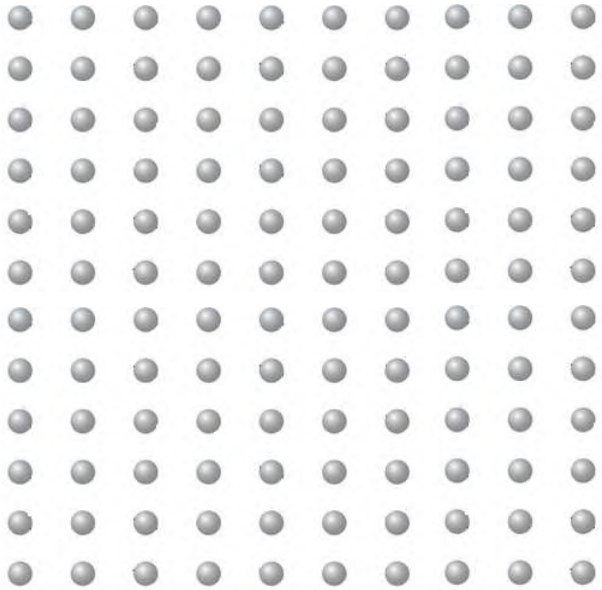
- Sound velocity
- Thermal properties: -specific heat
  -thermal expansion
  -thermal conductivity
- Hardness of perfect single crystals
- Vibrations

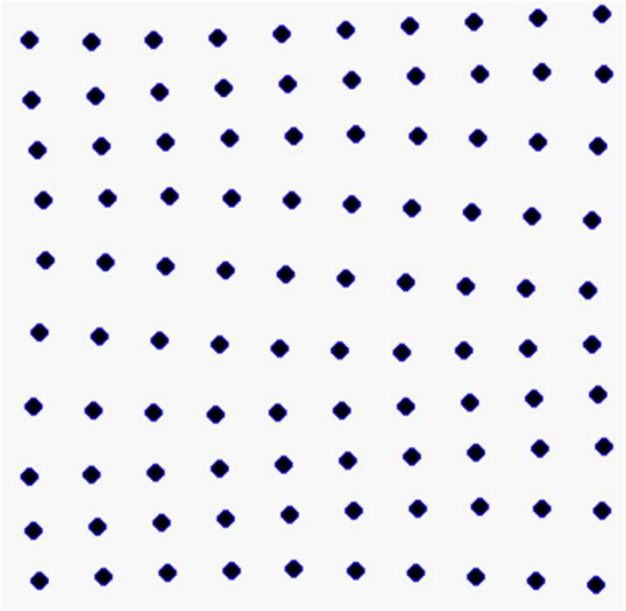
Vibrations of a 2D square lattice

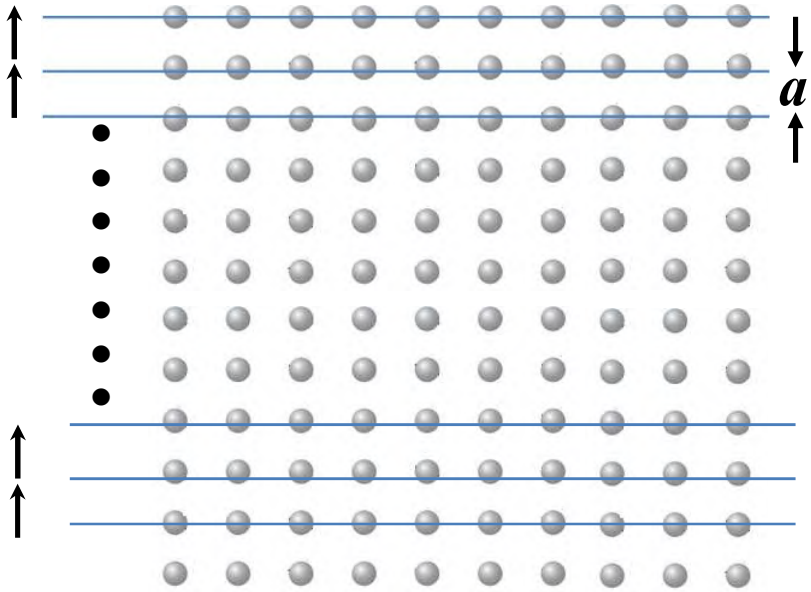


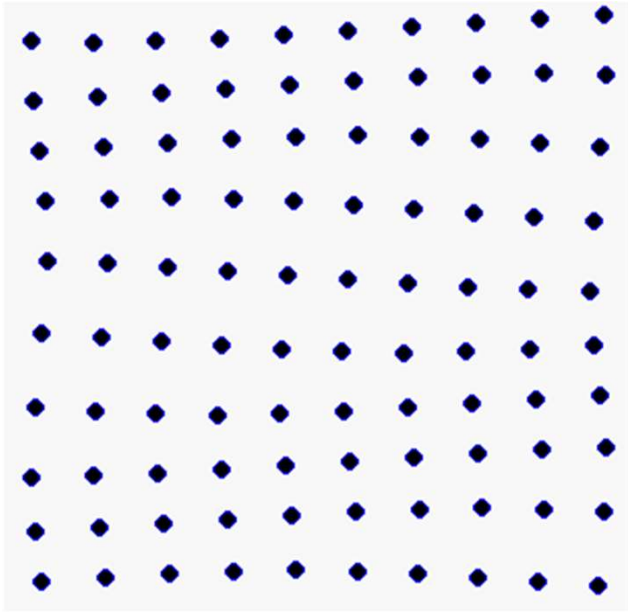
Vibrations of a 2D square lattice

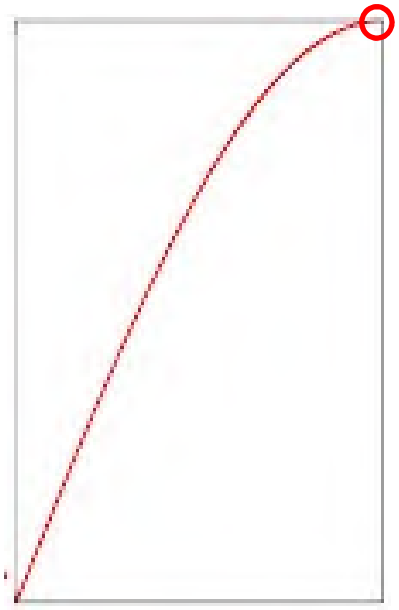












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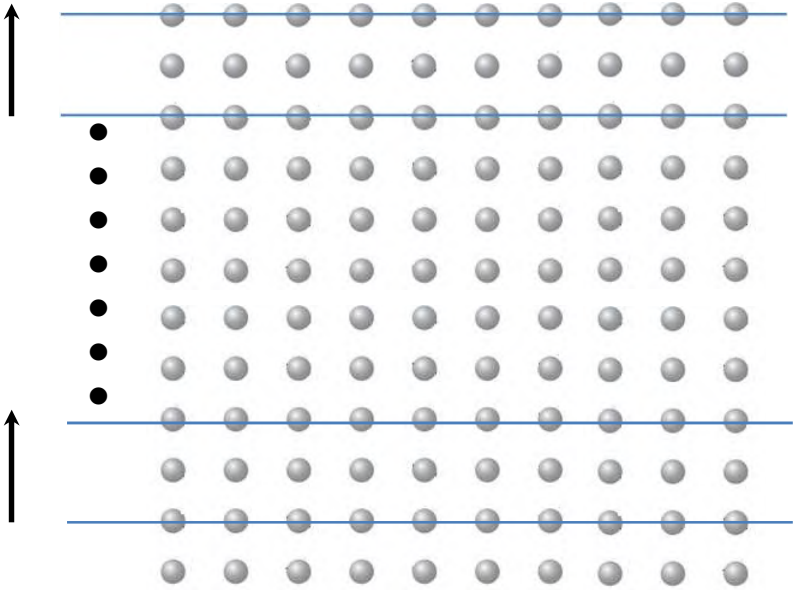

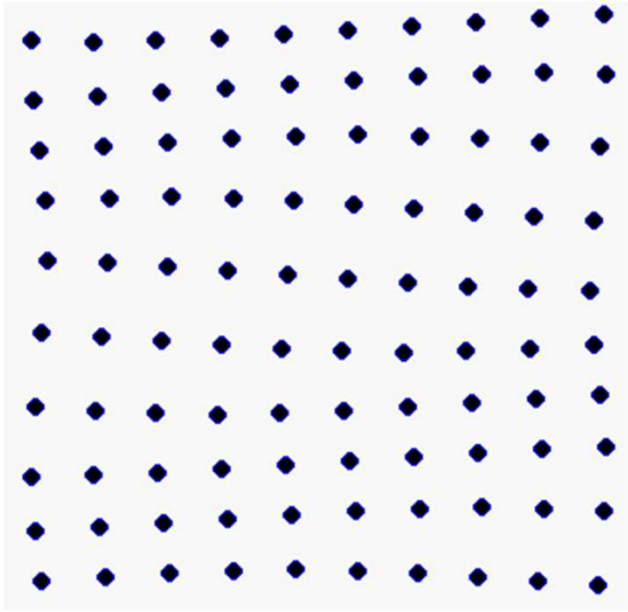

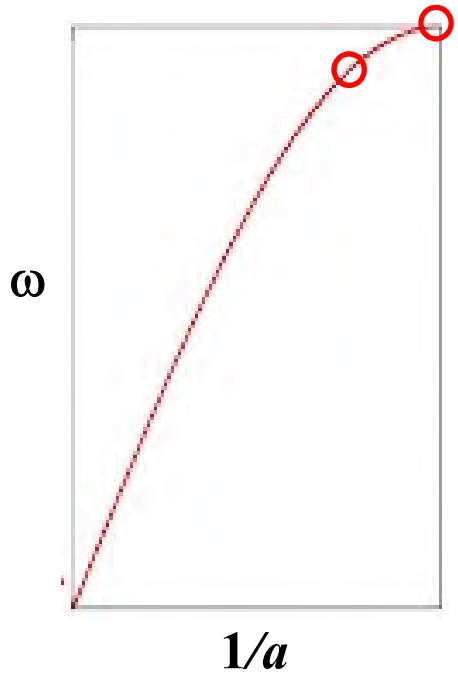
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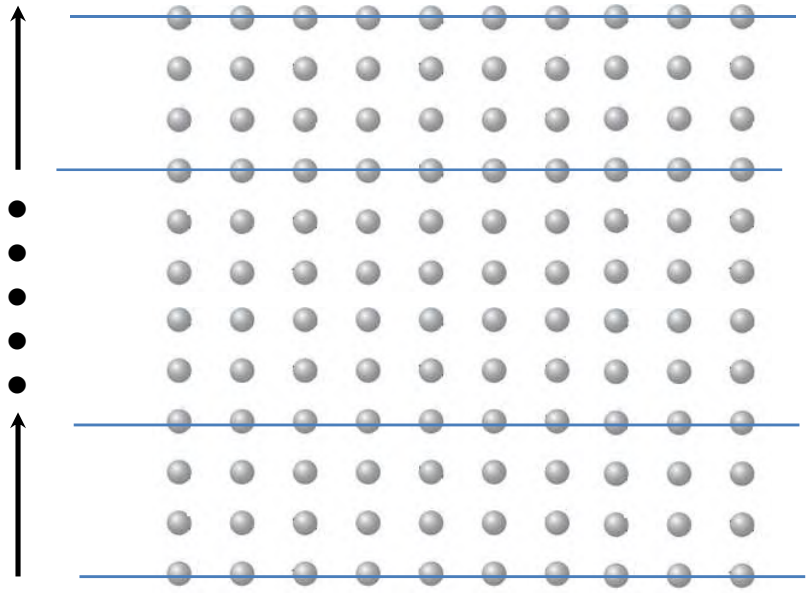

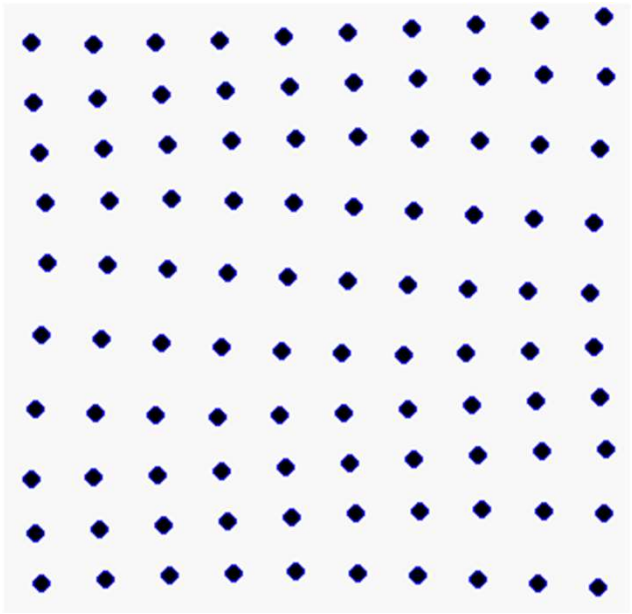

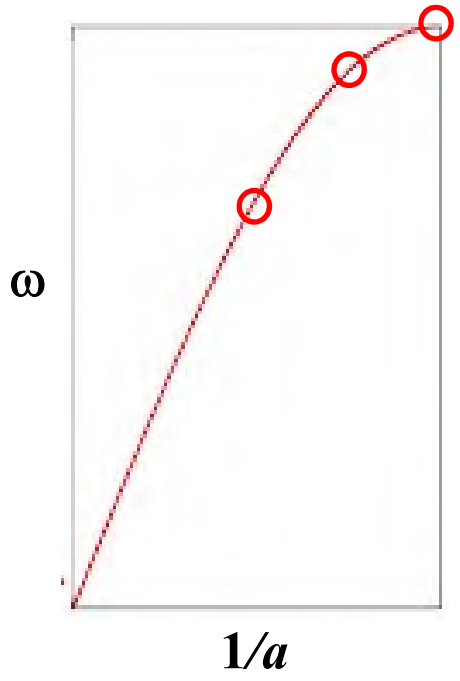
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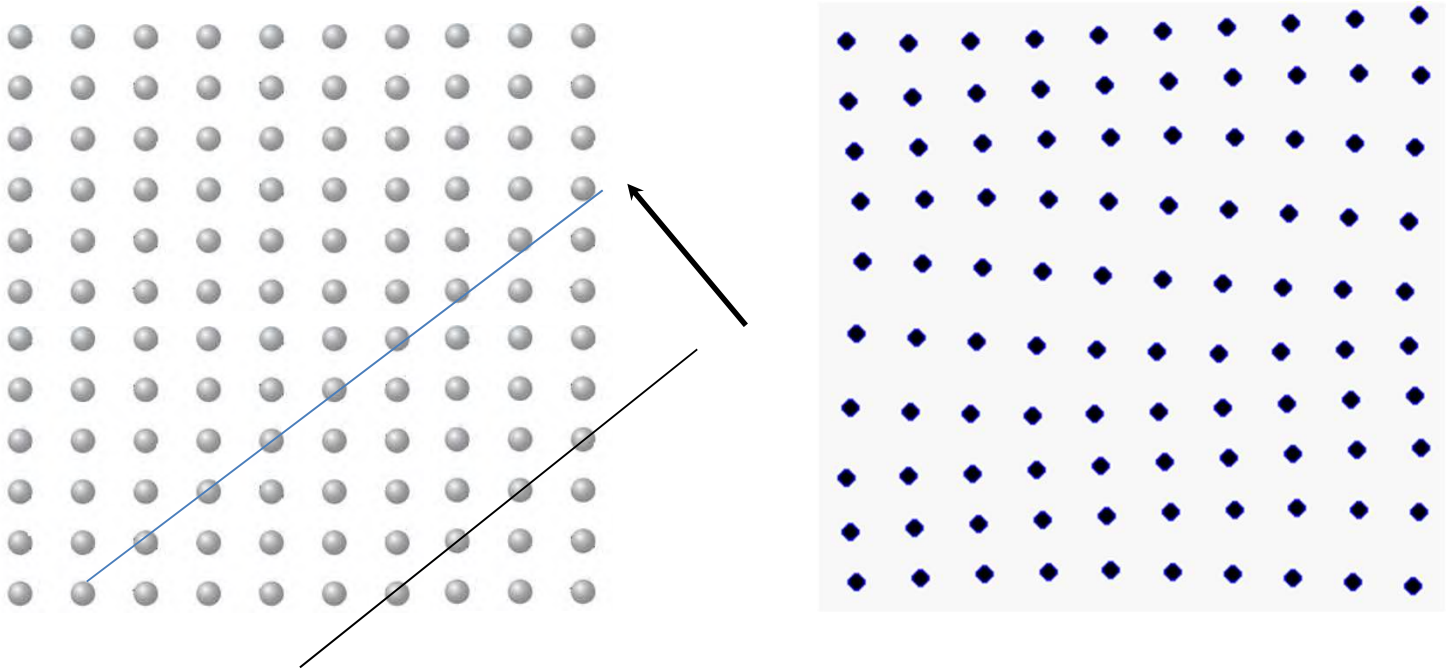

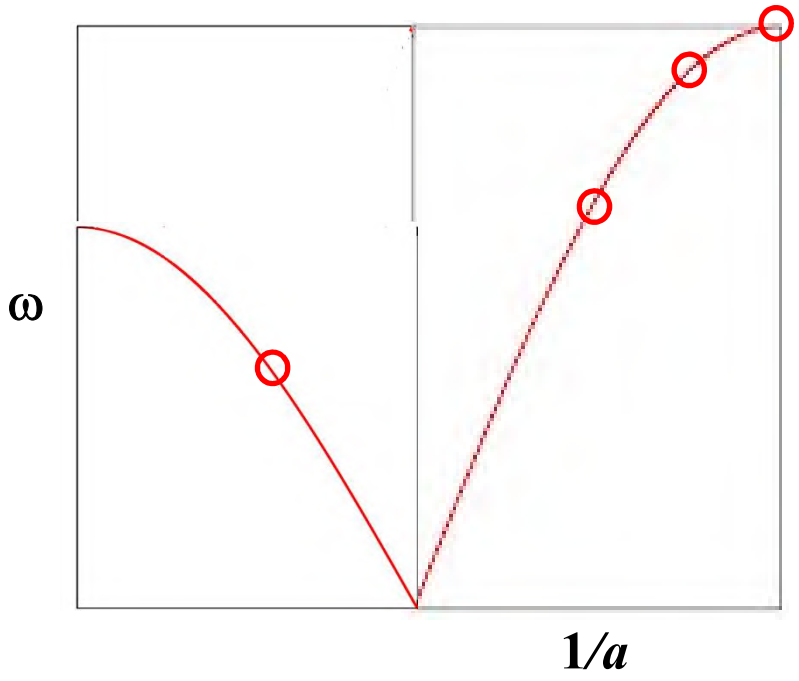
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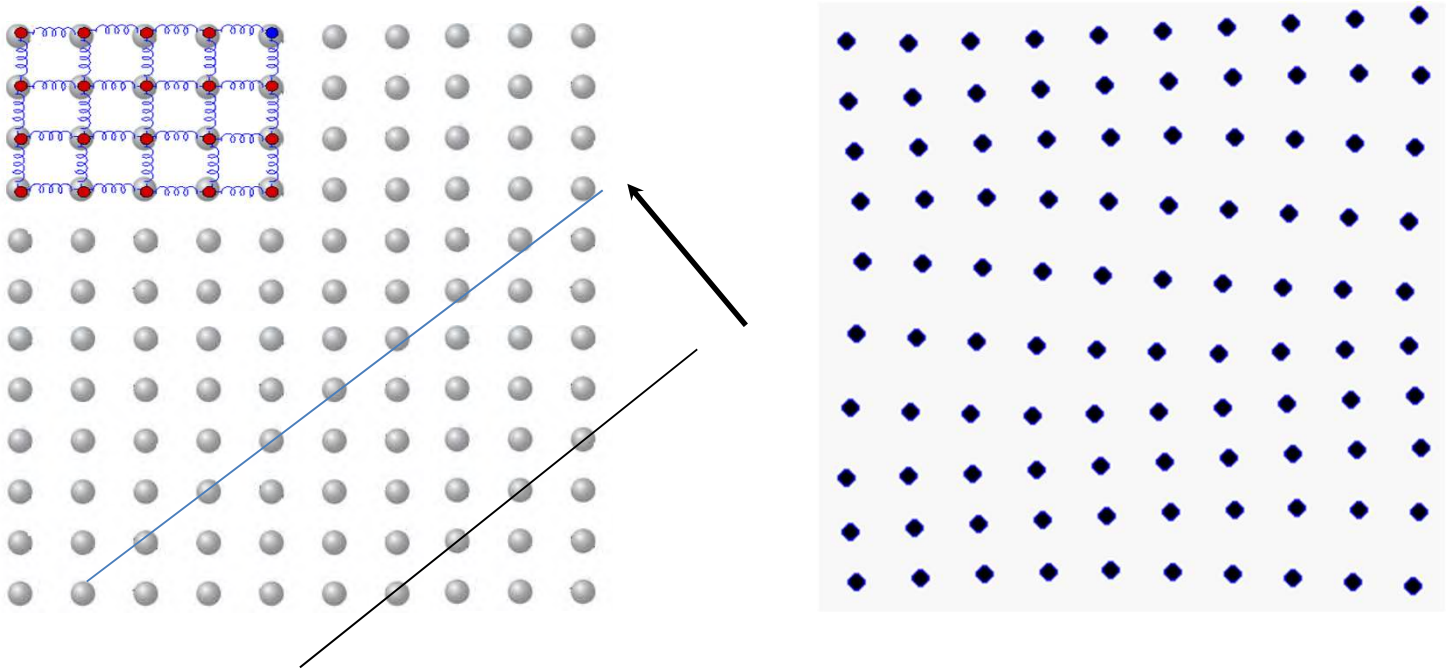
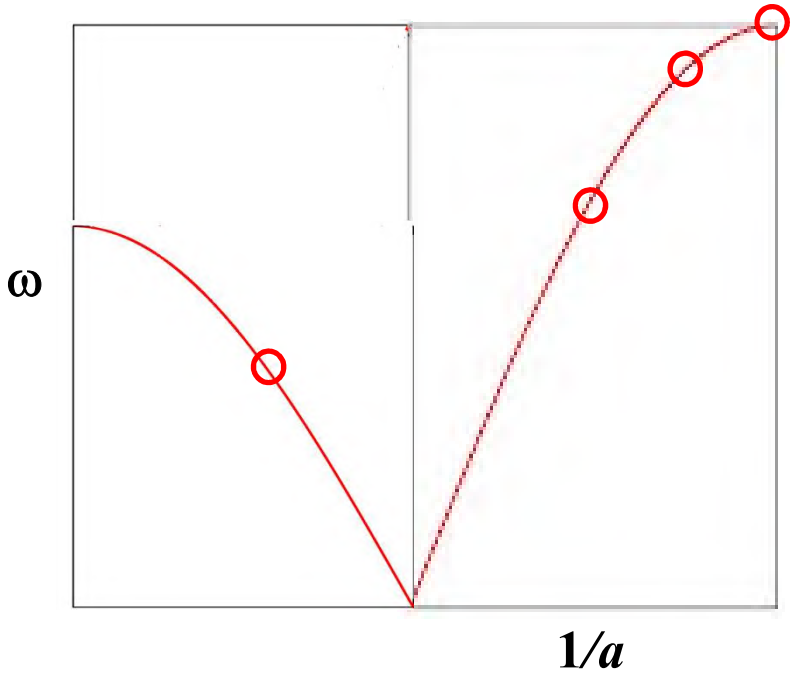
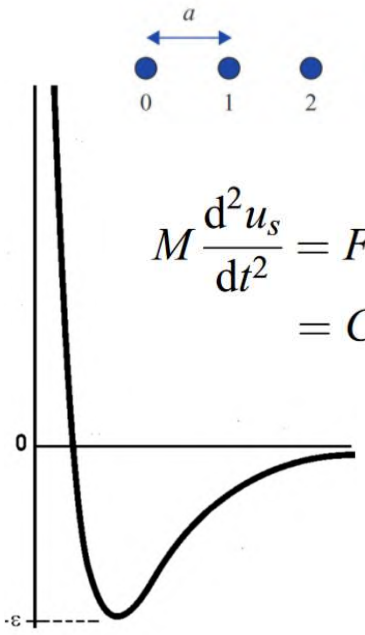






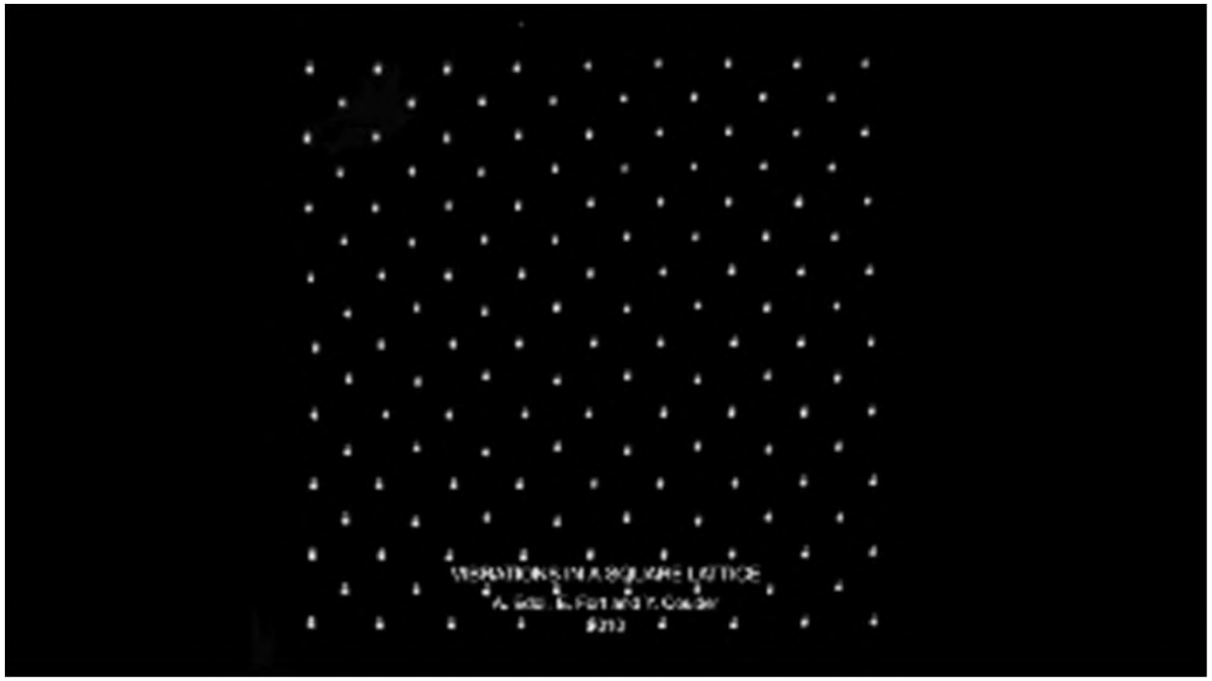
$$M\frac{\mathrm{d}^2 u_s}{\mathrm{d}t^2} = F_s$$

$$= C(u_{s+1} - U_s) + C(u_{s-1} - U_s)$$

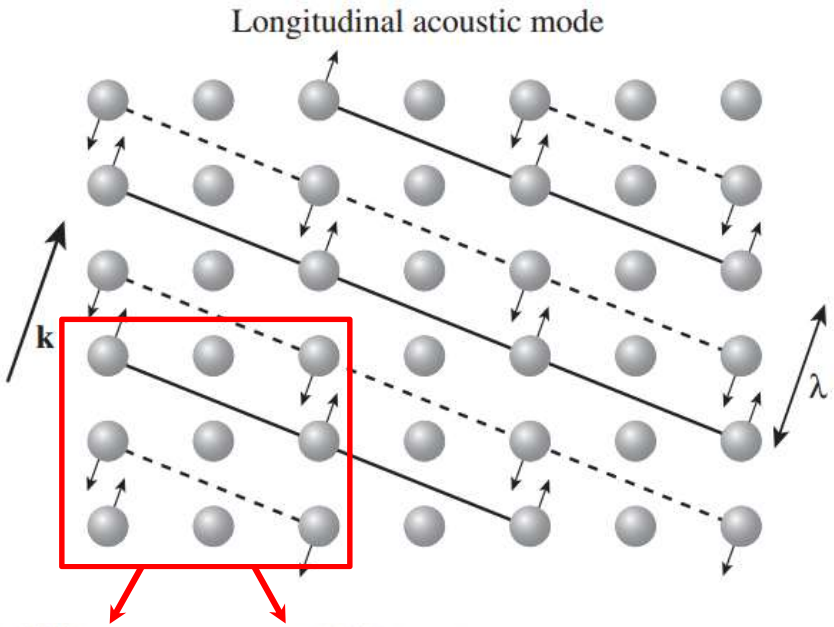
$$u_s \sim \mathrm{e}^{\mathrm{i}(qx-\omega t)}$$

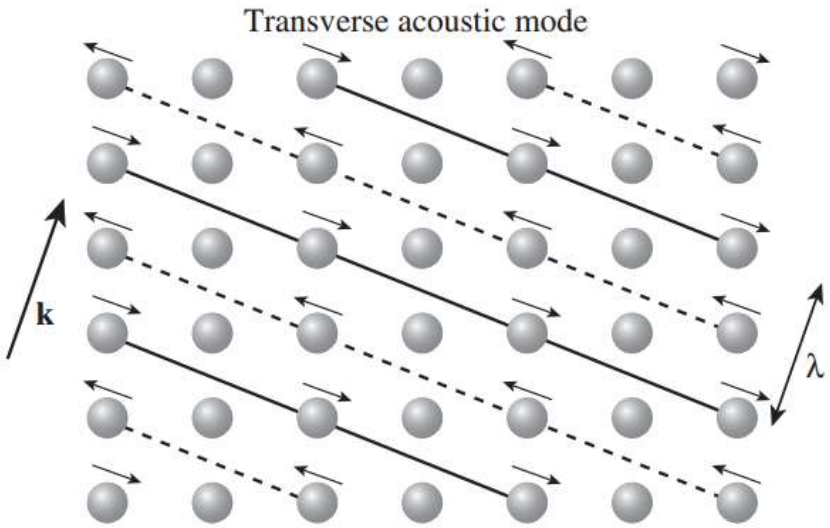
$$\omega^2 = \frac{4C}{M}\sin^2\left(\frac{qa}{2}\right)$$

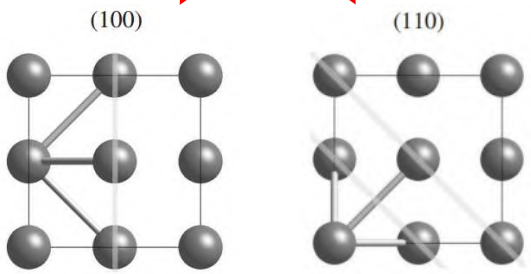
Normal mode vibrations of a 2D square lattice



Phonon band structure

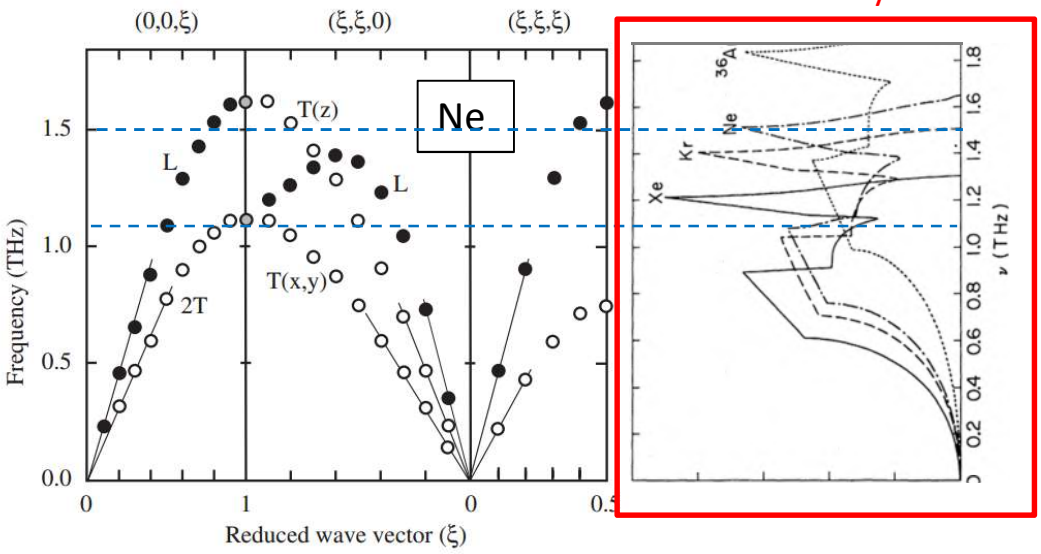




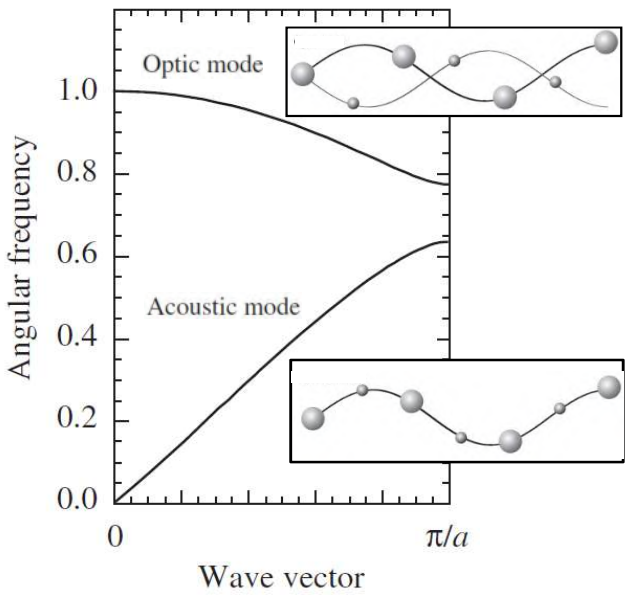


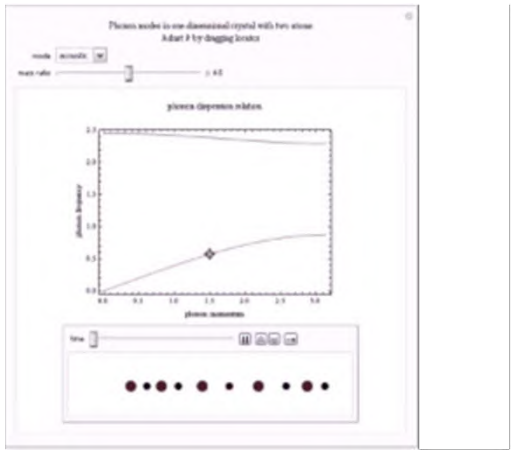
Density of states, $g(\omega) = dn/dE$
$= 1/(dE/dn)$

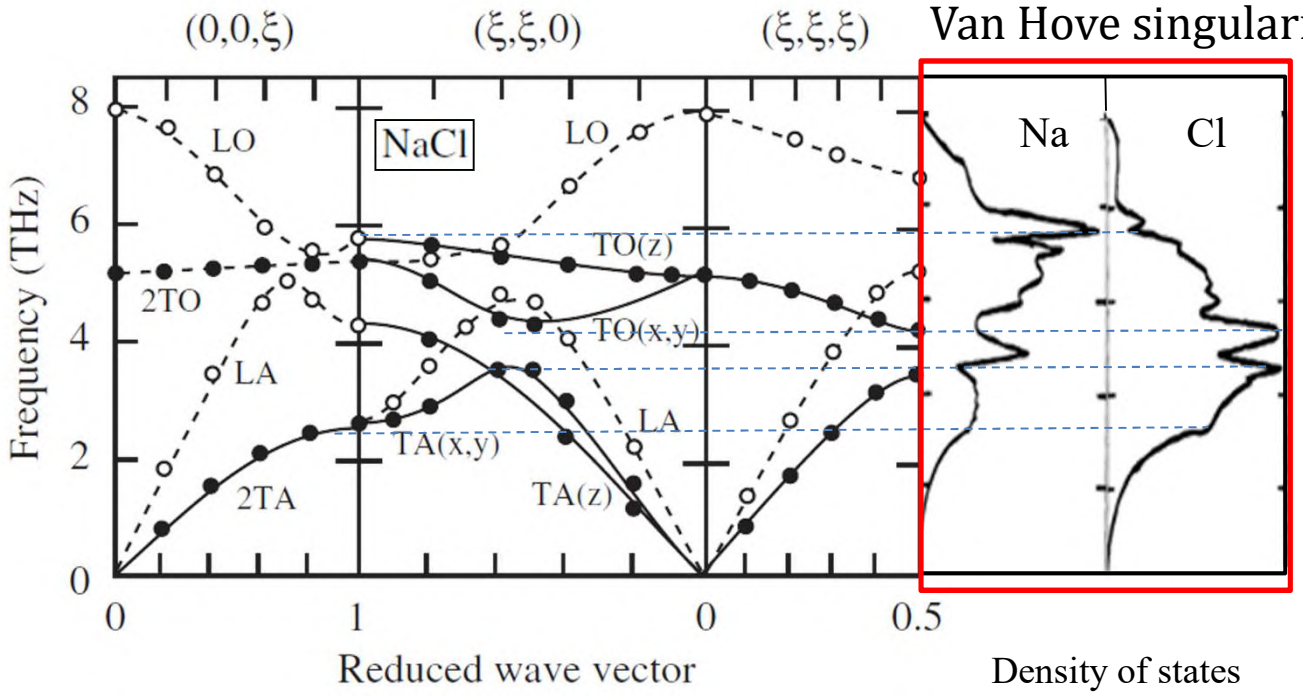
Vibrational density of states



Phonon band structure of polyatomic systems

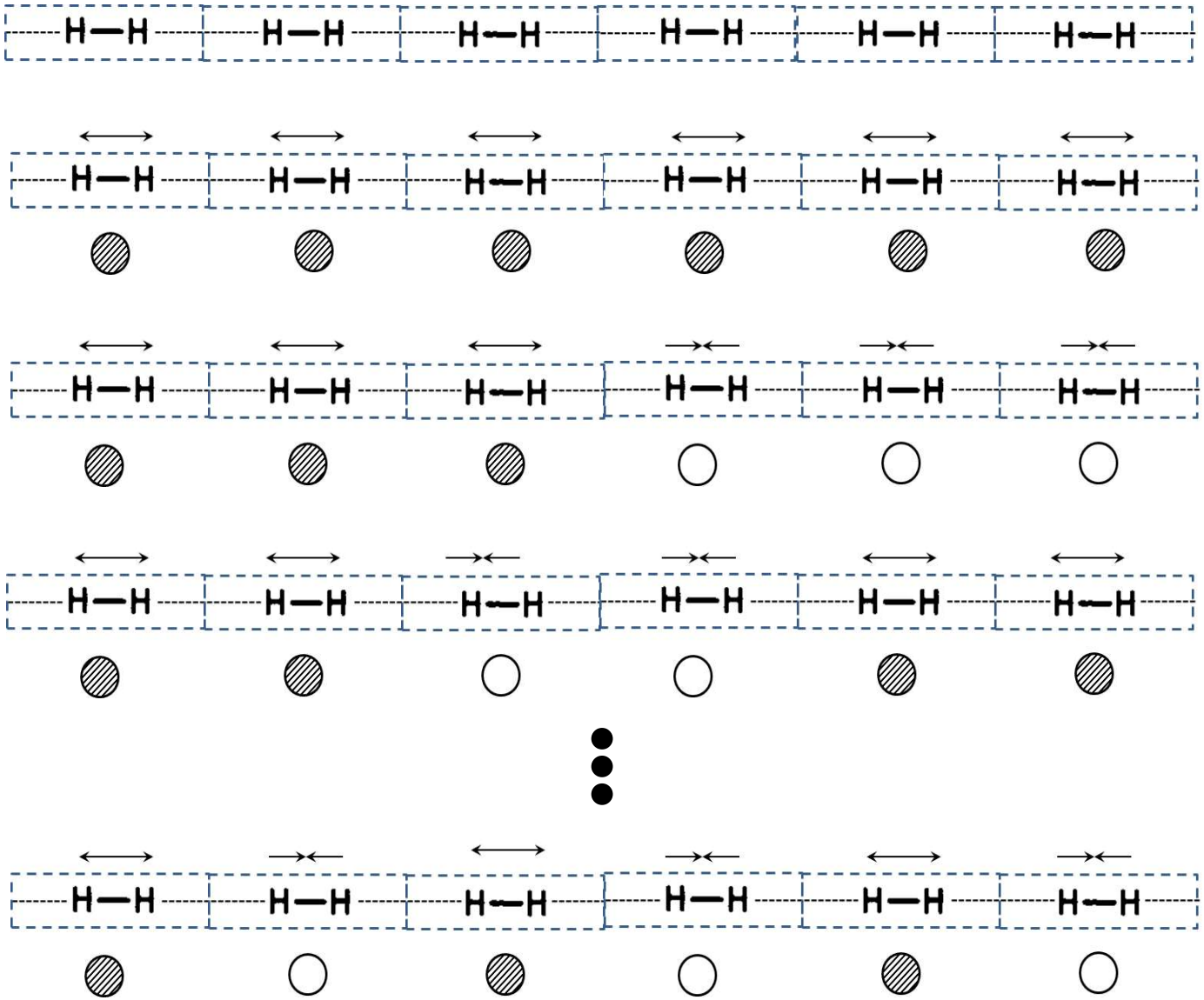






Van Hove singularity

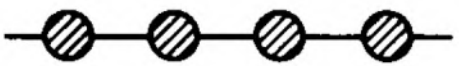
Phonon dispersion



Phonon dispersion – Bloch Theorem

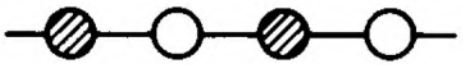
$k = 0 \qquad \psi_0 = \sum_n e^0 \chi_n = \sum_n \chi_n$

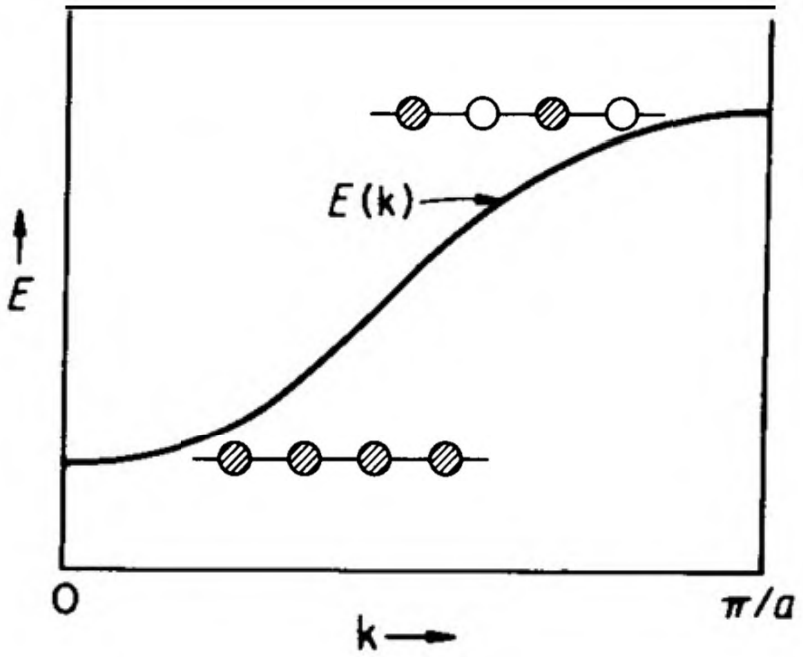
$= \chi_0 + \chi_1 + \chi_2 + \chi_3 + \cdots$



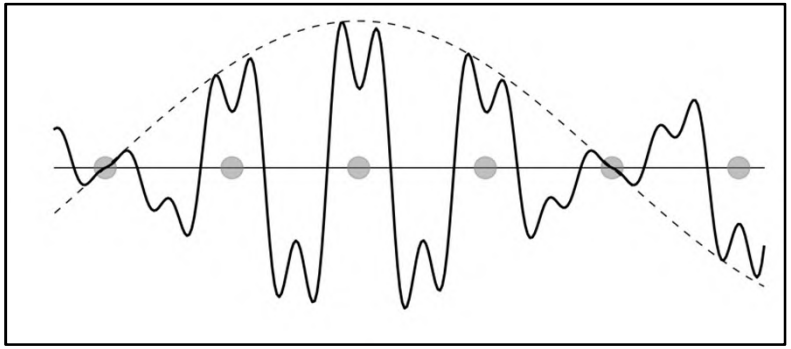
$k = \frac{\pi}{a} \qquad \psi_{\frac{\pi}{a}} = \sum_n e^{\pi i n} \chi_n = \sum_n (-1)^n \chi_n$

$= \chi_0 - \chi_1 + \chi_2 - \chi_3 + \cdots$

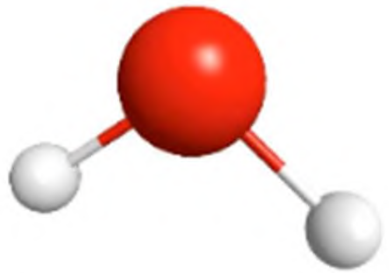




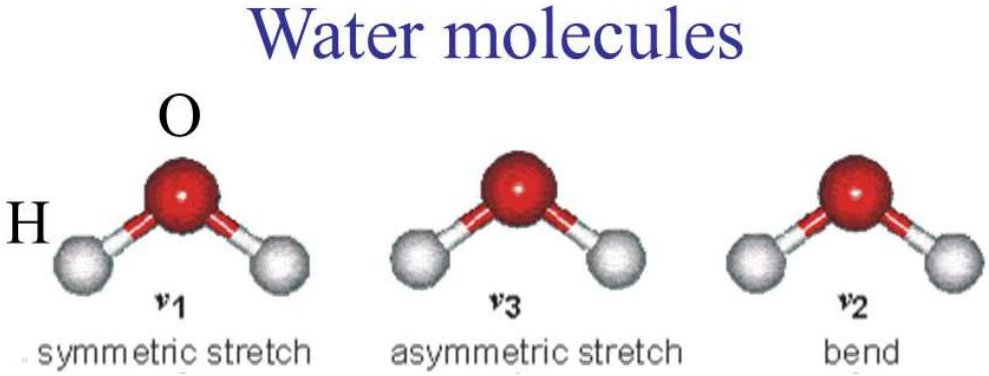
A Bloch wave has the form, $\psi = e^{i\boldsymbol{k}\cdot\boldsymbol{r}}u(\boldsymbol{r})$,
$\boldsymbol{k}$ is the crystal wave vector

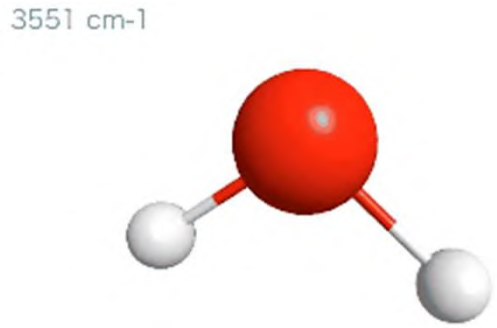


Vibrations of an isolated water

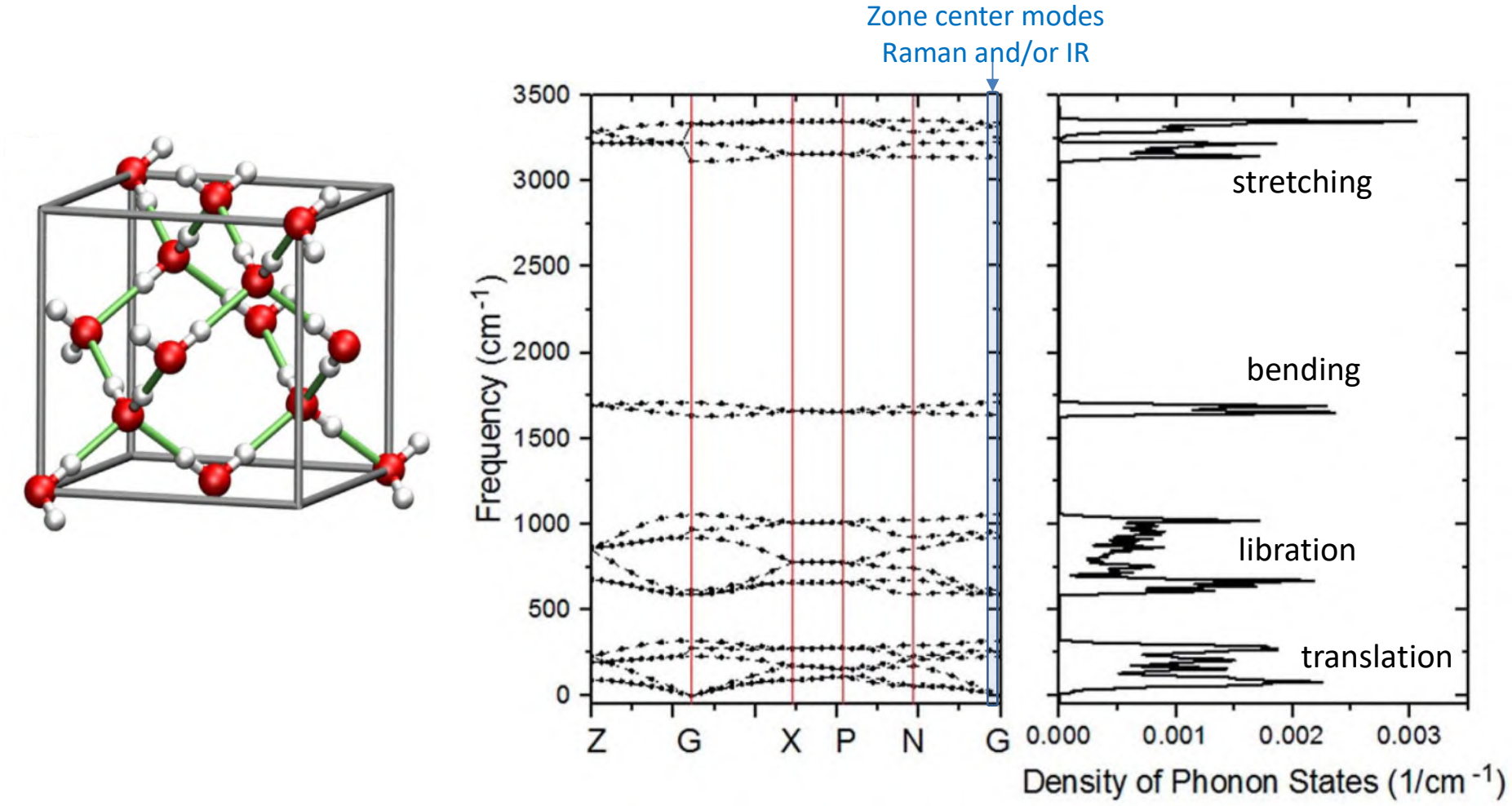


Vibrations of an isolated water



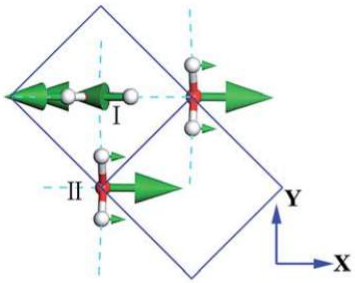


Vibrations of water in a crystal (ice Ic)

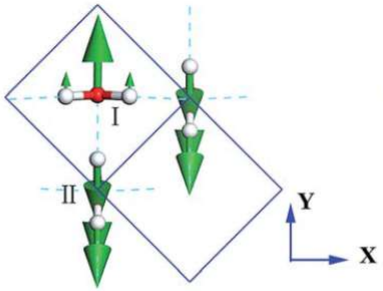


Vibrations of water in a crystal (ice Ic)

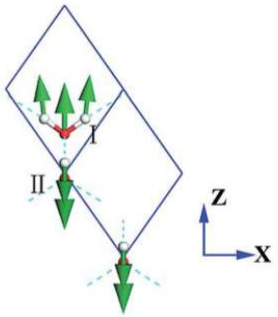
translational



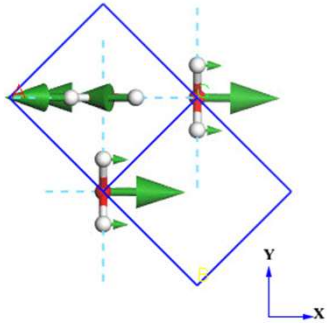
230(a) X(I - II)

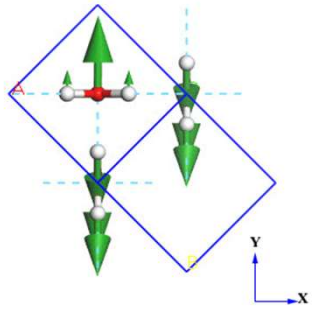


230(b) Y(I - II)

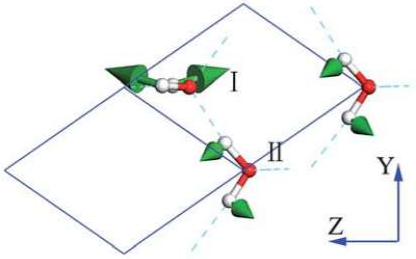


321 Z(I - II)

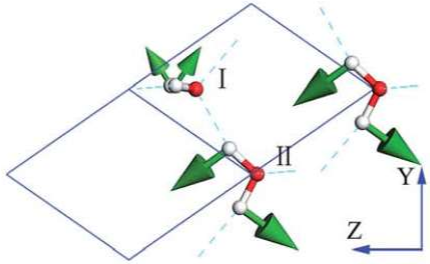




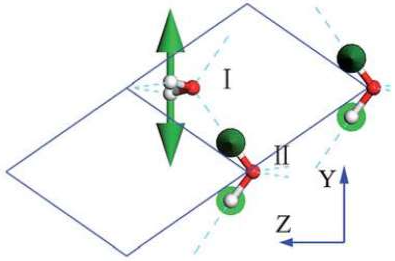
librational



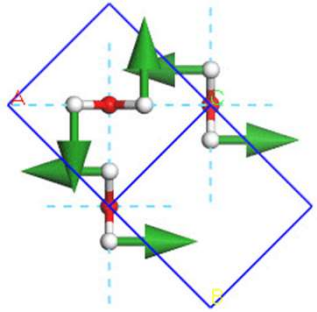
589(a) R I +W II

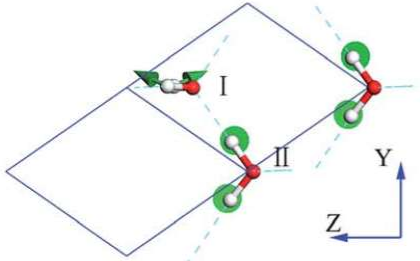


589(b) W I +R II

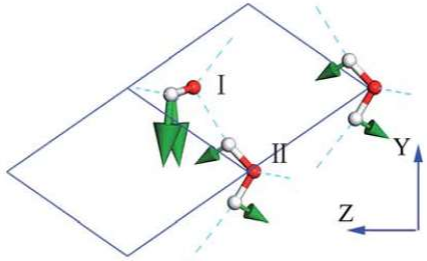


613 T I II

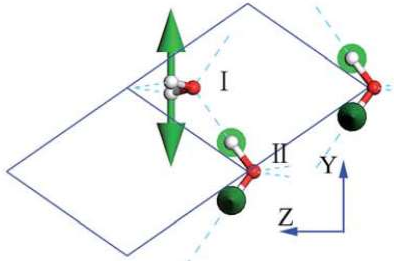




923(a) R I +W II



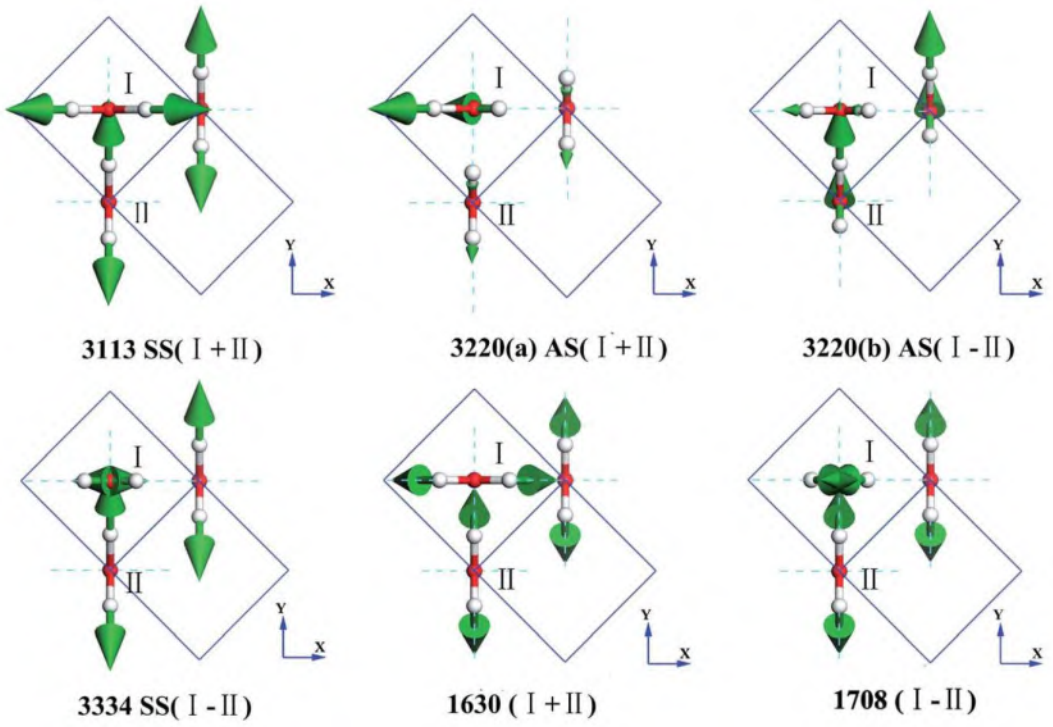
923(b) W I +R II

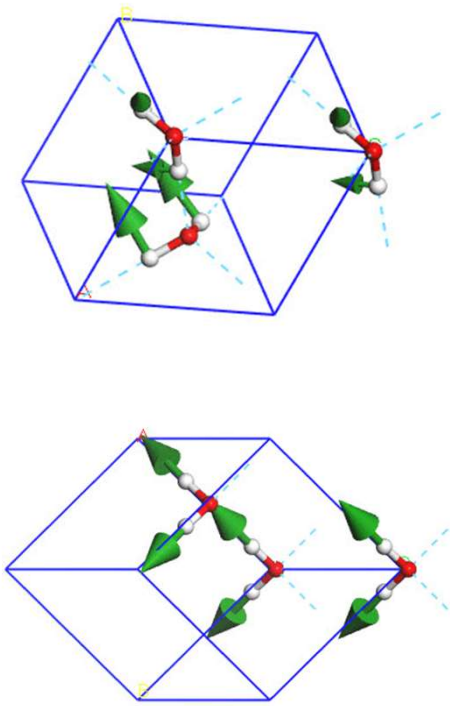


1053 T I II

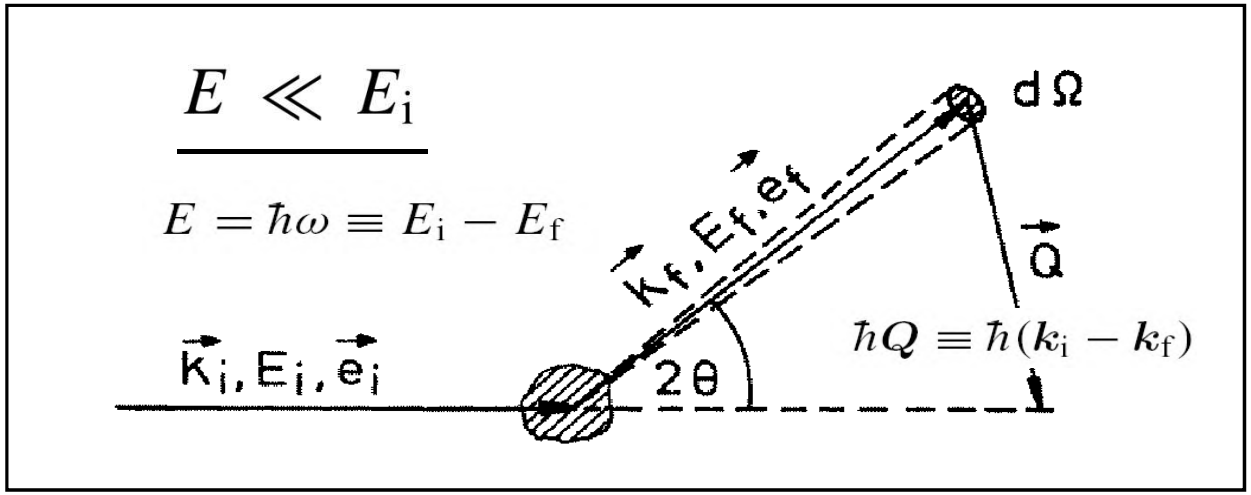
Vibrations of water in a crystal (ice Ic)

stretching and bending





Scattering by x-ray

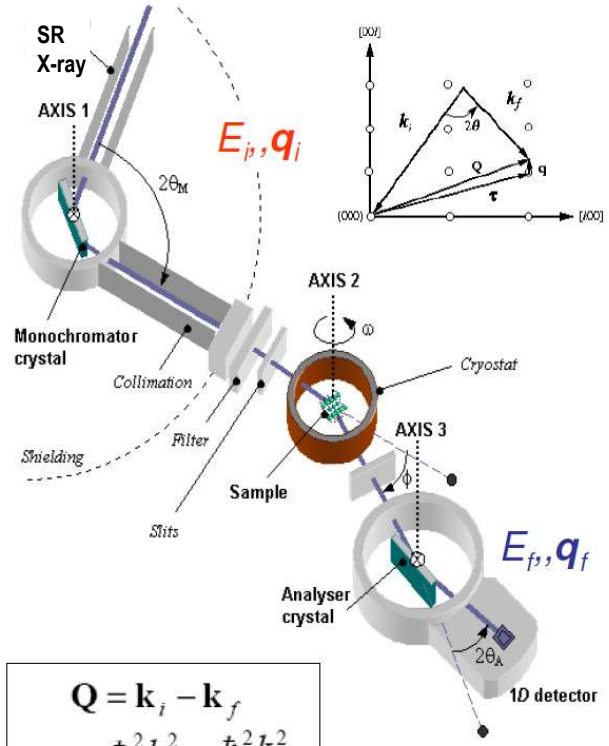


***Qr* << 1 collective dynamics**
***e.g.* phonons**

***Qr* >> 1 single atom dynamics**
***e.g.* Compton Scatttering**

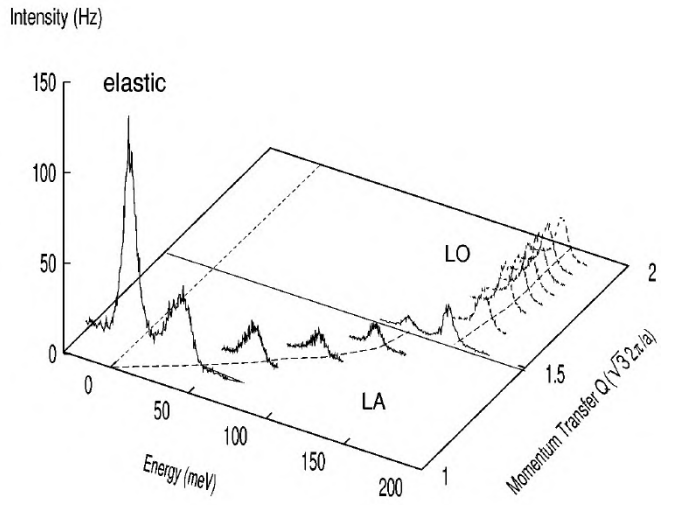
	Elastic "Static"	**Inelastic "Dynamics"**
	$\Delta\omega = 0$	$\Delta\omega \neq 0$
Coherent	**Bragg reflections**	**Phonon dispersion**
Incoherent	**Diffuse scattering**	**Vibration density of states**

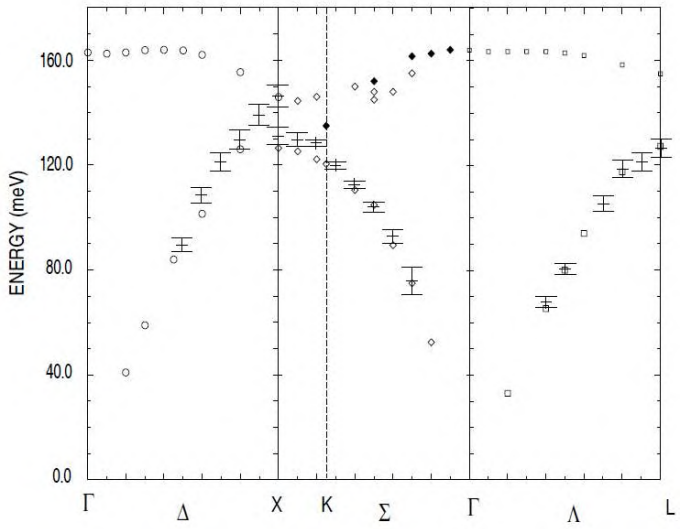
Phonon dispersion of single crystal diamond by Inelastic X-ray Scattering



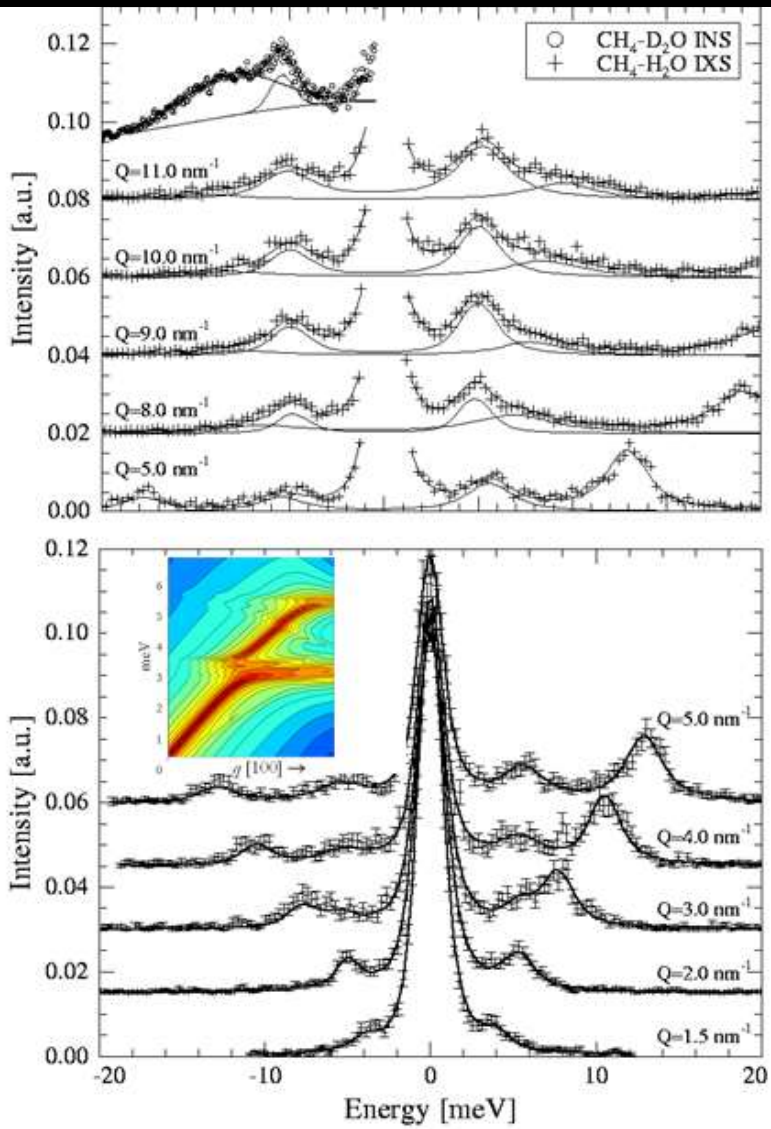
$$\mathbf{Q} = \mathbf{k}_i - \mathbf{k}_f$$

$$\Delta E = \frac{\hbar^2 k_i^2}{2m} - \frac{\hbar^2 k_f^2}{2m}$$

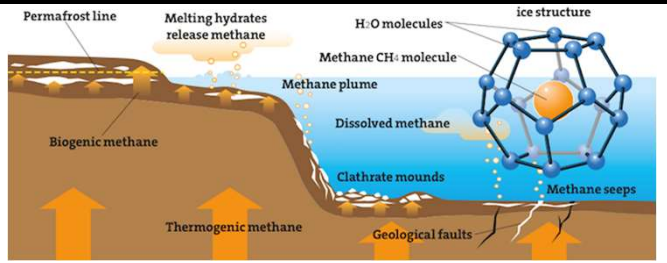


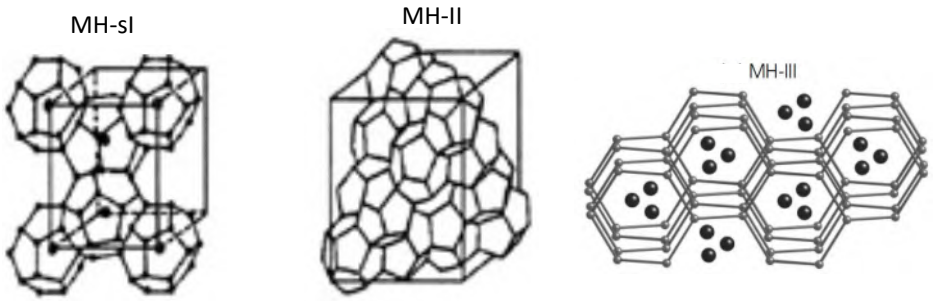


Phonon dispersion of polycrystals



J. Baumert, C. Gutt, V. P. Shpakov, J. S. Tse, M. Krisch, M. Müller, H. Requardt, D. D. Klug, S. Janssen, and W. Press, *Phys. Rev.* B 68, 174301 (2003)

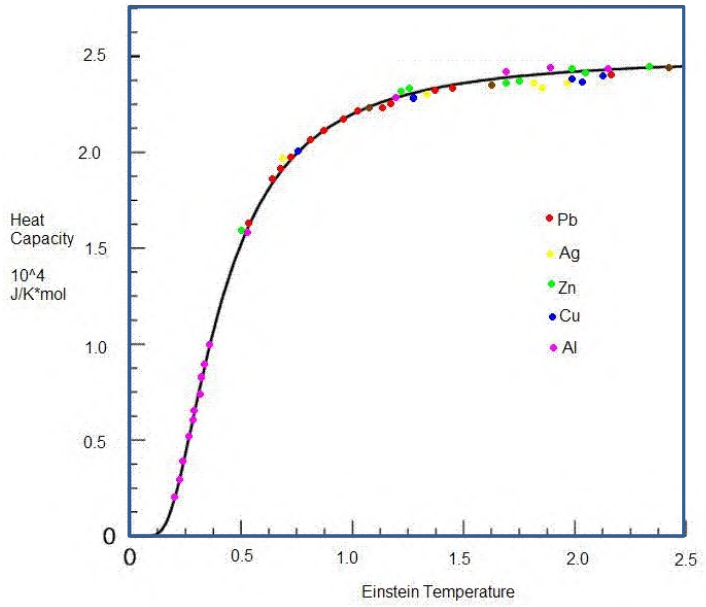




Hydrate pressure	MH-II 17 kbar	MH-III 21 kbar	MH-sI 0.2 kbar
ρ (g/cm^3)	1.07 (Ref. 4)	1.16 (Ref. 4)	0.90
B (GPa)	14.4 (Ref. 18)	23.5 (Ref. 4)	8.0
v_p (km/s)	4.2±0.1	4.6±0.1	3.7
C (GPa)	18.9±0.8	24.5±1.0	12.3
G (GPa)	3.4±0.6	0.8±0.7	3.3
v_s (km/s)	1.8±0.15	0.8±0.4	1.9

J. Baumert, C. Gutt, M. Krisch, H. Requardt,4 M. Müller, J. S. Tse, D. D. Klug, and W. Press, Phys. Rev., B 72, 054302 (2005)

Heat Capacity – Einstein model



$$U = \Sigma\, n_i \varepsilon_i$$

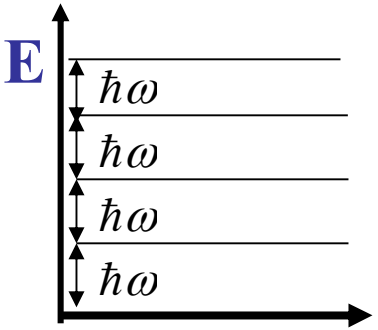
Number Distribution

Energy Distribution

There is a temperature dependence (*i.e.* distribution) of the oscillators!
Introduce Bose-Einstein distribution,

$$\bar{n} = \frac{1}{e^{\hbar\omega/k_B T} - 1}$$

Energy levels are equally spaced!

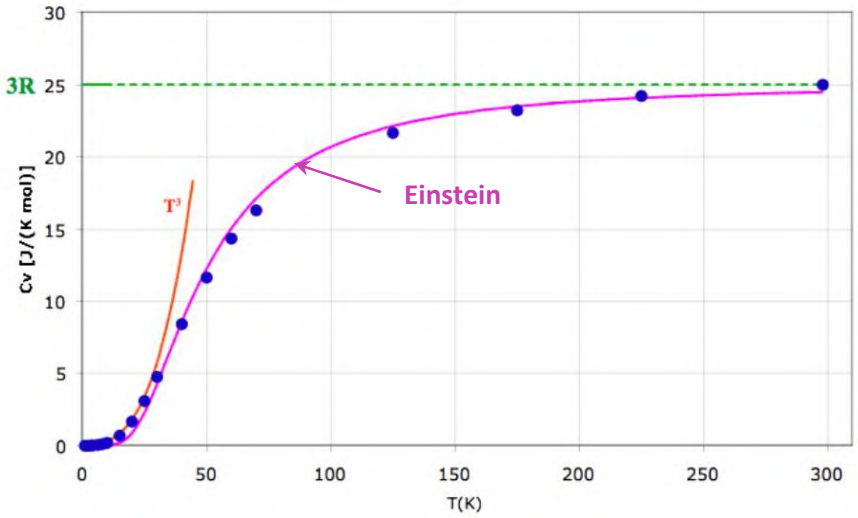


the total internal energy of the solid $U = 3N\hbar\omega\left(\bar{n} + \frac{1}{2}\right)$

$$C_v = \left(\frac{\partial U}{\partial T}\right)_v = 3Nk_B F_E\left(\frac{\hbar\omega}{k_B T}\right)$$

$$F(\ldots) \qquad x^2$$

Heat Capacity – Einstein/Debye model



Einstein Approximation: all modes (oscillators) have the same frequency $\Rightarrow \omega_E$

Debye approximation: In the low temperature limit acoustic modes dominate.
i.e. there is distribution of vibration modes !

Therefore the total internal energy should be,

$$U = \int_0^{\infty} \frac{\hbar\omega}{\exp(\hbar\omega/kT)-1} g(\omega)d\omega$$

No. of phonons in $d\omega$ at ω

Einstein statistic

Debye model – vibrational density of states

Debye assumed a dispersion relationship (phonon in a box)

$$\omega_j(k) = ck$$

and a phonon distribution function

$$g(\omega)d\omega \propto 4\pi k^2 dr$$

therefore,

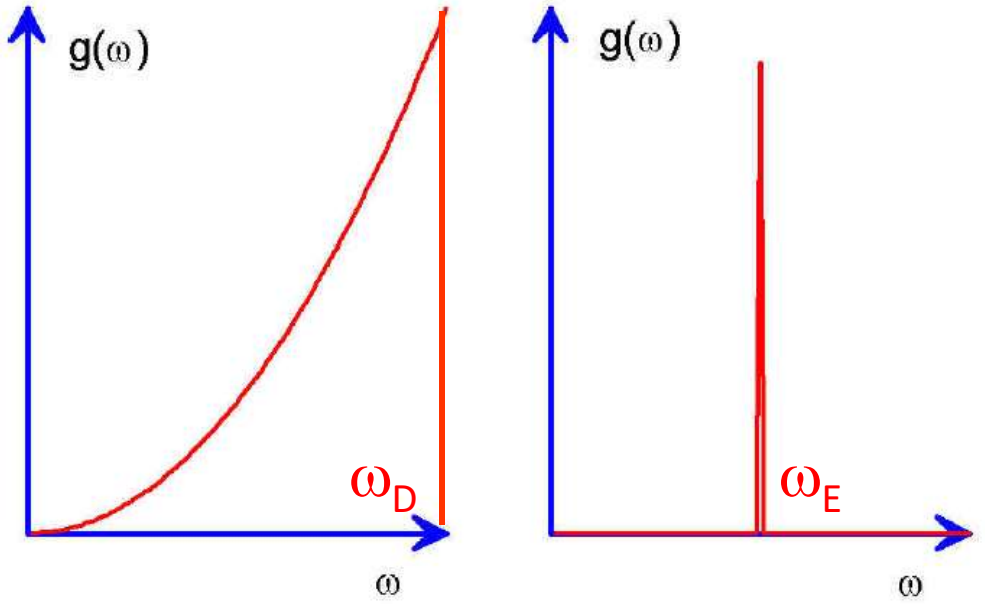
$$g(\omega) = D\omega^2$$

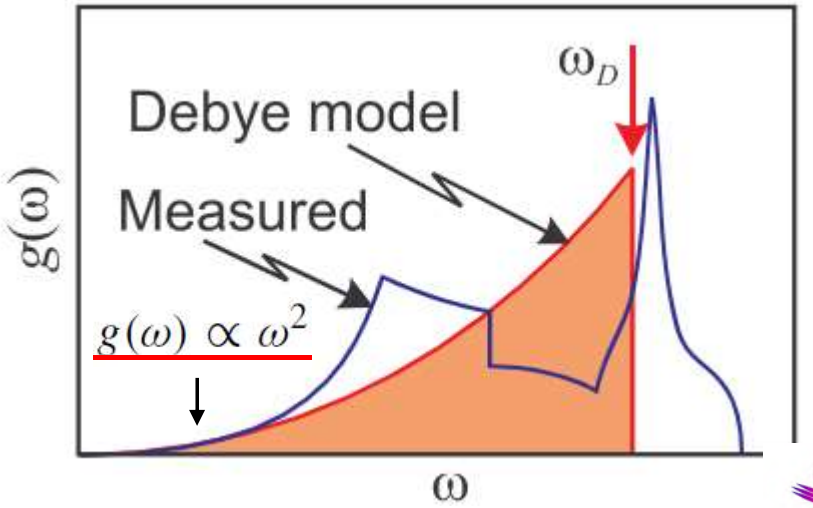
with a cutoff frequency, ω_D

$$g(\omega) = \frac{V}{2\pi^2}\left(\frac{1}{v_l^3} + \frac{2}{v_t^3}\right)\omega^2 = \frac{3V}{2\pi^2}\frac{\omega^2}{v_a^3}$$

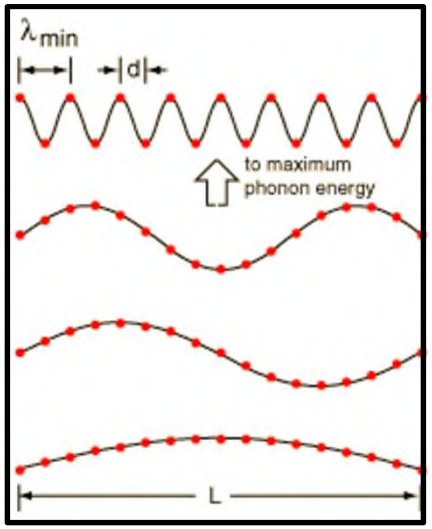
$$U = \frac{3V\hbar}{2\pi^2 v_s^3}\int_0^{\omega_D} \omega^3 \frac{1}{\exp(\hbar\omega/kT)-1}\,d\omega$$

$$c_V = \int_0^{\omega_D} \frac{3V\omega^2}{2\pi^2 c^3}\hbar\omega\frac{\partial n}{\partial T}\,d\omega$$





Phonon in a box

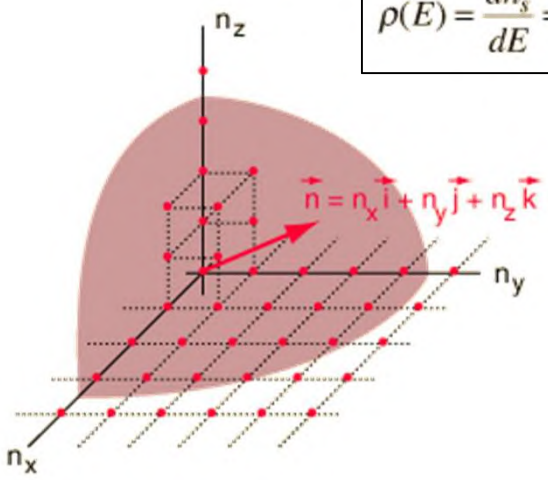


$\lambda_{min} = 2d$

$\lambda_n = \frac{2L}{n}$

$\lambda_{max} = 2L$

$$h\upsilon = \frac{hv_s}{\lambda} = \frac{hv_s n}{2L}$$



$$\rho(E) = \frac{dn_s}{dE} = \frac{8\pi}{(hc)^3} E^2$$

$$E = \frac{h^2k^2}{2m}$$

$$\rho(E) \propto k^2$$

the total energy in the lattice vibrations is of the form

$$U = 3\int_0^{E_{max}} \frac{E}{e^{E/kT} - 1} dE$$

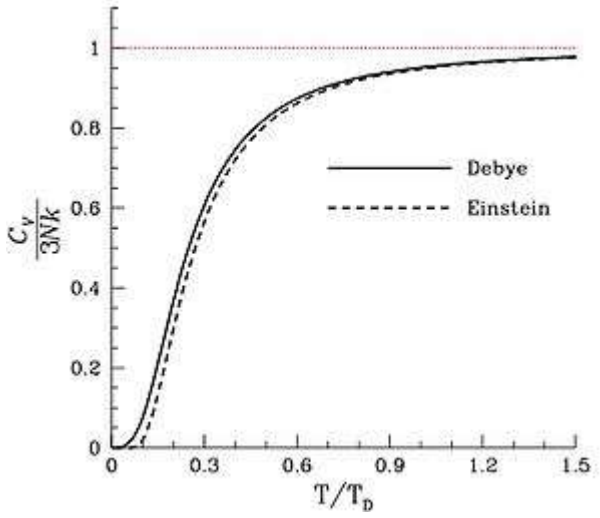
expressed in terms of the phonon modes by expressing the integral in terms of the mode number n.

$$U = \frac{3\pi}{2}\int_0^{n_{max}} \frac{hv_s n}{2L} \frac{n^2}{e^{hv_s n/2LkT} - 1} dn$$

let $x_{max} = \frac{hv_s n_{max}}{2LkT} = \frac{hv_s}{2kT}\left(\frac{6N}{\pi V}\right)^{1/3} = \frac{T_D}{T}$ the integral takes the form

$$U = \frac{9NkT^4}{T_D^3}\int_0^{T_D/T} \frac{x^3}{e^x - 1} dx$$

What can we learn from Debye temperature?



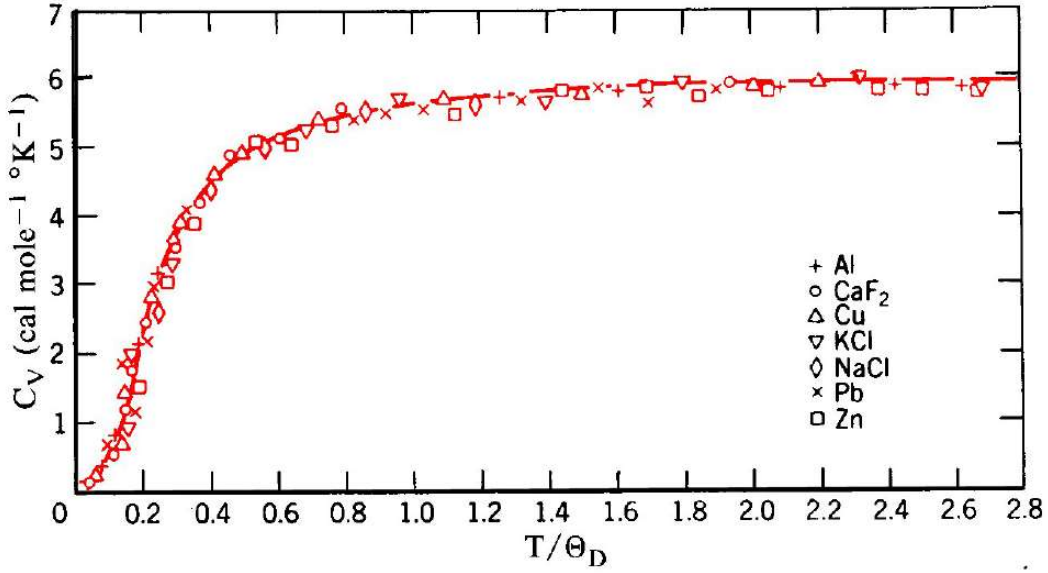


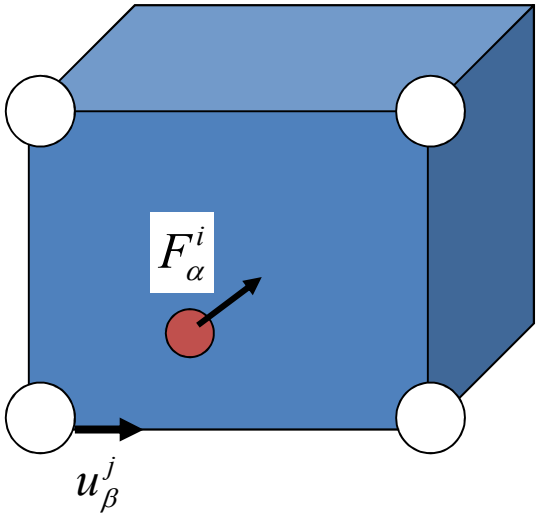
Table 4.5 Debye temperatures T_D, heat capacities, and thermal conductivities of selected elements

	Crystal							
	Ag	**Be**	**Cu**	**Diamond**	**Ge**	**Hg**	**Si**	**W**
T_D (K)*	215	1000	315	1860	360	100	625	310
C_m (J K^{-1} mol^{-1})†	25.6	16.46	24.5	6.48	23.38	27.68	19.74	24.45
c_s (J K^{-1} g^{-1})†	0.237	1.825	0.385	0.540	0.322	0.138	0.703	0.133
κ (W m^{-1} K^{-1})†	429	183	385	1000	60	8.65	148	173

Theoretical lattice dynamics - Harmonic approximation

Force constant, Hooke's Law

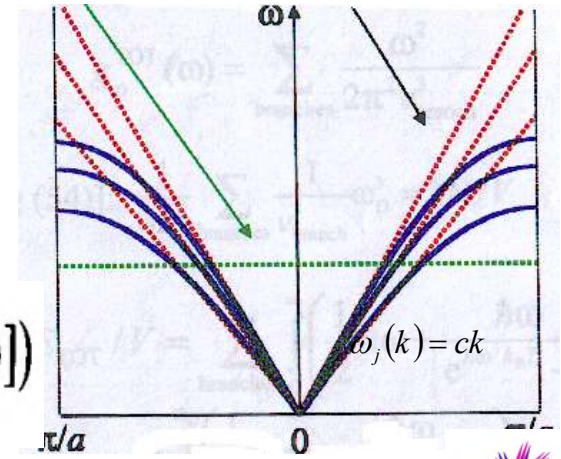
$$\Phi_{\alpha\beta}^{ij} = \frac{\partial^2 E_{tot}}{\partial u_\alpha^i \partial u_\beta^j} = -\frac{\partial F_\alpha^i}{\partial u_\beta^j} \approx -\frac{F_\alpha^i}{u_\beta^j} \qquad i, j = 1, N \qquad \alpha, \beta = x, y, z$$



Dynamic matrix is the Fourier transformation of force constants

$$D_{\alpha\beta}^{ij}(q) = \frac{1}{\sqrt{M_i M_j}} \sum_L \Phi_{\alpha\beta}^{i,j+L} e^{-iq\cdot(R^{j+L}-R^i)}$$

Einstein approximation | Debye approximation



Diagonalize Dynamic matrix to get phonon dispersions, and DOS

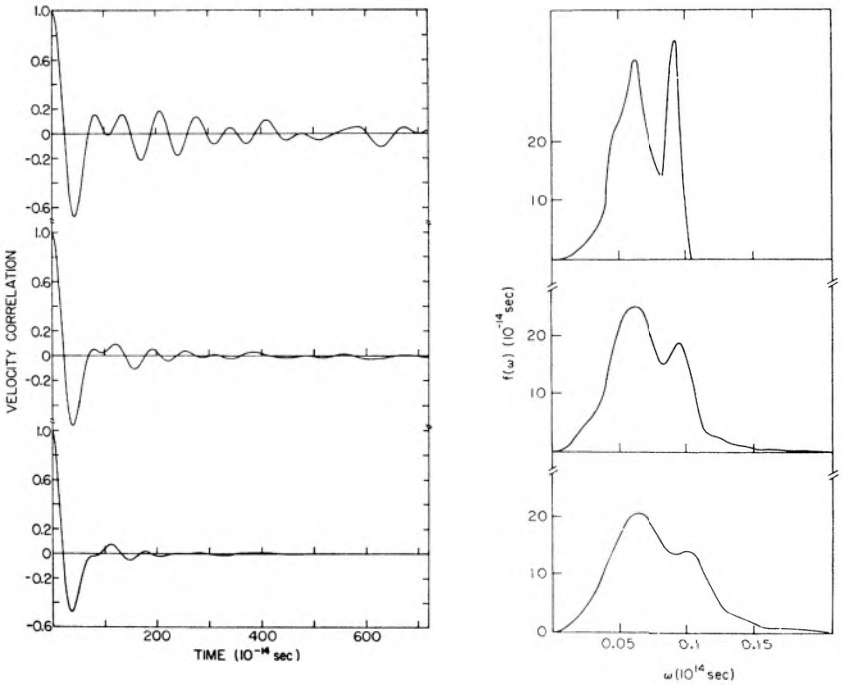
$$m_j\omega^2(\mathbf{k},\nu)\mathbf{U}(j,\mathbf{k},\nu) = \sum_{j'l'} \Phi\begin{pmatrix} jj' \\ 0l' \end{pmatrix} \cdot \mathbf{U}(j',\mathbf{k},\nu) \exp\left(i\mathbf{k}\cdot[\mathbf{r}(j'l') - \mathbf{r}(j0)]\right)$$

Theoretical molecular dynamics
Beyond harmonic approximation

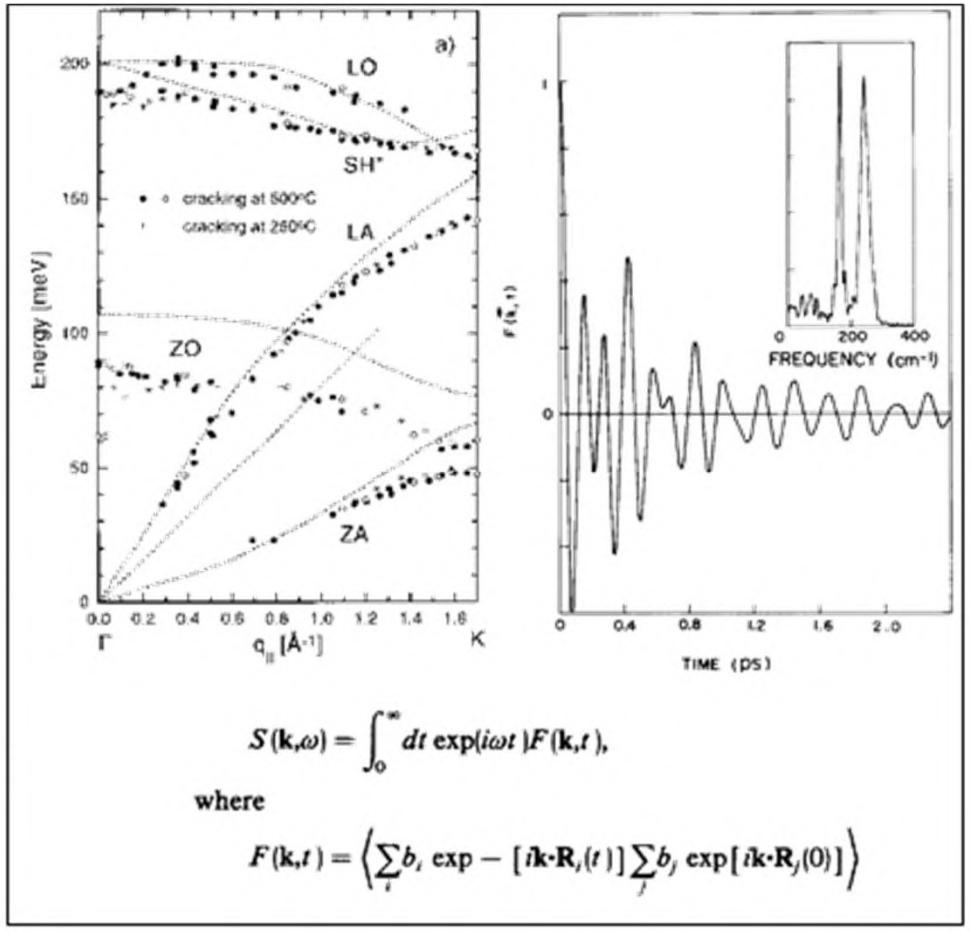
Time correlation function formalism

$$P(\omega) = m \int \langle \dot{\boldsymbol{r}}(\tau)\dot{\boldsymbol{r}}(t+\tau)\rangle_{\tau} \mathrm{e}^{-i\omega t}\mathrm{d}t$$

$$\langle \dot{\boldsymbol{r}}(\tau)\dot{\boldsymbol{r}}(t+\tau)\rangle_{\tau} \Rightarrow P(\omega)$$



J. M. Dickey and A. Paskein, *Phys. Rev*. 188, 1407 (1969)



$$S(\mathbf{k},\omega) = \int_0^{\infty} dt \exp(i\omega t) F(\mathbf{k},t),$$

where

$$F(\mathbf{k},t) = \left\langle \sum_i b_i \exp - [i\mathbf{k}\cdot\mathbf{R}_i(t)] \sum_j b_j \exp[i\mathbf{k}\cdot\mathbf{R}_j(0)] \right\rangle$$

J.S. Tse and M.L. Klein *and* I.R. McDonald, *J. Chem. Phys*,. 81, 6124 (1984)

End of Part I

Outline

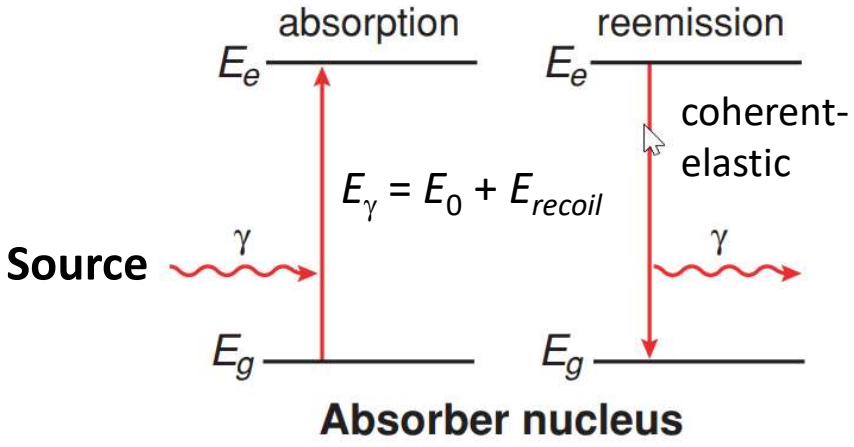
Day 1

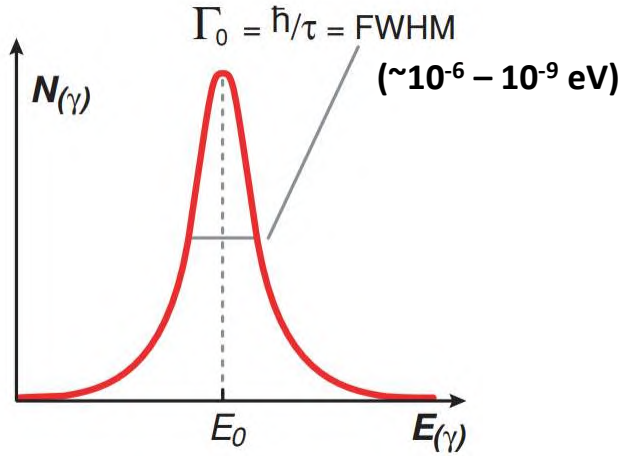
- Interatomic interaction and vibrations
- Lattice vibrations and phonons
- Vibrational spectrum and properties

Day 2

- Mossbauer effect
- Vibrational density of states
- Isomer shift, Quadrupole splitting and Hyperfine interaction
- Applications

Recoilless Nuclear Resonance Absorption of Radiation - Mossbauer Effect

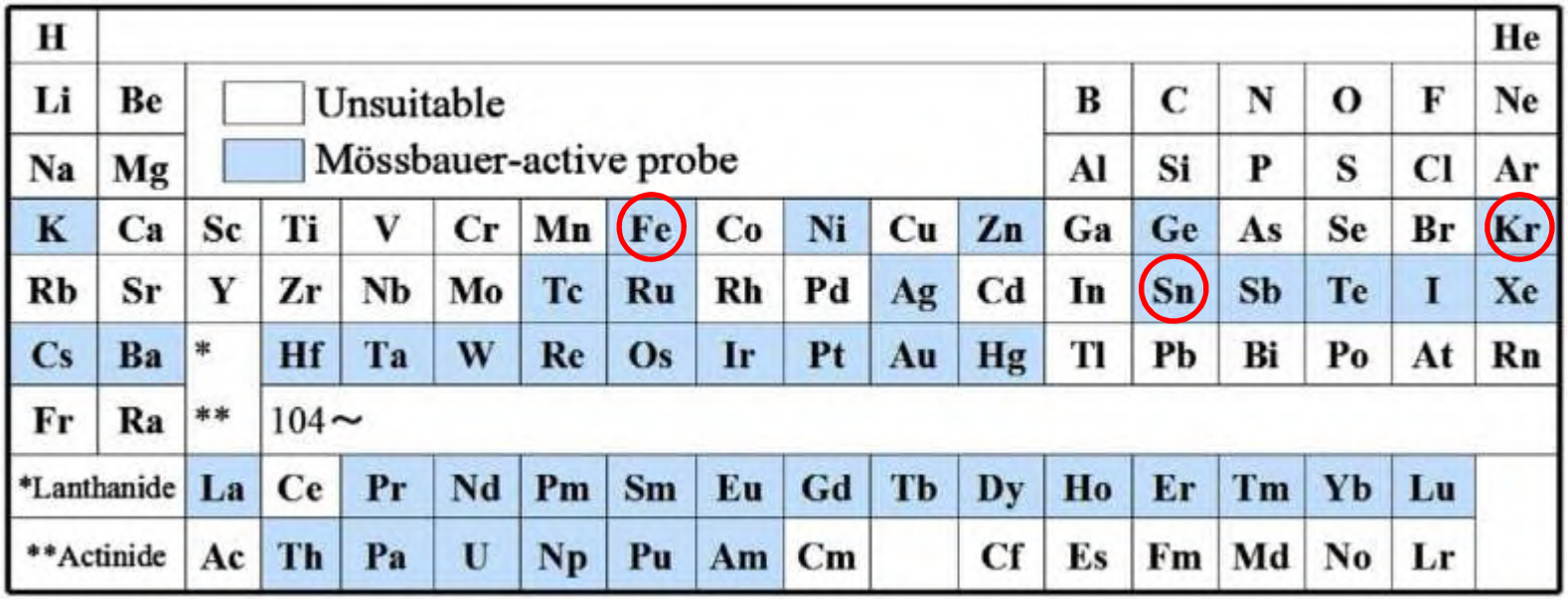




Before 1958 it was thought impossible for nuclei to absorb and emit γ-rays resonantly. Due to conservation of momentum, the emitting and absorbing nuclei would lose some of the γ-ray energy by recoiling, $p_{\text{nucleus}} = -p_\gamma$, therefore eliminating any chance of the γ-ray being absorbed again by another nucleus - this due to the very narrow linewidth of some nuclear energy levels (due to their long lifetime - the uncertainty principle!) However, Mossbauer showed that if the absorber and emitting atoms are embedded in a lattice (as in a solid) the ***recoil due to the γ-ray may in fact be taken up by the entire solid***, making the energy loss negligible. Effectively, the γ radiation emitted by their nuclei are very close to being recoil-free. This implies that the emitted photon has the exact frequency that corresponds to the transition energy between the nuclear ground state and the excited state. This is the essence of Mossbauer Spectroscopy: the discovery of ***recoil-free*** nuclear resonance emission and absorption.

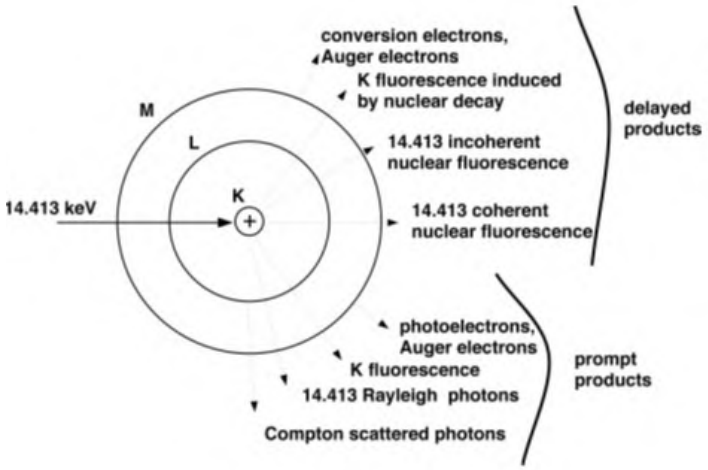
$$E_{recoil} = \frac{1}{2}mv^2 = \frac{p^2}{2m} = \frac{p^2c^2}{2mc^2} = \frac{(14.4keV)^2}{2(53.022GeV)} \cong 0.002eV$$

Mossbauer active nuclei

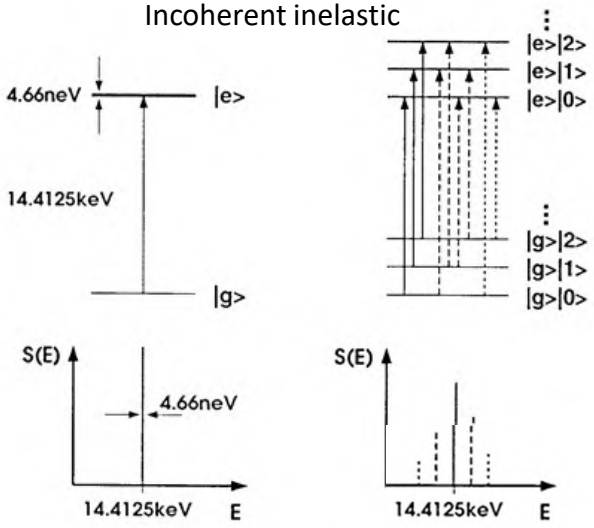


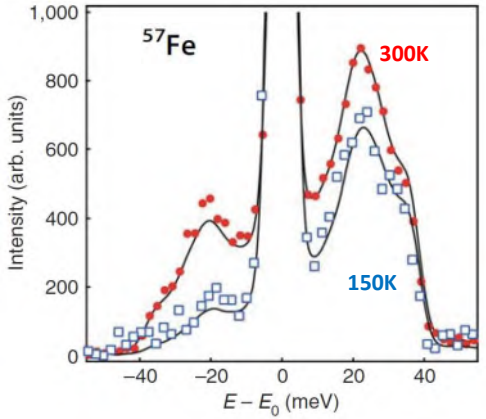
H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	*	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	**	104～														
*Lanthanide		La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	
**Actinide		Ac	Th	Pa	U	Np	Pu	Am	Cm		Cf	Es	Fm	Md	No	Lr	

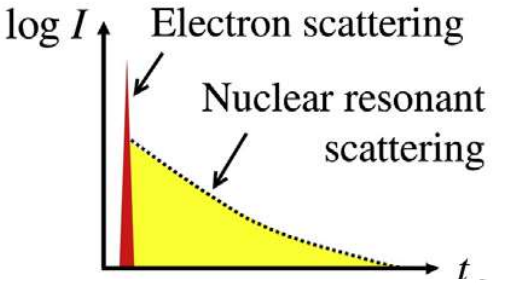
Non-resonant Inelastic X-ray Scattering (NRIXS)

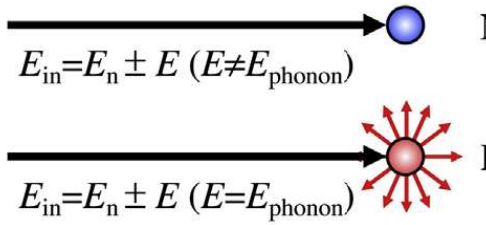


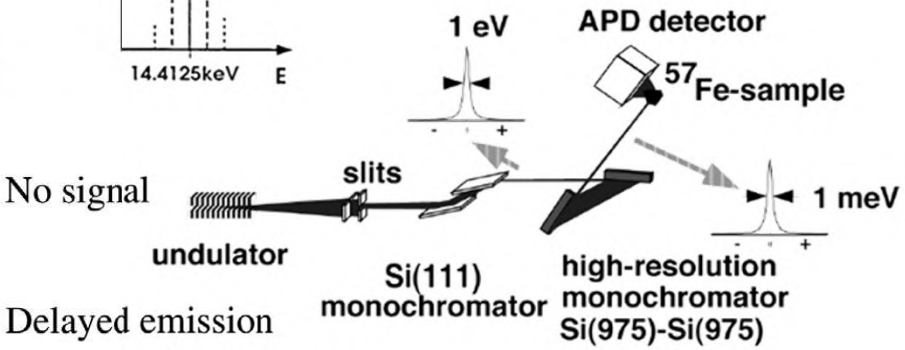
Incoherent inelastic

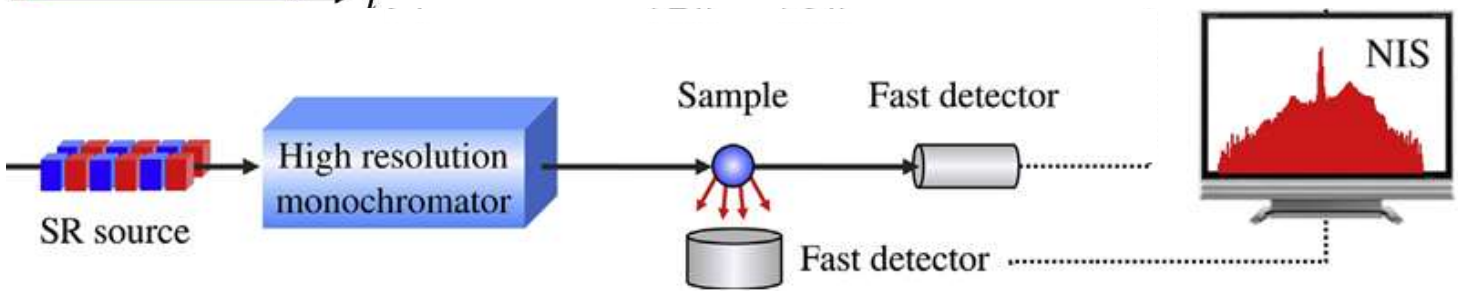




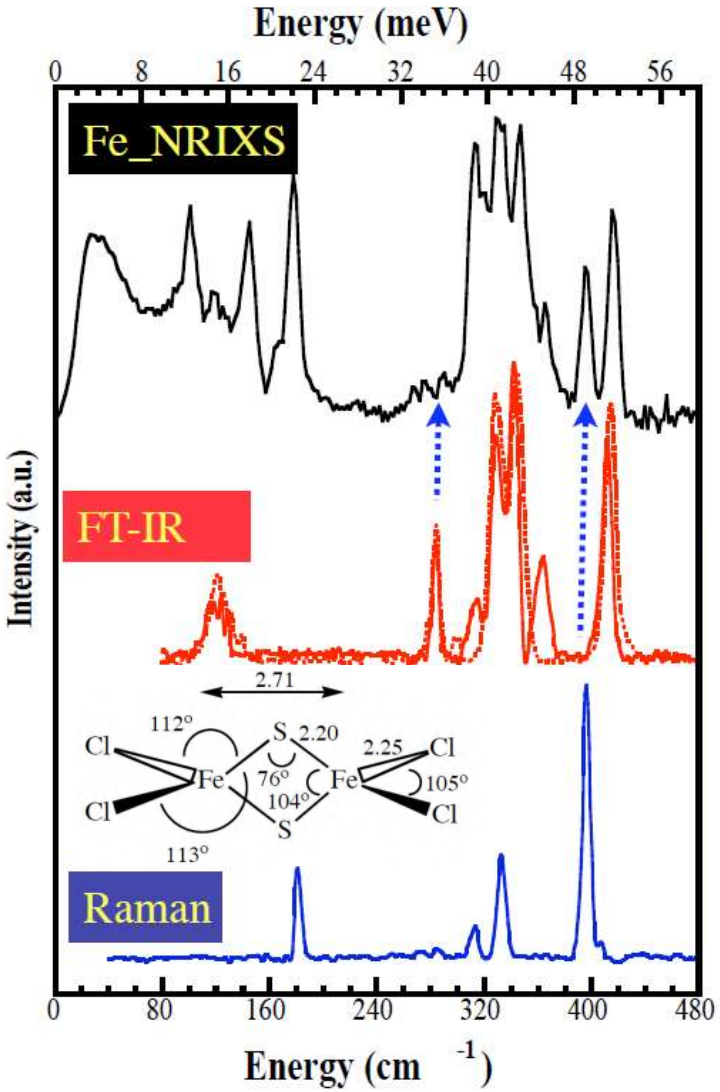








Advantage of VDOS – no selection rules



Selection rules:

- Infrared
  Only "*u*" modes are active
  $I \propto |\partial\mu/\partial q|^2$

- Raman
  Only "*g*" modes are active
  $I \propto |\partial\alpha/\partial q|^2$

- NRVS
  All modes are active
  $I \propto$ VDOS

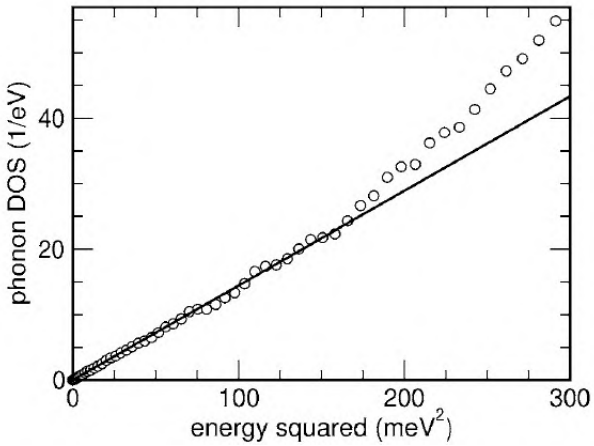
Extraction of sound velocity

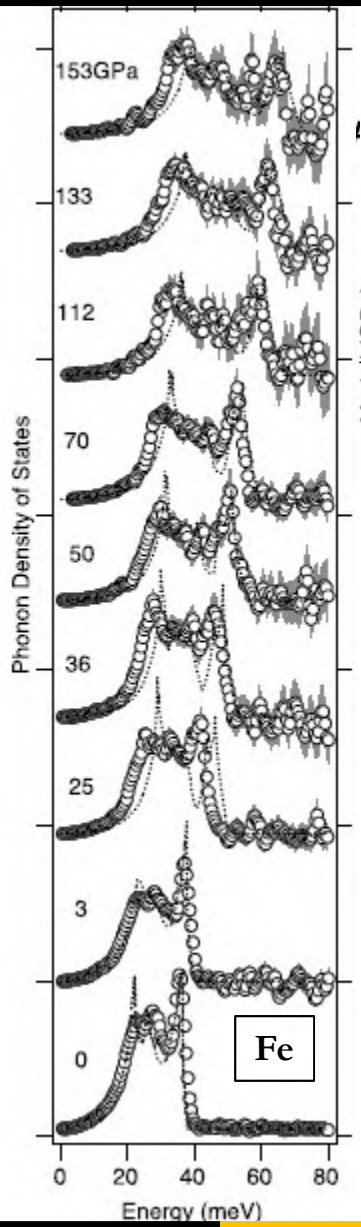
$$g(\omega) = \frac{V\omega^2}{2\pi^2}\frac{1}{v_D^3} \Rightarrow g(\omega) = \frac{V\omega^2}{2\pi^2}\left(\frac{1}{v_P^3} + \frac{2}{v_S^3}\right)$$

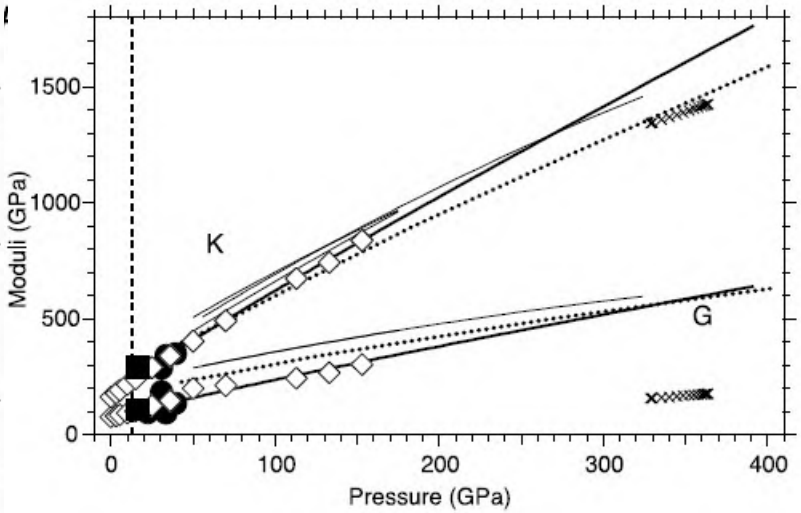
$$\frac{3}{V_D^3} = \frac{1}{V_P^3} + \frac{2}{V_S^3}$$

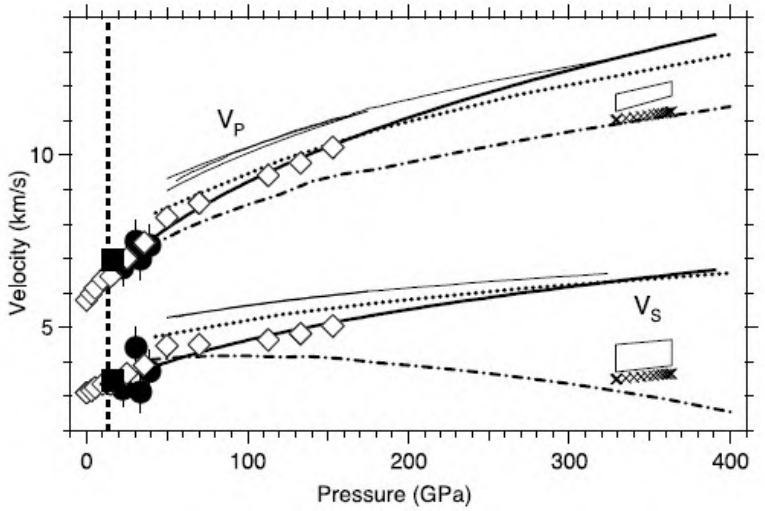
$$\frac{K}{\rho} = V_P^2 - \frac{4}{3}V_S^2$$

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









Properties derived from vibrational density of states

The partition function for the harmonic lattice is given by

$$\ln Z^N = -3N \int \ln\left(2\sinh\frac{\beta E}{2}\right) g(E)\,\mathrm{d}E$$

the vibrational energy per atom

$$U = -\frac{\partial \ln Z}{\partial \beta} = \frac{3}{2}\int E\coth\frac{\beta E}{2} g(E)\,\mathrm{d}E$$

vibrational entropy per atom S

$$S = k_\mathrm{B}\beta U + k_\mathrm{B}\ln Z$$

the free energy per atom F

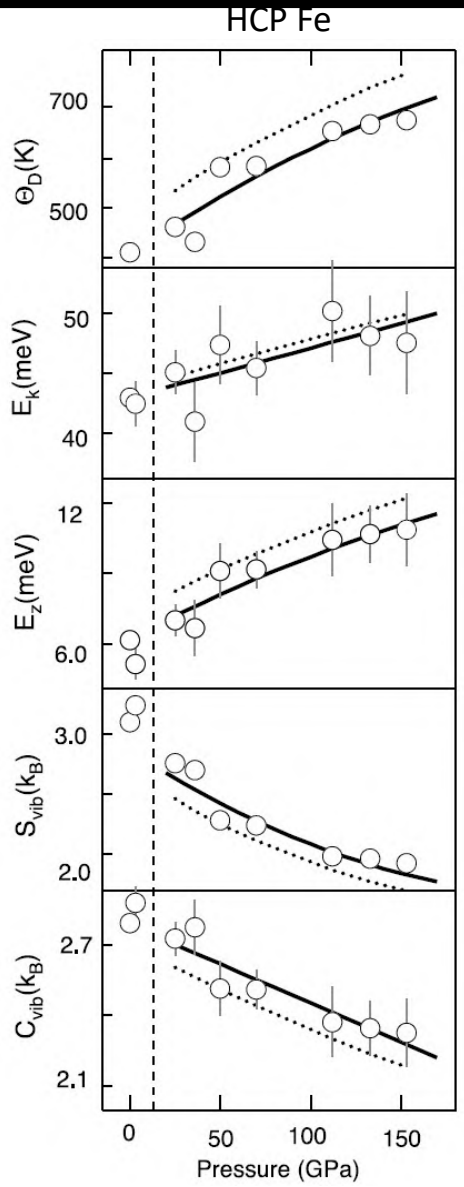
$$F = -\frac{1}{\beta}\ln Z$$

the specific heat per atom at constant volume

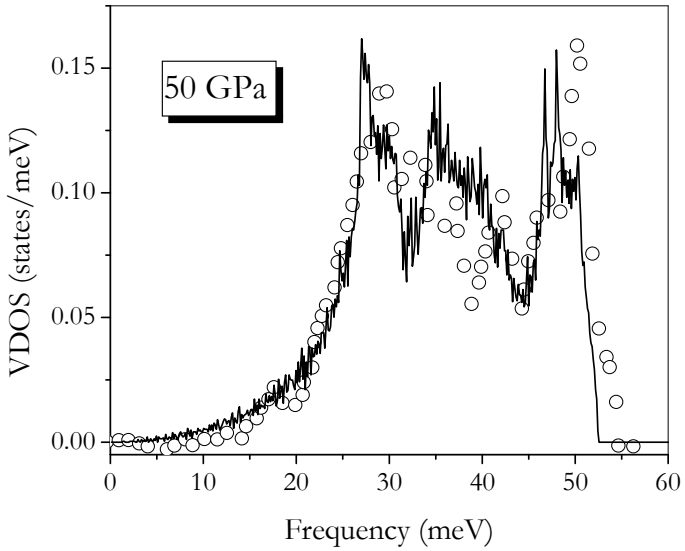
$$c_V = \frac{\partial U}{\partial T} = k_\mathrm{B}\beta^2\frac{\partial^2 \ln Z}{\partial \beta^2} = 3k_\mathrm{B}\int\left(\frac{\beta E}{2\sinh(\beta E/2)}\right)^2 g(E)\,\mathrm{d}E$$

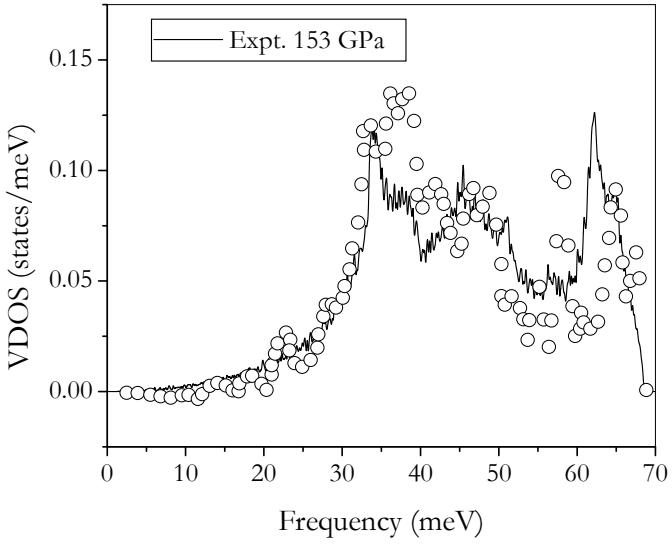
mean force constant

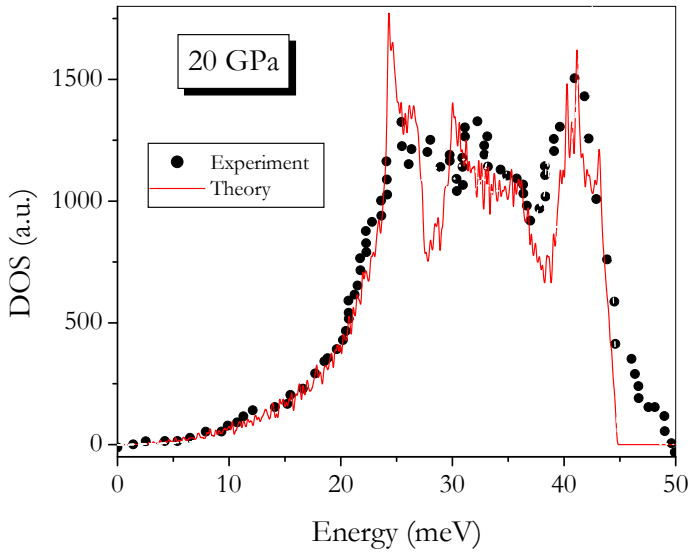
$$F_m = \frac{9}{10}\frac{k^2}{E_r}k_\mathrm{B}^2\theta_\mathrm{D}^2$$

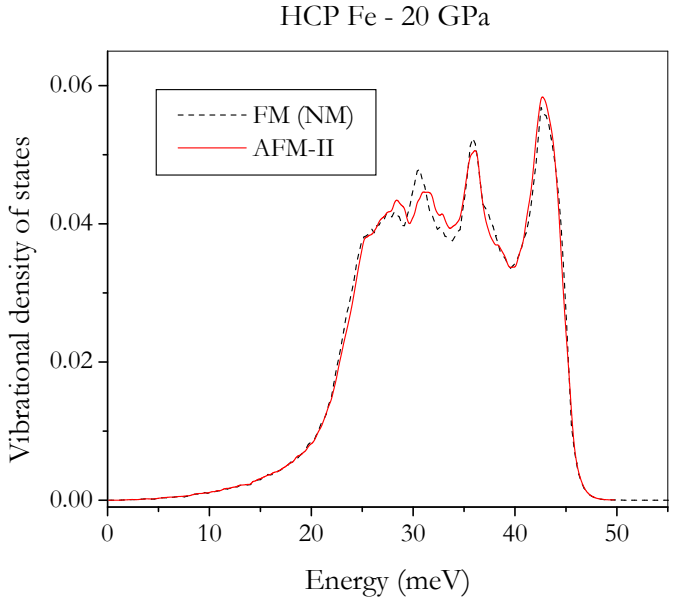


Improved calculated vibrational DOS for ε-Fe

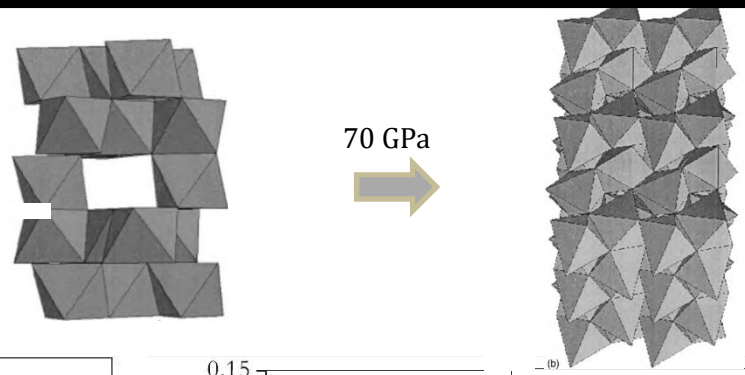


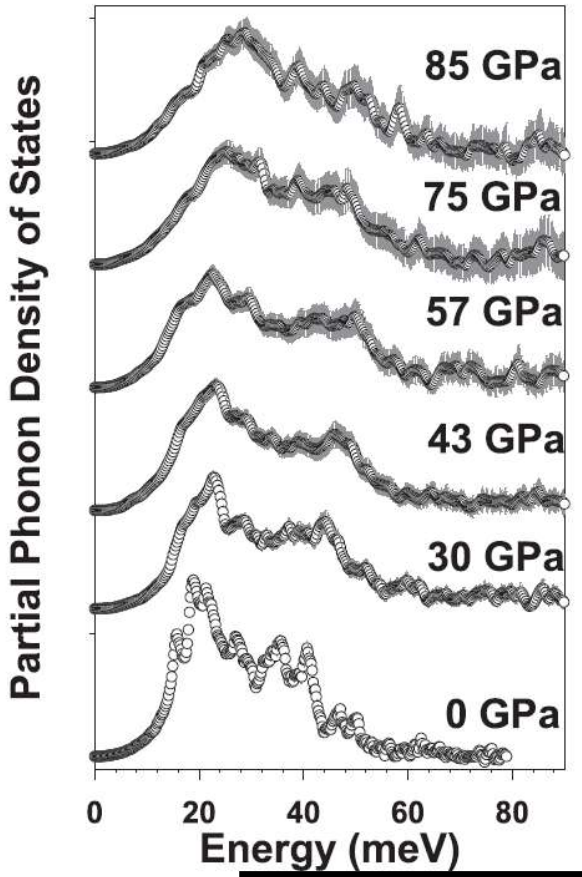


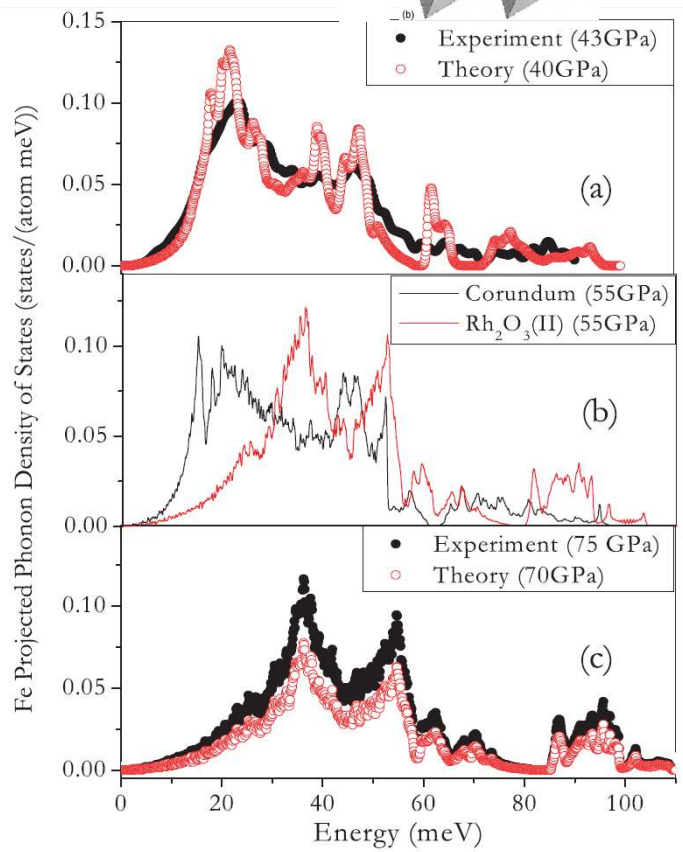


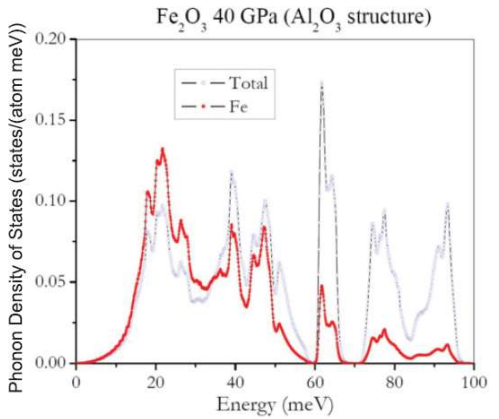


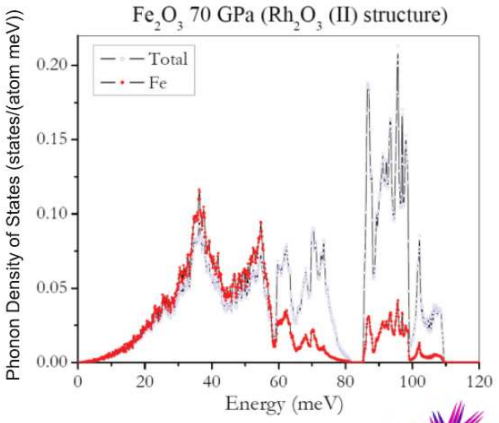
Phase stability - Hematite Fe_2O_3











University of Saskatchewan

J.F. Lin, J.S. Tse, *et.al.*, *Phys. Rev.* B 84, 064424 (2011).

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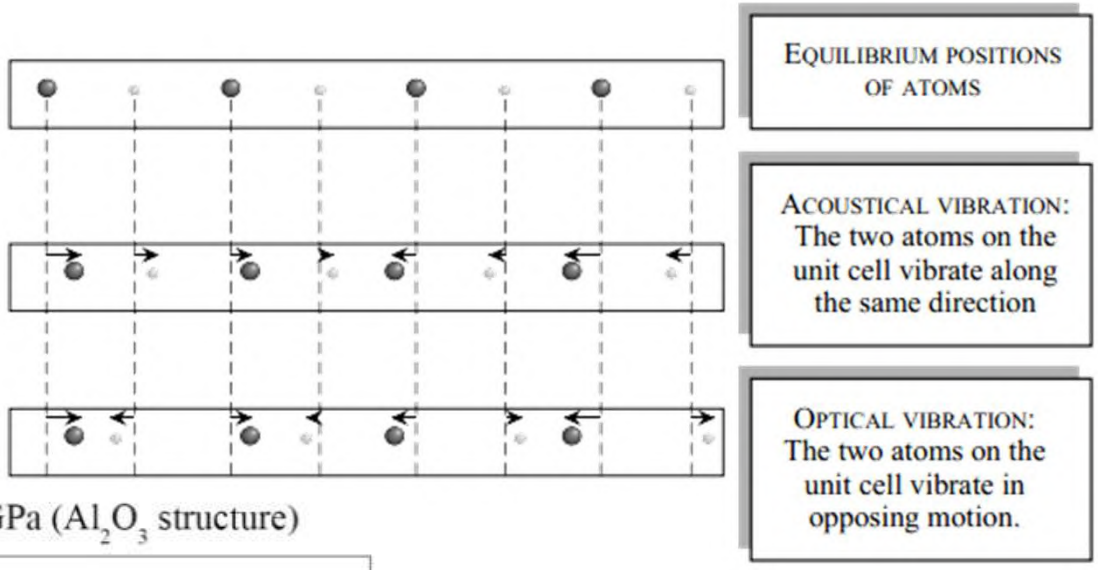
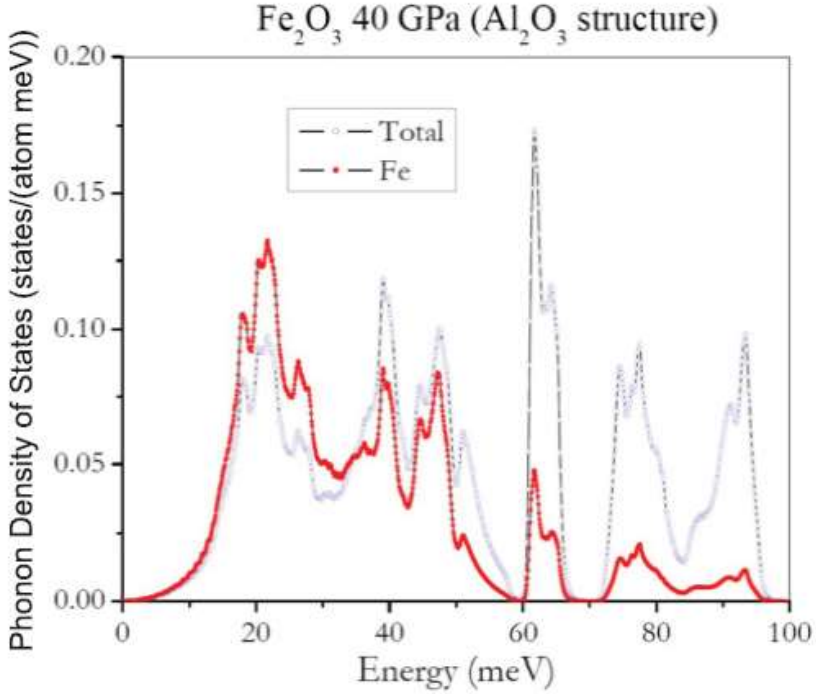
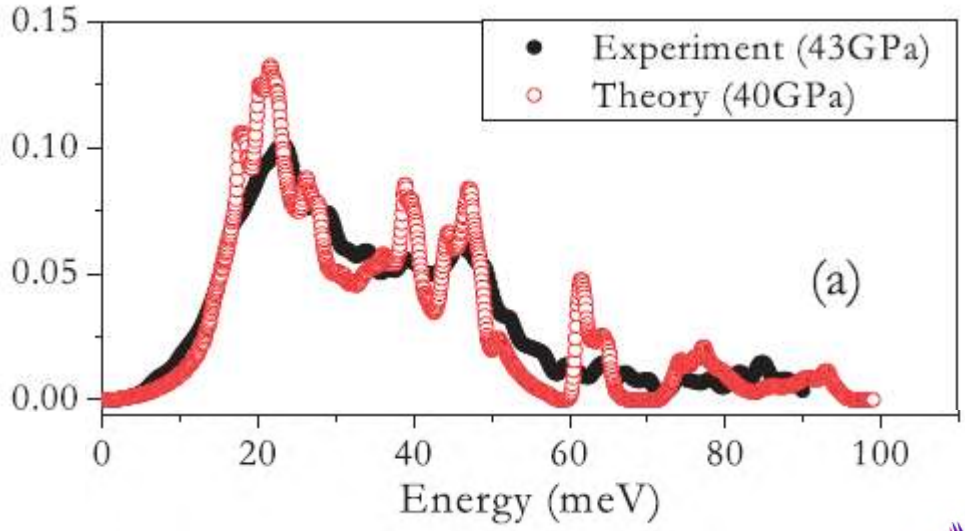
Why it also work for multi-component systems?



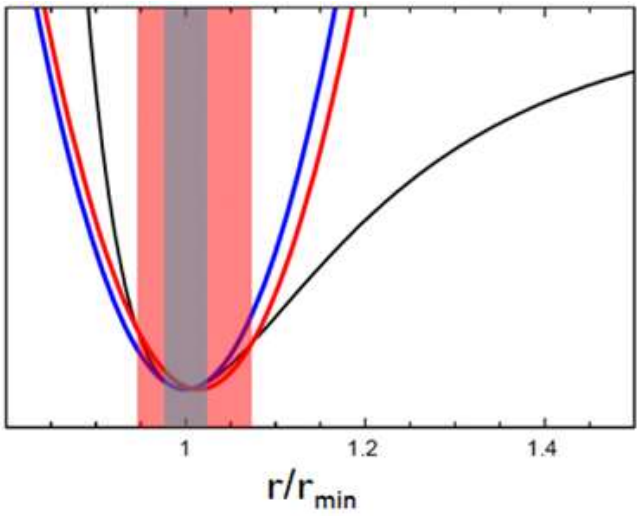


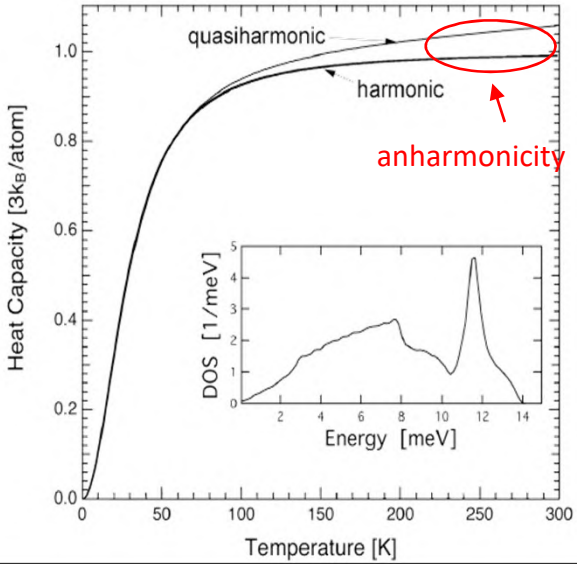


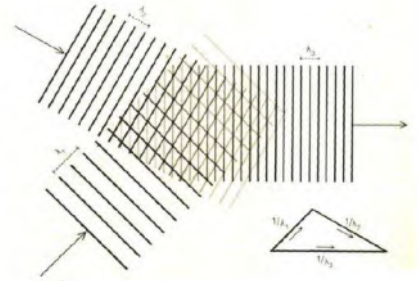
Phonon anharmonicity

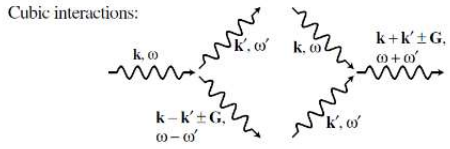
1. The heat capacity becomes T independent for $T>T_D$.
2. There is no thermal expansion of solids.
3. Thermal conductivity of solids is infinite

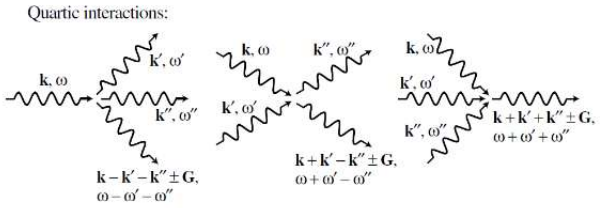
$$U(x) = U_{harm}(x) + U_{anharm}(x) = cx^2 - gx^3 - fx^4$$









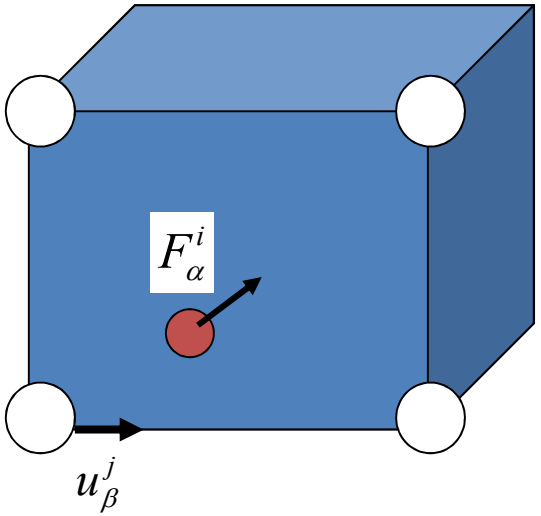


If the lattice potential is harmonic, the phonon frequencies are volume-independent, and the thermal expansion coefficient is zero at all temperatures.

Theoretical lattice dynamics - Harmonic approximation

Force constant, Hooke's Law

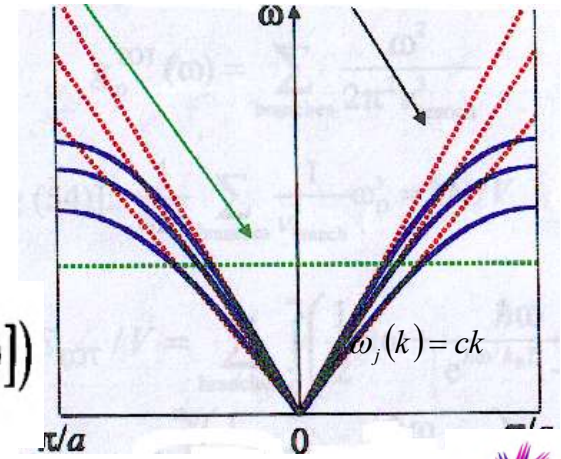
$$\Phi_{\alpha\beta}^{ij} = \frac{\partial^2 E_{tot}}{\partial u_\alpha^i \partial u_\beta^j} = -\frac{\partial F_\alpha^i}{\partial u_\beta^j} \approx -\frac{F_\alpha^i}{u_\beta^j} \qquad i, j = 1, N \qquad \alpha, \beta = x, y, z$$



Dynamic matrix is the Fourier transformation of force constants

$$D_{\alpha\beta}^{ij}(q) = \frac{1}{\sqrt{M_i M_j}} \sum_L \Phi_{\alpha\beta}^{i,j+L} e^{-iq\cdot(R^{j+L}-R^i)}$$

Einstein approximation | Debye approximation



Diagonalize Dynamic matrix to get phonon dispersions, and DOS

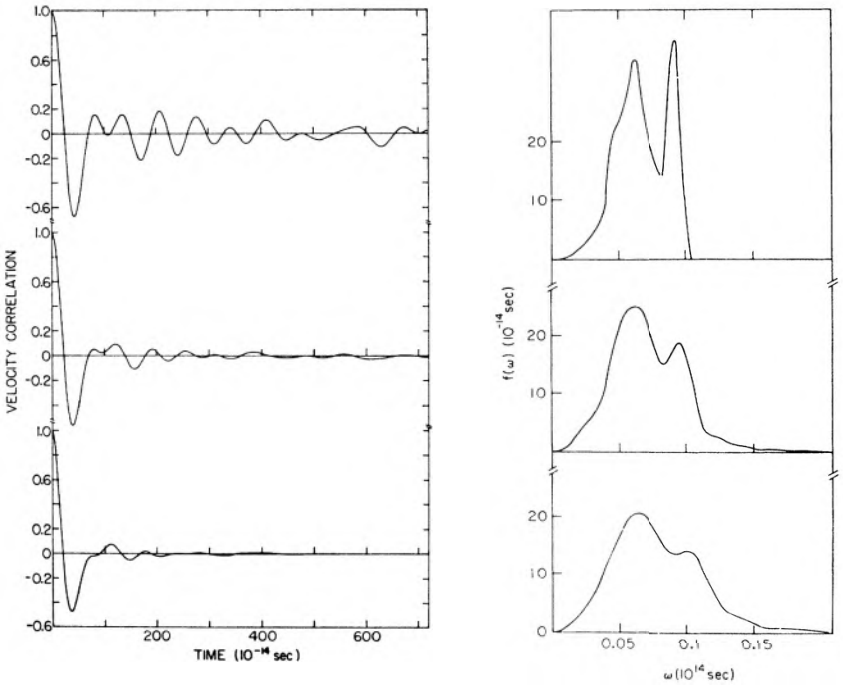
$$m_j\omega^2(\mathbf{k},\nu)\mathbf{U}(j,\mathbf{k},\nu) = \sum_{j'l'} \Phi\begin{pmatrix} jj' \\ 0l' \end{pmatrix} \cdot \mathbf{U}(j',\mathbf{k},\nu) \exp\left(i\mathbf{k}\cdot[\mathbf{r}(j'l') - \mathbf{r}(j0)]\right)$$

Theoretical molecular dynamics
Beyond harmonic approximation

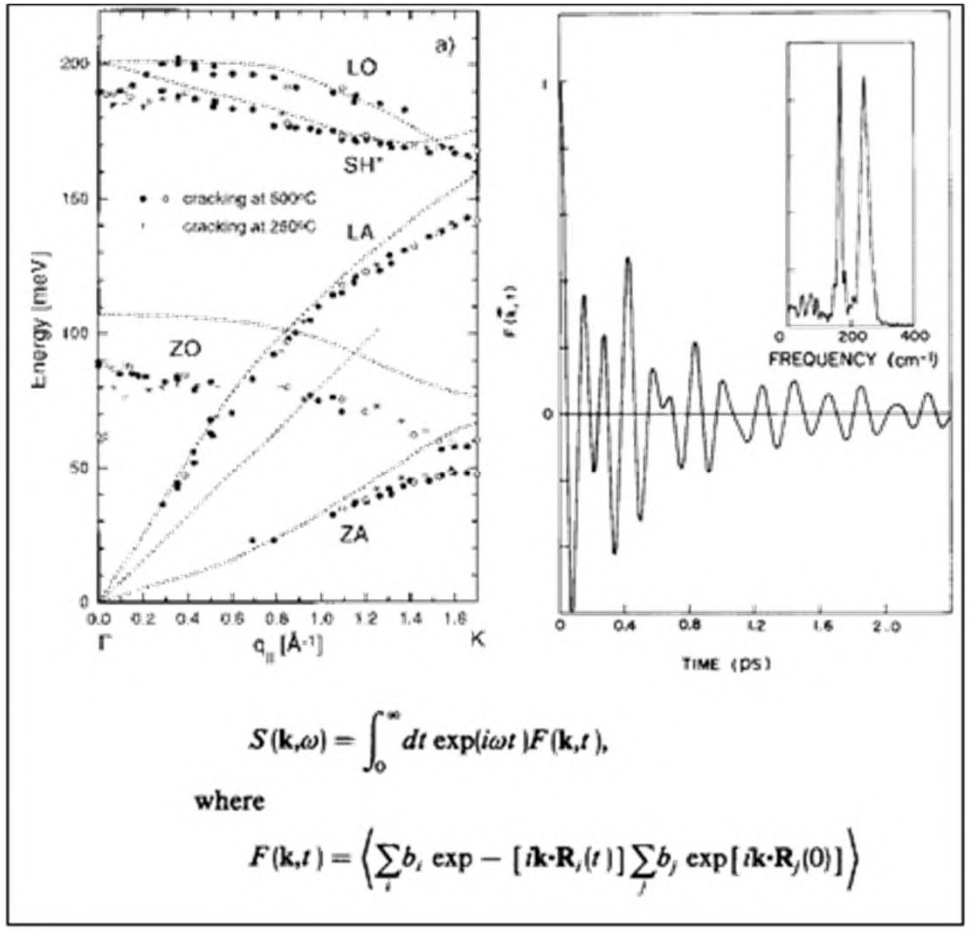
Time correlation function formalism

$$P(\omega) = m \int \langle \dot{\boldsymbol{r}}(\tau)\dot{\boldsymbol{r}}(t+\tau)\rangle_{\tau} \mathrm{e}^{-i\omega t}\mathrm{d}t$$

$$\langle \dot{\boldsymbol{r}}(\tau)\dot{\boldsymbol{r}}(t+\tau)\rangle_{\tau} \Rightarrow P(\omega)$$



J. M. Dickey and A. Paskein, *Phys. Rev*. 188, 1407 (1969)



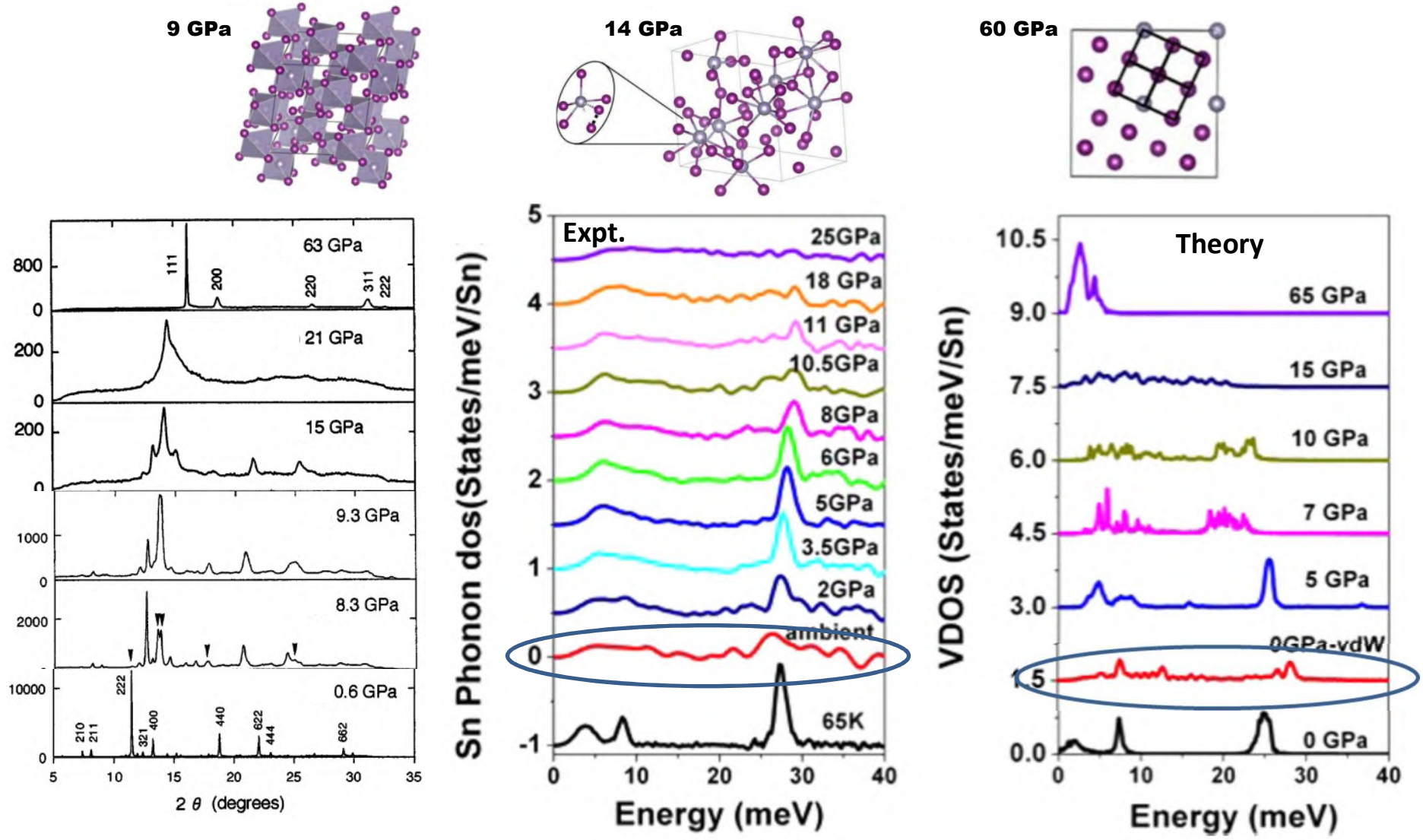
$$S(\mathbf{k},\omega) = \int_0^{\infty} dt \exp(i\omega t) F(\mathbf{k},t),$$

where

$$F(\mathbf{k},t) = \left\langle \sum_i b_i \exp - [i\mathbf{k}\cdot\mathbf{R}_i(t)] \sum_j b_j \exp[i\mathbf{k}\cdot\mathbf{R}_j(0)] \right\rangle$$

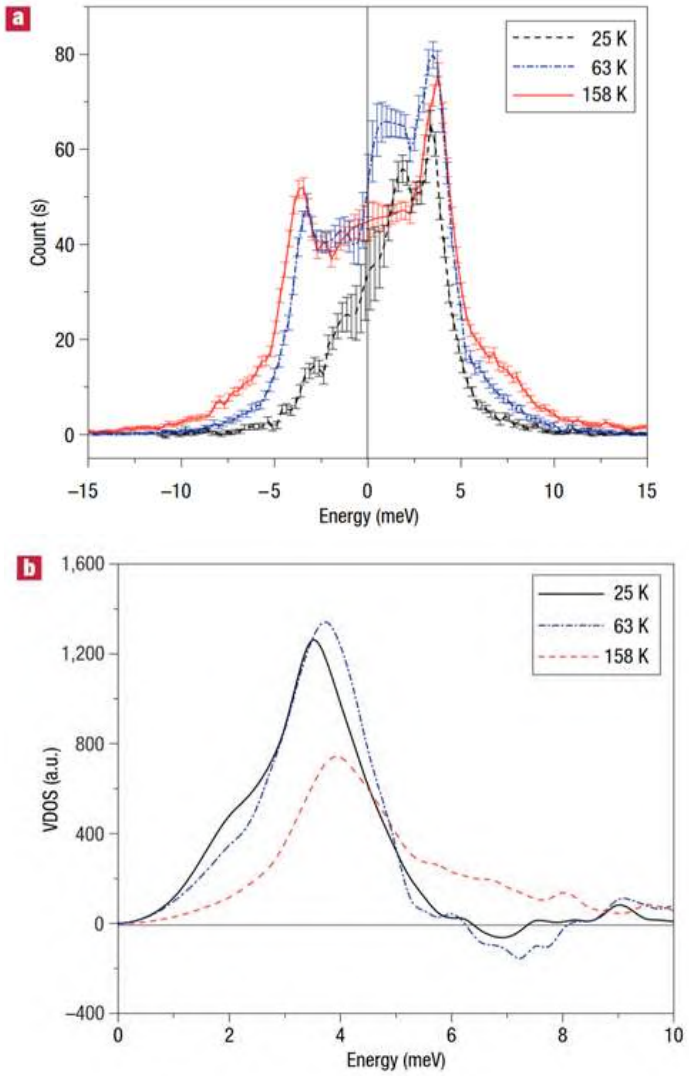
J.S. Tse and M.L. Klein *and* I.R. McDonald, *J. Chem. Phys*,. 81, 6124 (1984)

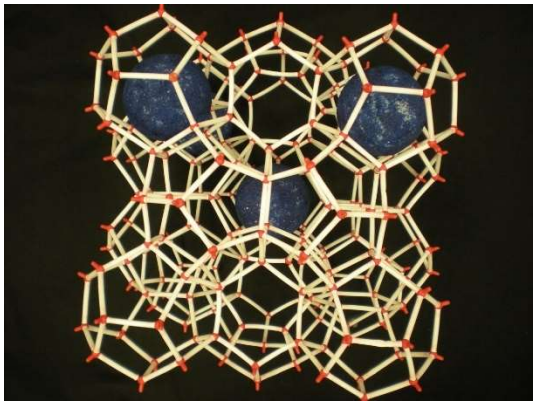
SnI_4 – effect of temperature

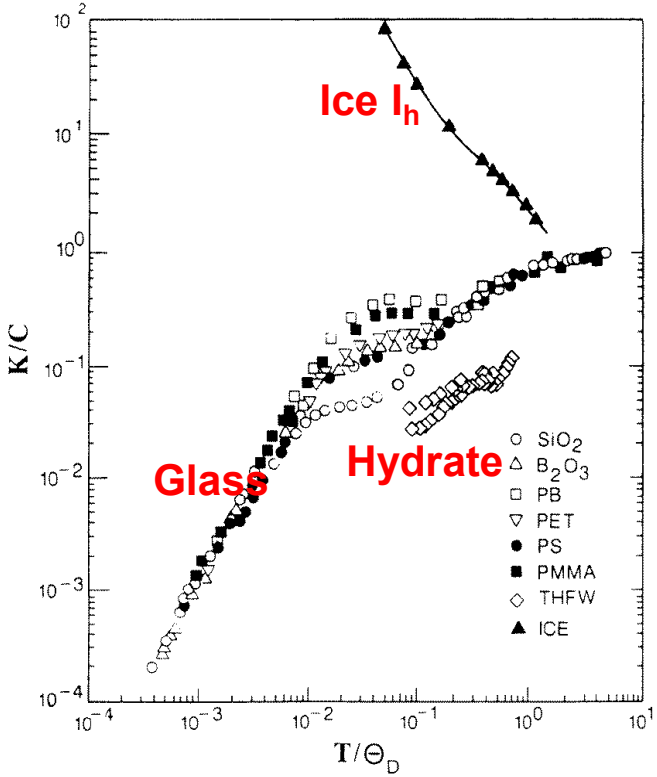


H. Liu, J. S. Tse, M. Y. Hu, W. Bi, J. Zhao, E. E. Alp, M. Pasternak, R. D. Taylor, and J. C. Lashley
J. Chem. Phys., **143**, 164508 (2015);

Anharmonic motions of Kr in the clathrate hydrate







J. S. Tse, D. D. Klug, J. Y. Zhao, W. Sturhahn, E. E. Alp, J. Baumert, C. Gutt, M. R. Johnson and W. Press, *Nature Materials,* 4, 917 - 921 (2005)

Analysis of the VDOS - Anharmonicity

The **Lamb–Mössbauer factor** is the ratio of recoil-free to total nuclear resonant. The Debye–Waller factor describes the attenuation of x-ray scattering or coherent neutron scattering caused by thermal motion.

The Lamb-Mössbauer factor or recoil free fraction is

$$f_{\mathrm{LM}} = \exp\left[-E_R \int \frac{g(E)}{E} \coth\frac{\beta E}{2} dE\right],$$

where $g(E)$ is the density of phonon states at energy E and $\beta = (k_B \mathrm{T})^{-1}$, k_B is the Boltzmann constant, T is the temperature, $E_R = \hbar^2 k^2/2M$ is the recoil energy of a free nucleus. M is the mass of the free nucleus and k is the magnitude of the wave vector of the x-ray photon.

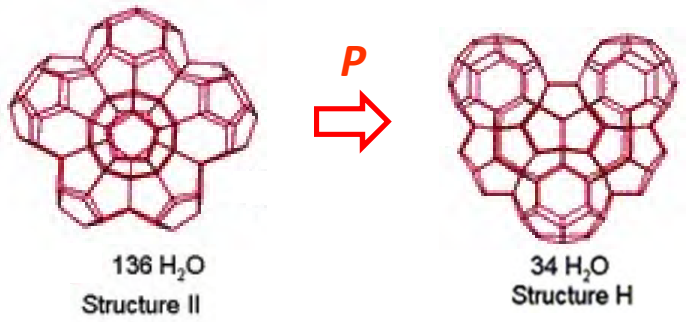
The Lamb-Mössbauer factor describes scattering from Mössbauer nuclei and is defined as

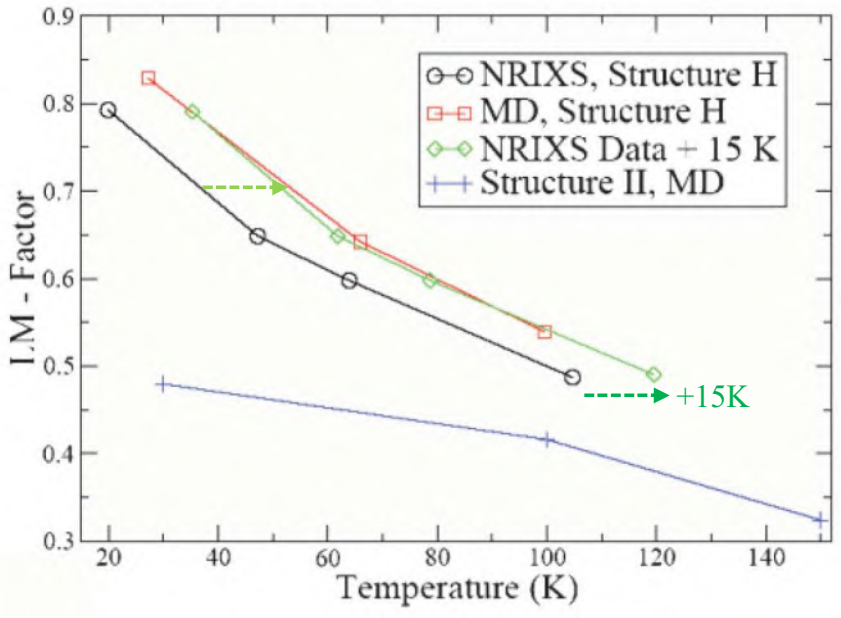
$$f = \langle e^{i\mathbf{k}_f\cdot\mathbf{r}}\rangle\langle e^{-i\mathbf{k}_i\cdot\mathbf{r}}\rangle \approx e^{-\frac{1}{2}[\langle(\mathbf{k}_f\cdot\mathbf{r})\rangle^2+\langle(-\mathbf{k}_i\cdot\mathbf{r})^2\rangle]},$$

$\mathbf{q} = \mathbf{k}_f - \mathbf{k}_i$ is the momentum transfer,

Debye-Waller factor is defined as

$$e^{-2M} = \langle e^{i\mathbf{q}\cdot\mathbf{r}}\rangle^2 \approx e^{-\langle(\mathbf{q}\cdot\mathbf{r})^2\rangle},$$





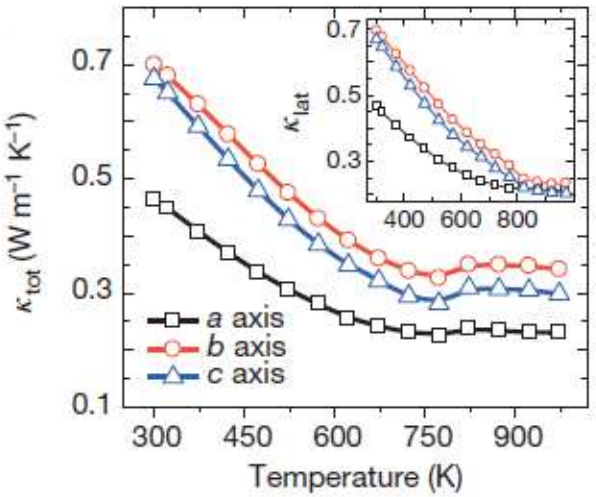
Anharmonicity and Thermal conductivity - SnSe

LETTER

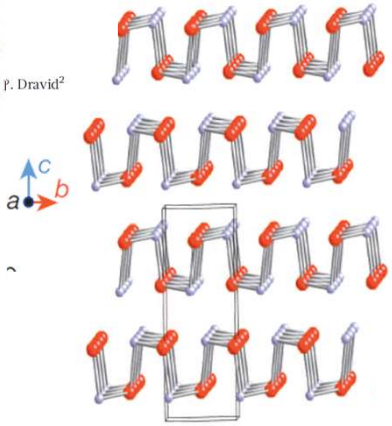
doi:10.1038/nature13184

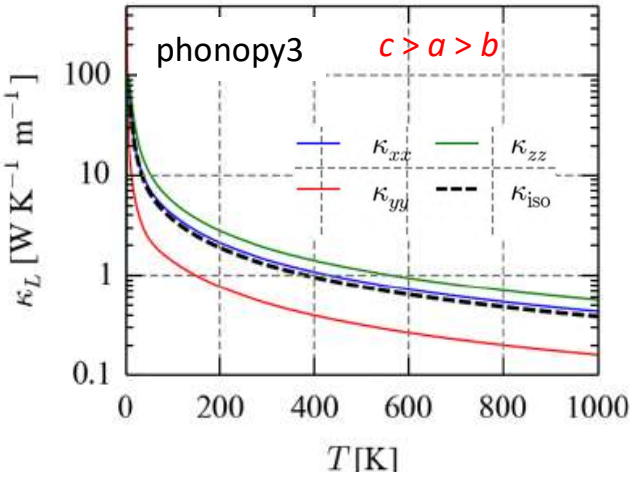
Ultralow thermal conductivity and high thermoelectric figure of merit in SnSe crystals

Li-Dong Zhao[1], Shih-Han Lo[2], Yongsheng Zhang[2], Hui Sun[3], Gangjian Tan[1], Ctirad Uher[3], C. Wolverton[2], Vinayak P. Dravid[2] & Mercouri G. Kanatzidis[1]



Experiment: $b \approx c > a$





PRL **117,** 075502 (2016)

Molecular dynamics:

300 K: $a = 1.27 \pm 0.18$, $b = 1.51 \pm 0.23$, $c = 1.53 \pm 0.24$

600 K: $a = 0.56 \pm 0.08$, $b = 0.74 \pm 0.10$, $c = 0.76 \pm 0.11$

800 K: $a = 0.45 \pm 0.05$, $b = 0.57 \pm 0.07$, $c = 0.56 \pm 0.08$

$b \approx c > a$

Analysis of the momentum of the dynamics structure factor

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

$$f = \langle e^{i\mathbf{k}_f\cdot\mathbf{r}}\rangle\langle e^{-i\mathbf{k}_i\cdot\mathbf{r}}\rangle \approx e^{-\frac{1}{2}[\langle(\mathbf{k}_f\cdot\mathbf{r})\rangle^2+\langle(-\mathbf{k}_i\cdot\mathbf{r})^2\rangle]}$$

$$S(\mathbf{k},E) \equiv \frac{1}{2\pi\hbar}\int dt d\mathbf{r}\, e^{i(\mathbf{kr}-\frac{E}{\hbar}t)} G_a(\mathbf{r},t)$$

$$f_{DW} \propto e^{-2M} = \langle e^{i\mathbf{q}\cdot\mathbf{r}}\rangle^2 \approx e^{-\langle(\mathbf{q}\cdot\mathbf{r})^2\rangle}$$

$$R_l(\mathbf{k}) \equiv \int_{-\infty}^{+\infty} (E-E_R)^l\, S(\mathbf{k},E)\, dE$$

$$\frac{\partial^2 V}{\partial z^2} = K_{\hat{\mathbf{k}}} + A_{\hat{\mathbf{k}}} z + \frac{B_{\hat{\mathbf{k}}}}{2} z^2$$

$$R_3 = \frac{\hbar^2 E_R}{\tilde{m}}\left(K_{\hat{\mathbf{k}}} + \frac{B_{\hat{\mathbf{k}}}}{2}\langle z^2\rangle\right)$$

$$f(\mathbf{k},T) = e^{-k^2\langle z^2(T)\rangle}$$

$$R_0 = 1\,,$$

$$R_1 = 0\,,$$

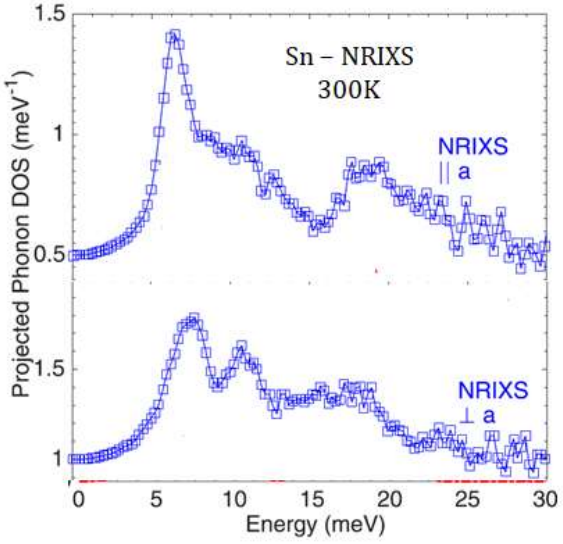
$$R_2 = 4\, E_R\, T_{\hat{\mathbf{k}}}\,,$$

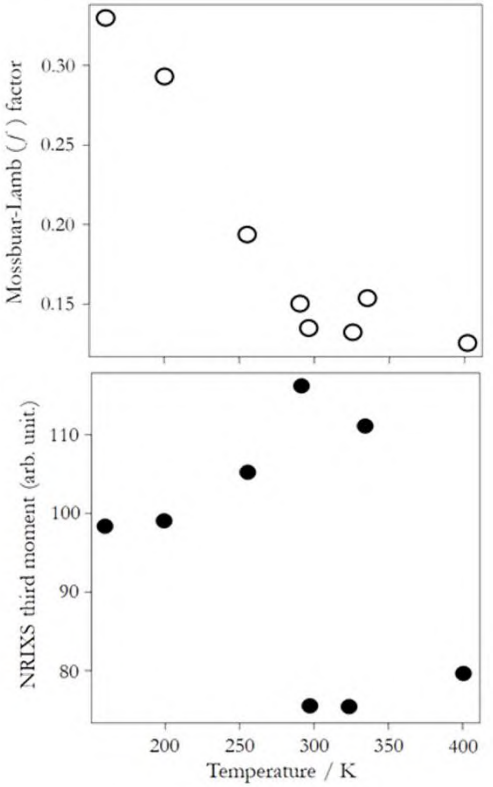
$$R_3 = \frac{\hbar^2 E_R}{\tilde{m}}\left\langle \frac{\partial^2 V}{\partial z^2}\right\rangle$$

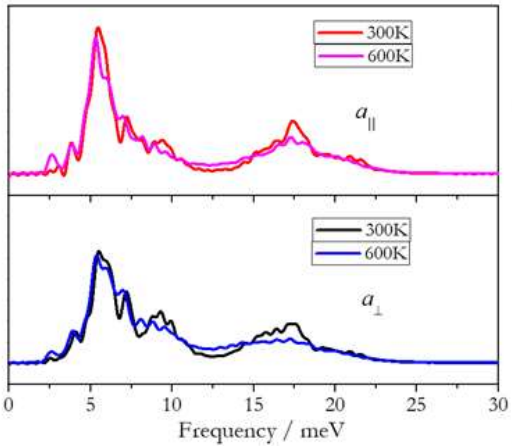
$$K_{\hat{\mathbf{k}}} = \left.\frac{\partial^2 V}{\partial z^2}\right|_{\text{eq}}$$

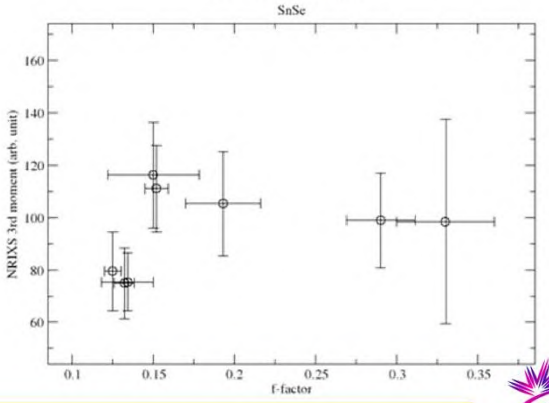
$$A_{\hat{\mathbf{k}}} = \left.\frac{\partial^3 V}{\partial z^3}\right|_{\text{eq}}$$

$$B_{\hat{\mathbf{k}}} = \left.\frac{\partial^4 V}{\partial z^4}\right|_{\text{eq}}$$



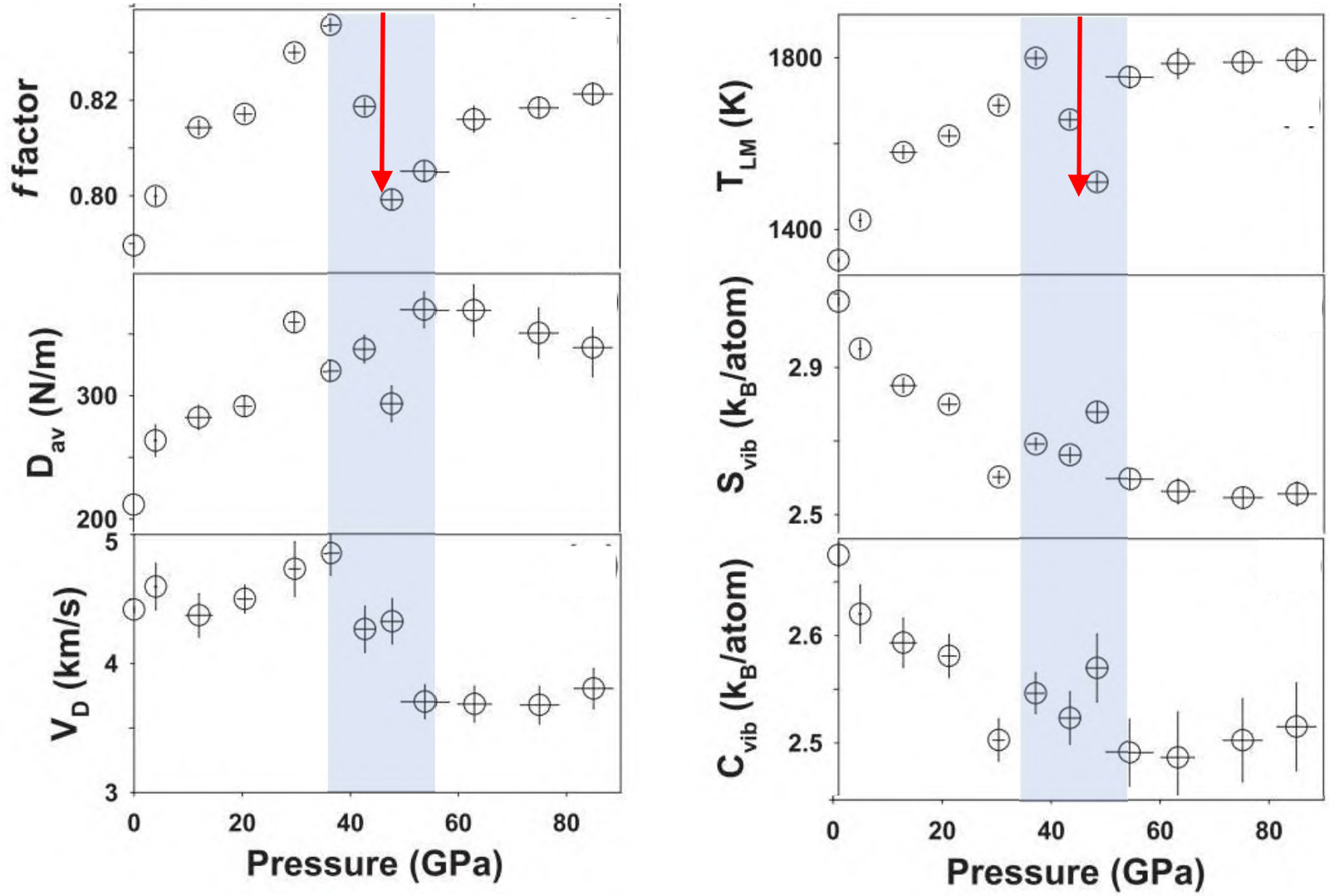






Soft mode and anharmonicity at structural phase transition

Hematite Fe_2O_3 Corundum (Al_2O_3) → Rh_2O_3



Hyperfine Interactions

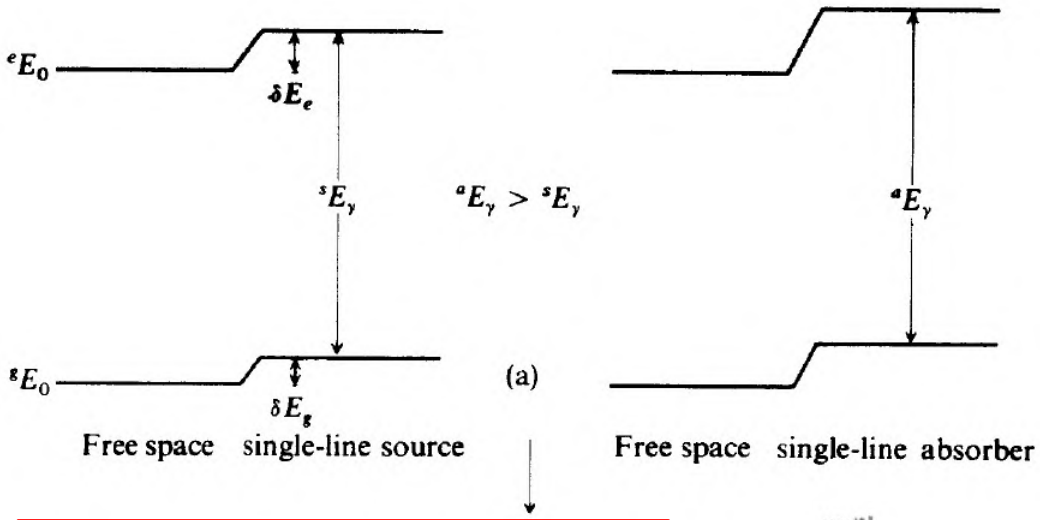
Hyperfine interactions are interactions between the nucleus and the electromagnetic fields produced by the surrounding electrons. In a solid, we need to include the *electromagnetic* fields produced by the neighboring atoms or ions.

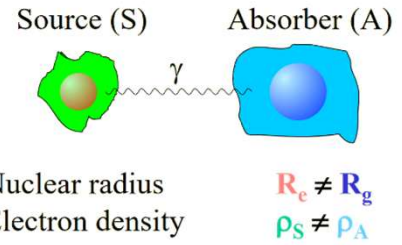
In the Mossbauer effect, there are mainly three types of hyperfine interactions:

1. Electric monopole interaction, which causes isomer shift, a shift of the entire resonance spectrum.
2. Electric quadrupole interaction, which causes quadrupole splitting of the spectral lines.
3. Magnetic dipole interaction, which causes Zeeman splitting of the spectral lines – magnetic hyperfine splitting.

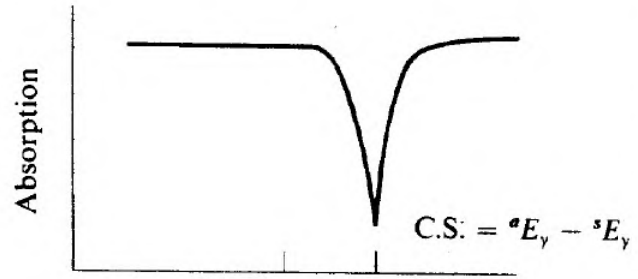
Isomer shift

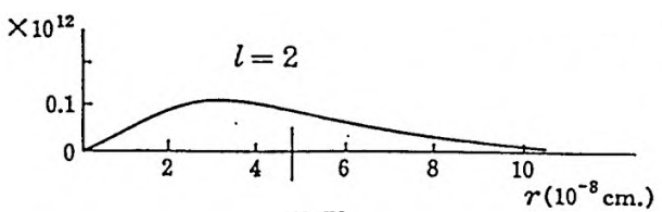
The Mössbauer isomeric shift is the shift observed when one compares two different nuclear isomeric states in two different physical, chemical or biological environments (e.g. between the source and absorber). The magnitude of the difference is dependence on the *total s*-electron density at the nucleus, $|\psi_s(0)|^2$.

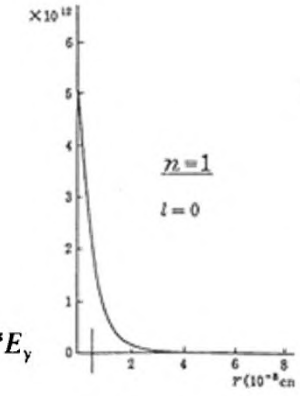


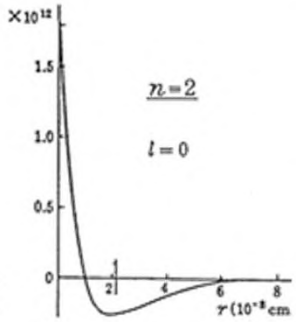


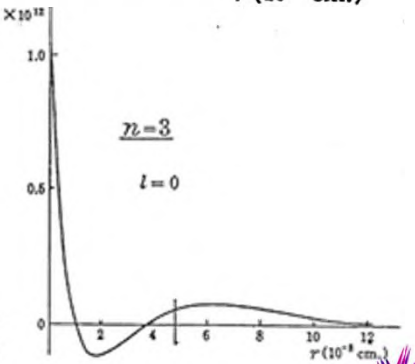
$$\text{I.S} = K\left(R_e^2 - R_g^2\right)\left(|\psi_s(0)|_a^2 - |\psi_s(0)|_s^2\right)$$





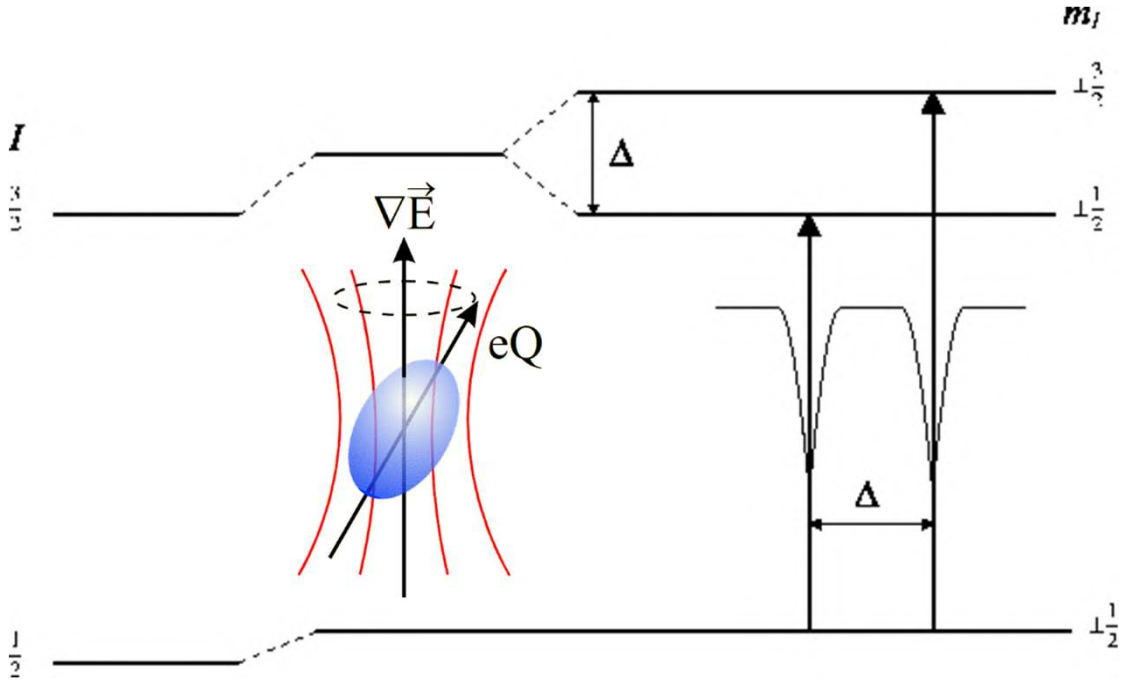






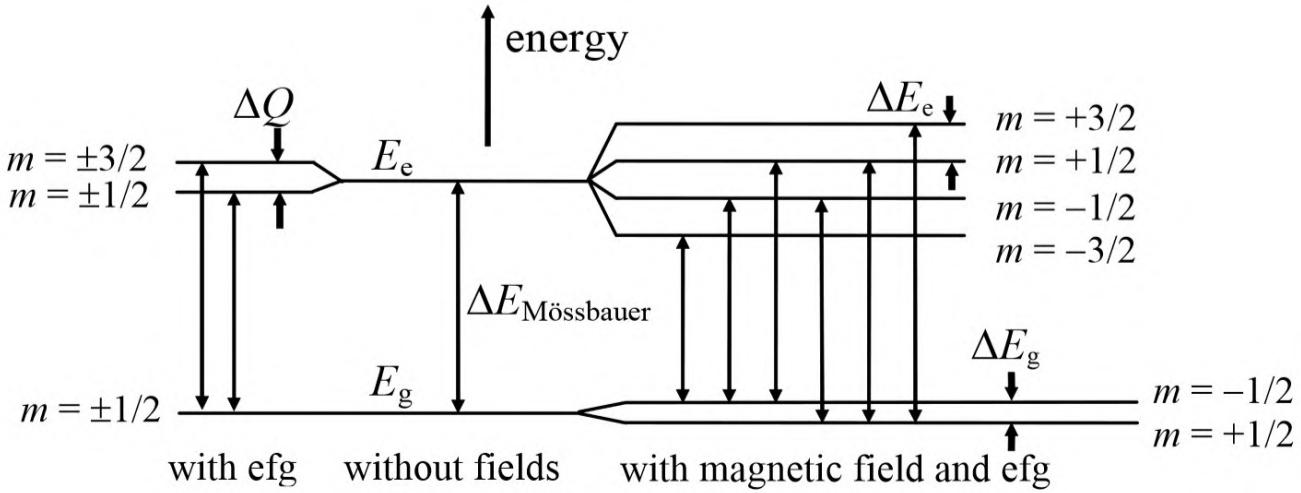
Quadrupole splitting

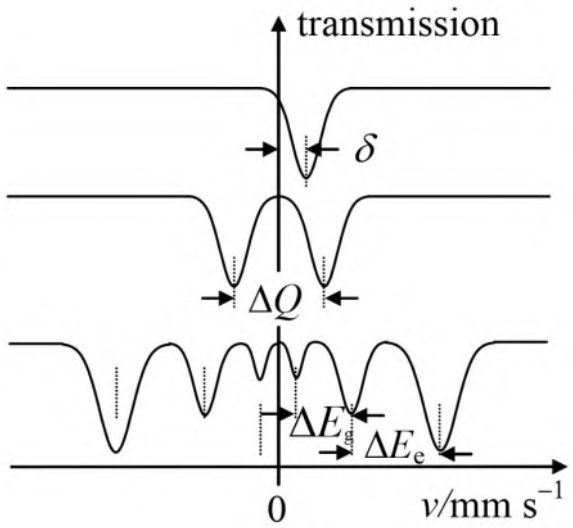
A nucleus that has a spin quantum number $I > ½$ has a non-spherical charge distribution Q. An asymmetric charge distribution around the nucleus causes an asymmetric electric field at the nucleus, characterised by a tensor quantity called the Electric Field Gradient (EFG), ∇E. The electric quadrupole interaction between these two quantities gives rise to a splitting in the nuclear energy levels.

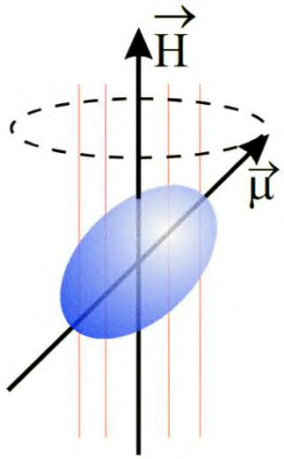


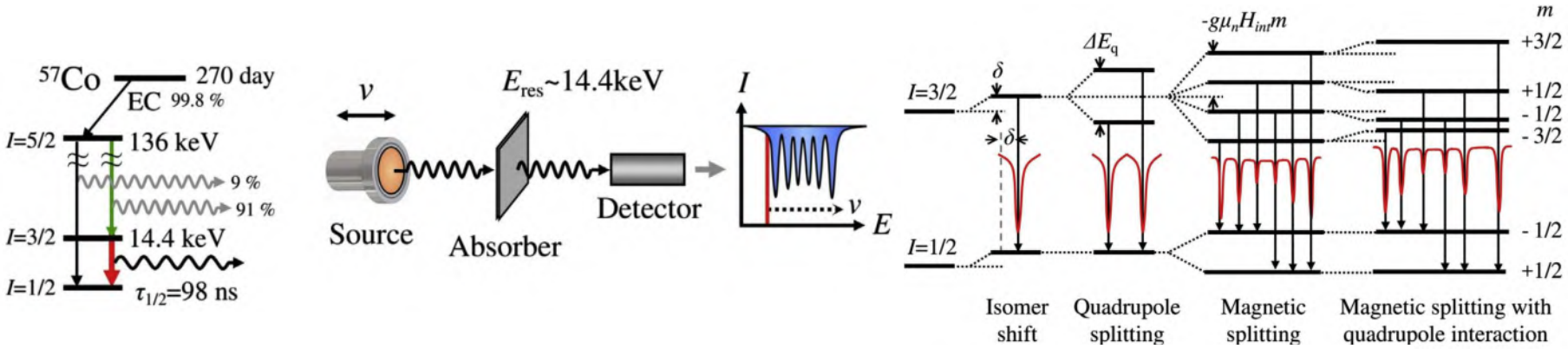
Magnetic splitting

A magnetic splitting occurs through the interaction between the nuclear dipole moment and the magnetic field.

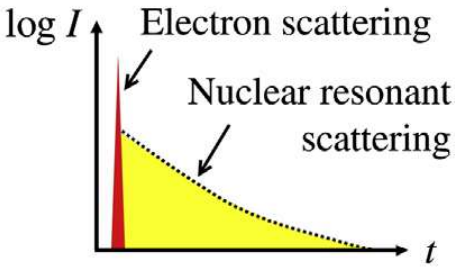




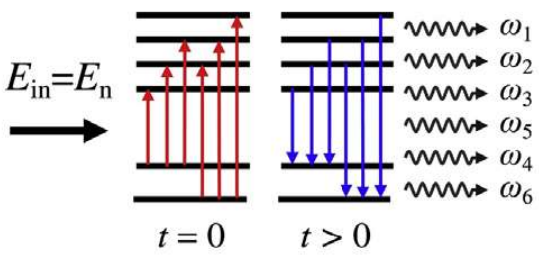


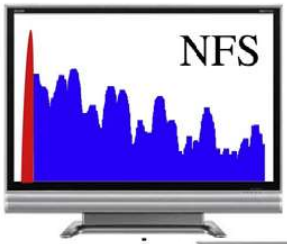


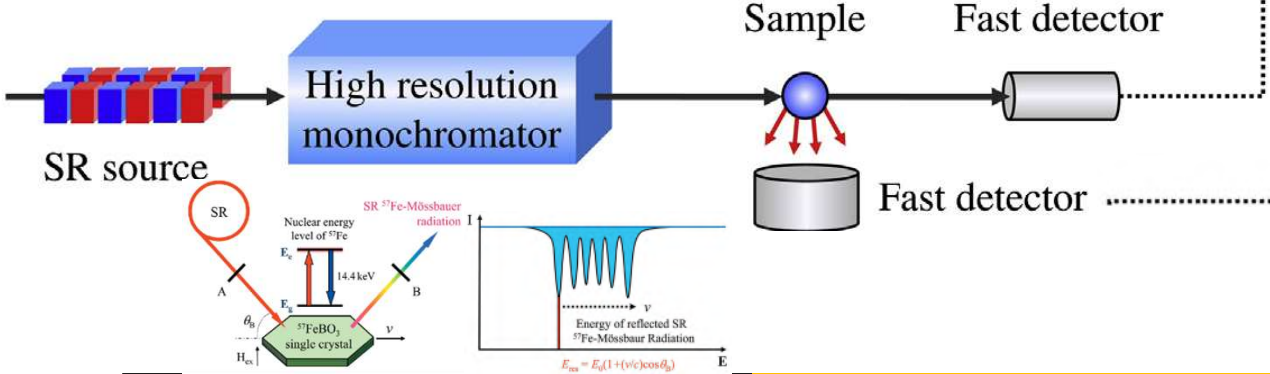
Scattering Intensity vs Time



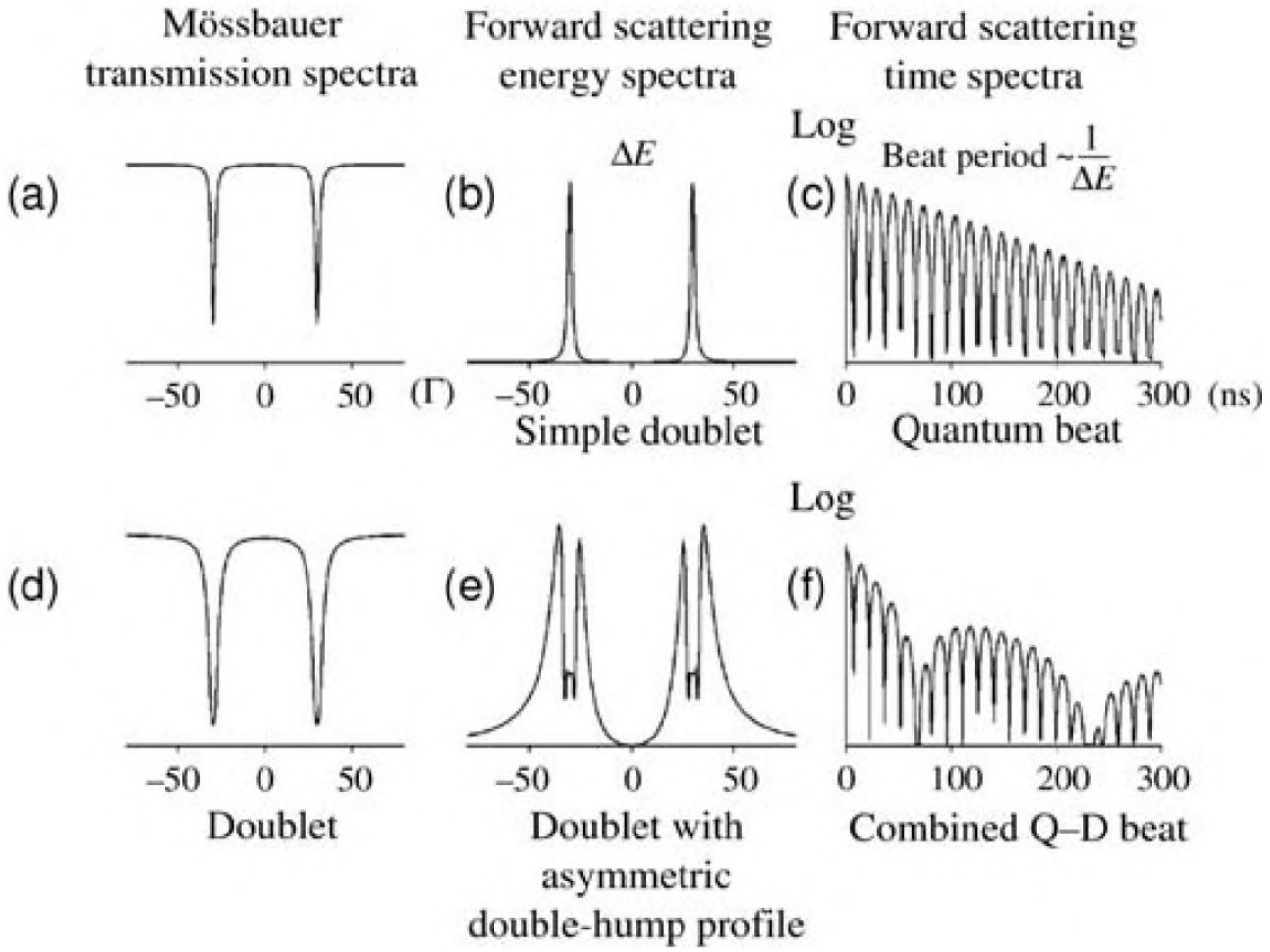
Nuclear Forward Scattering





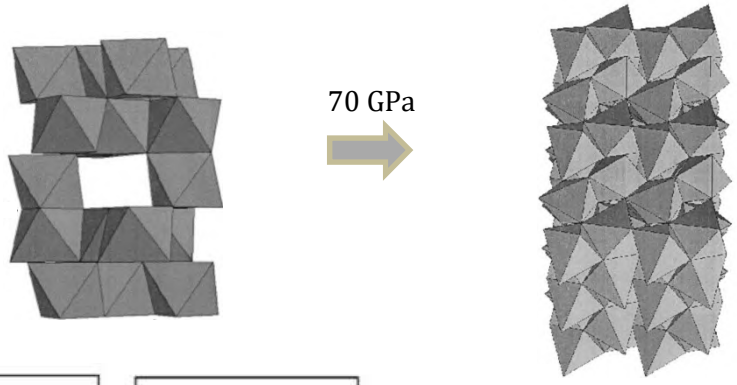


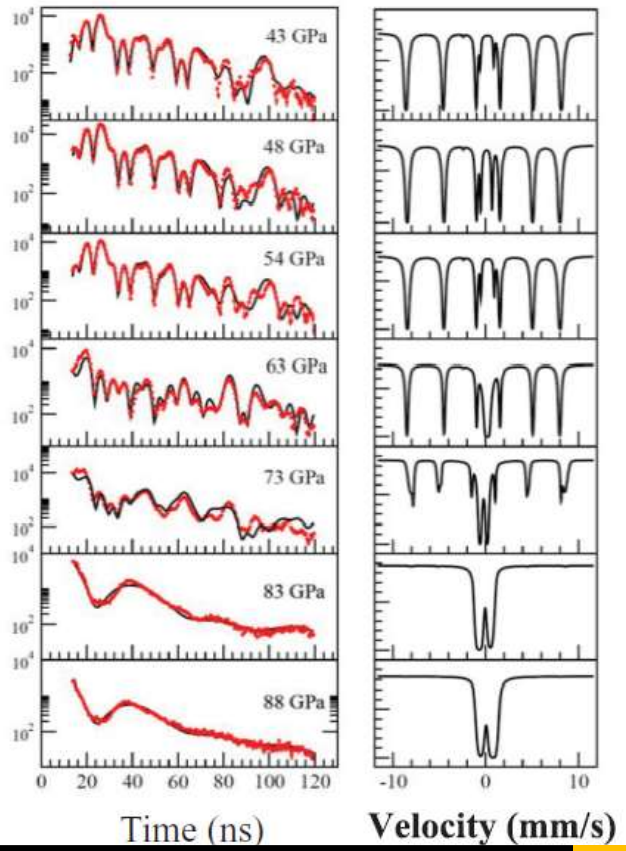
Synchrotron based Experimental techniques

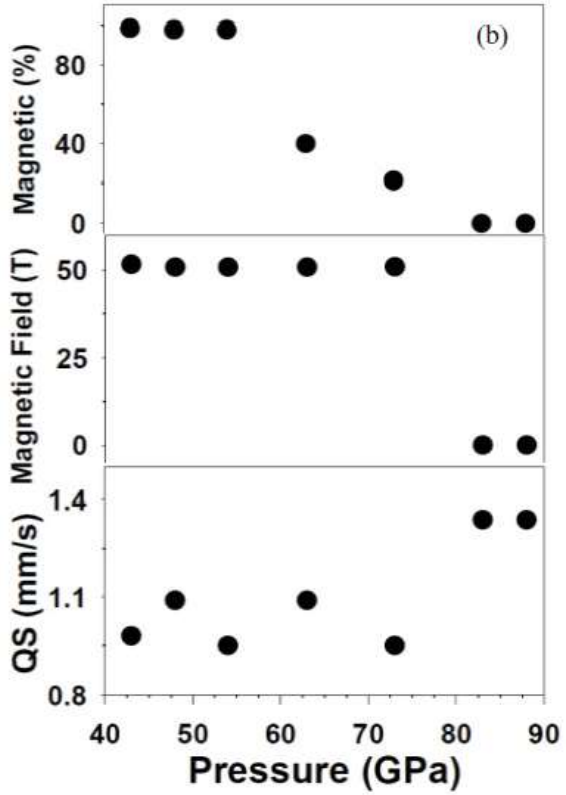


Calculated Mossbauer transmission spectra (a), nuclear forward scattering spectra in energy (b) and in time (c) domain for the case of a quadrupole doublet in a 0.2 mm thick stainless steel foil 100% enriched in ^{57}Fe. (d), (e), and (f) are the corresponding spectra for a 3.0mmthick stainless steel foil 100% enriched in ^{57}Fe.

HS → LS trtansiytion in Hematite Fe_2O_3

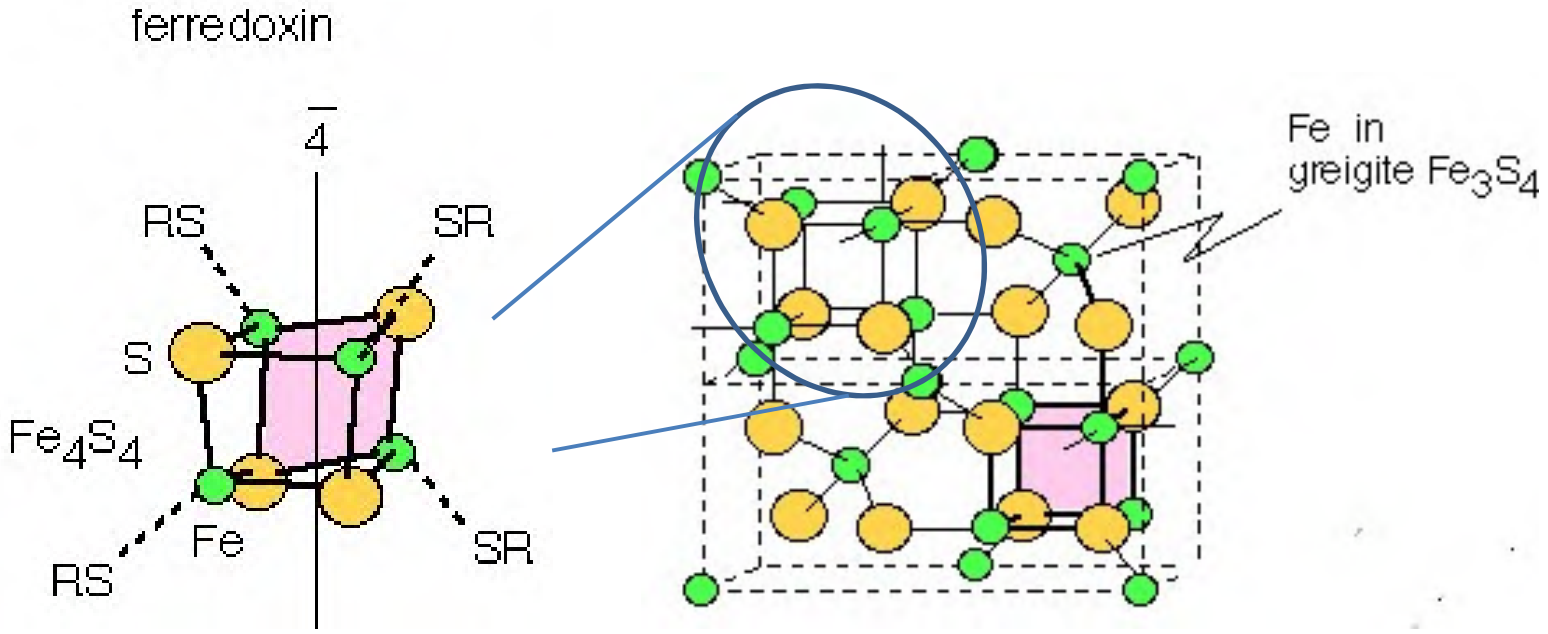


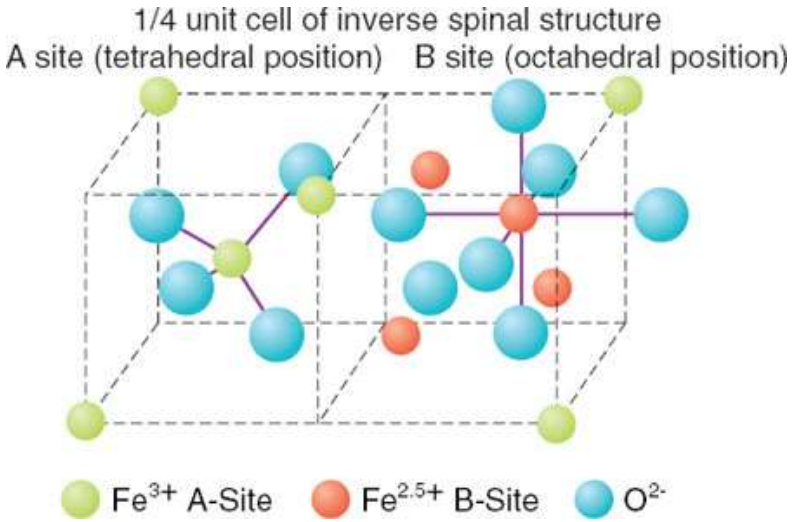




J.F. Lin, J.S. Tse, et.al., *Phys. Rev*. B 84, 064424 (2011).

Fe_3S_4 - the ubiquitous $[Fe_4S_4]$ cube





Inverse spinels ($B(AB)O_4$):
The A^{II} ions occupy the octahedral voids, whereas half of B^{III} ions occupy the tetrahedral voids.

It can be represented $(B^{III})^{tet}(A^{II}B^{III})^{oct}O_4$

$$(Fe^{3+}_{T}(Fe^{2+}_{O}Fe^{3+}_{O})S^{2-}_{4})$$

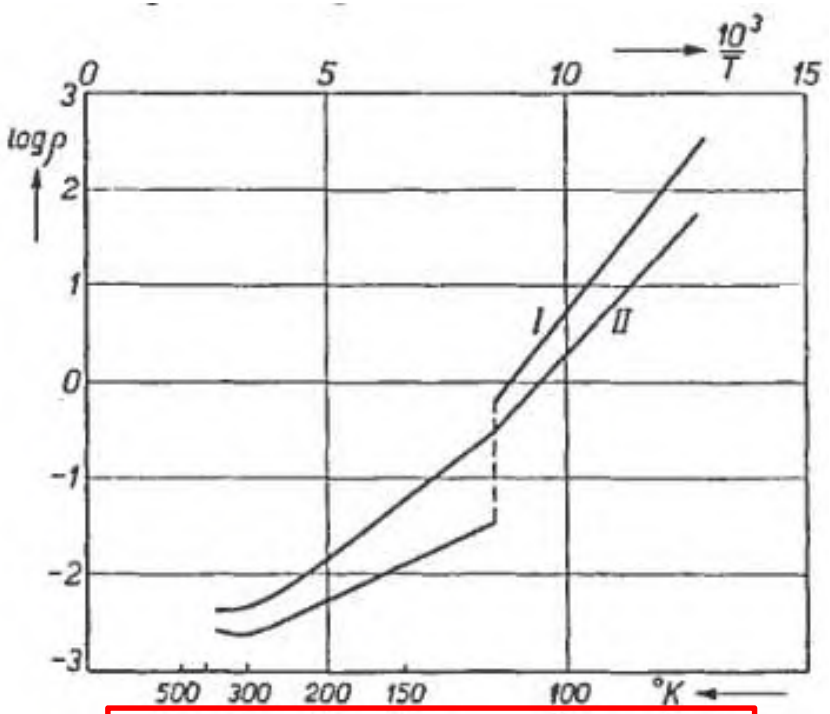
Is there a Verwey transition in gregeite?

No. 3642, AUGUST 19, 1939 NATURE 327

Electronic Conduction of Magnetite (Fe_3O_4) and its Transition Point at Low Temperatures

E. J. W. VERWEY.

Natuurkundig Laboratorium,
N. V. Philips' Gloeilampenfabrieken,
Eindhoven.



I with $FeO : Fe_2O_3 = 1 : 1{\cdot}025$,
II with $FeO : Fe_2O_3 = 1 : 1{\cdot}08$.

SCIENTIFIC REPORTS

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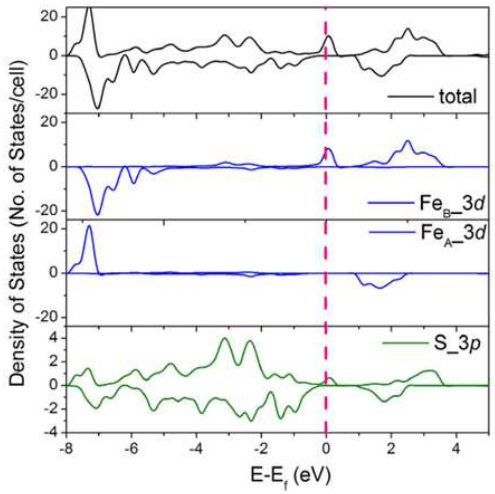
Electronic structures of greigite (Fe_3S_4): A hybrid functional study and prediction for a Verwey transition

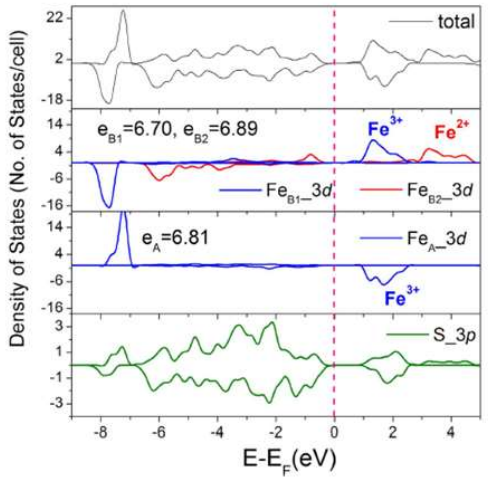
Min Wu[1,2,3], John S Tse[2] & Yuanming Pan[3]

total energy difference of 0.377 eV per Fe_3S_4 formula unit

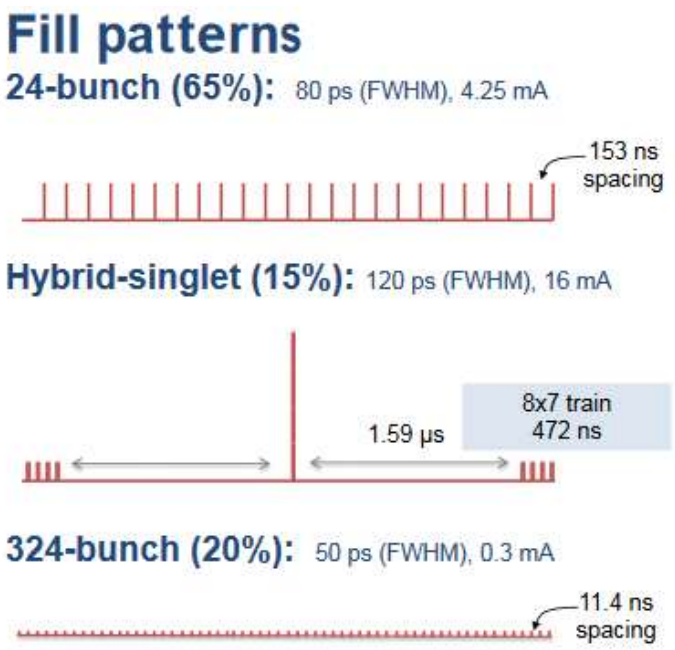
$Fe_A^{3+}(Fe_B^{2.5+}, Fe_B^{2.5+})S^{2-}_4$ $(Fe^{3+})_A(Fe^{2+}{}_B Fe^{3+}{}_B)S^{2-}_4$

cubic $a = 10.109$ Å $a = 7.120$ Å, $b = 7.090$ Å, $c = 10.080$ Å and $\beta = 90.010°$

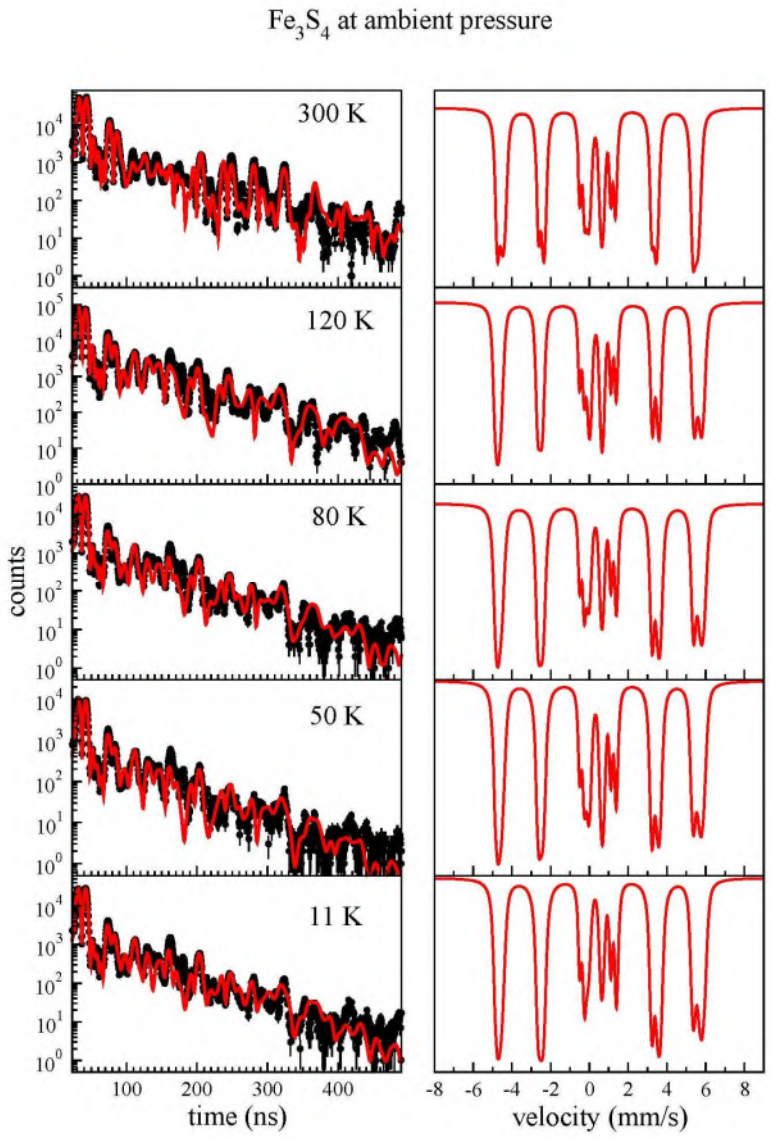




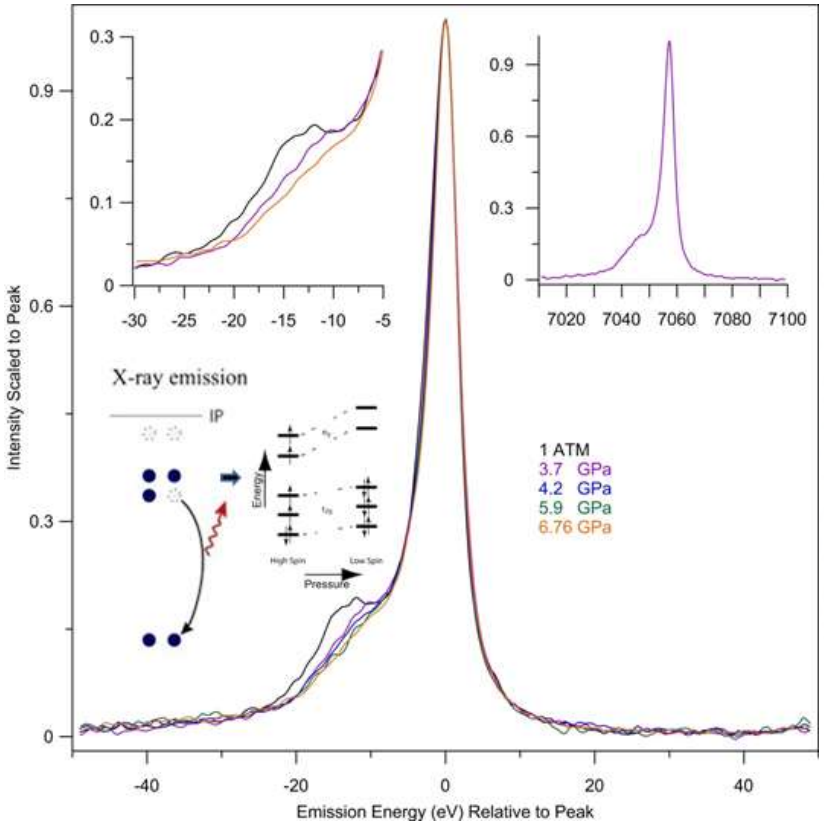
High resolution Mossbauer spectra

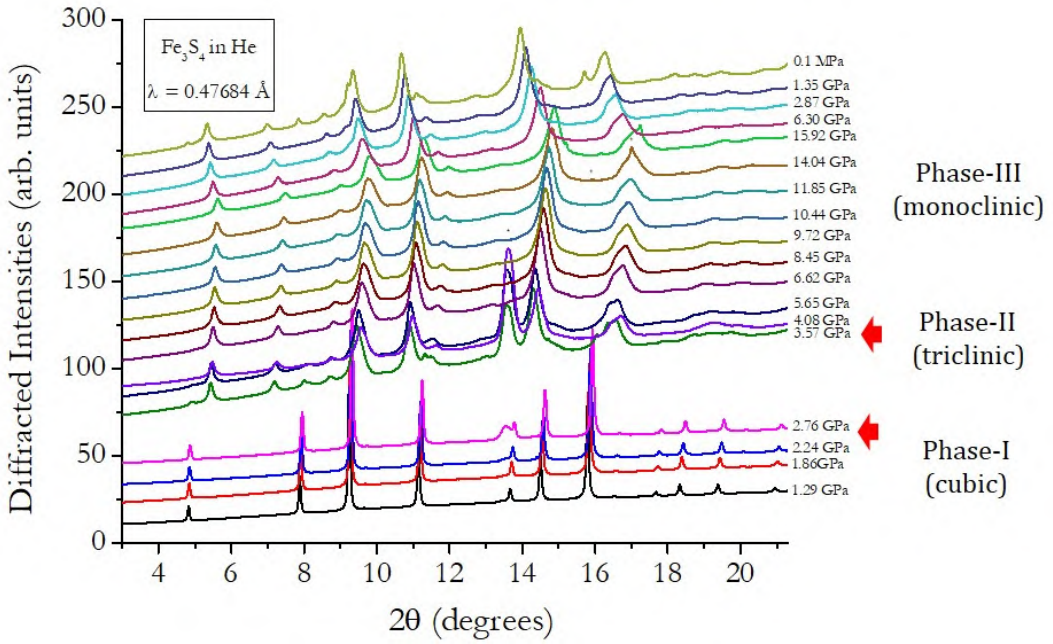


A single X-ray pulse followed 1.594 µs later by a 493 ns-long segmented pulse-train. This pattern repeats with a frequency of 271.554 kHz (period of 3.6825 µs)

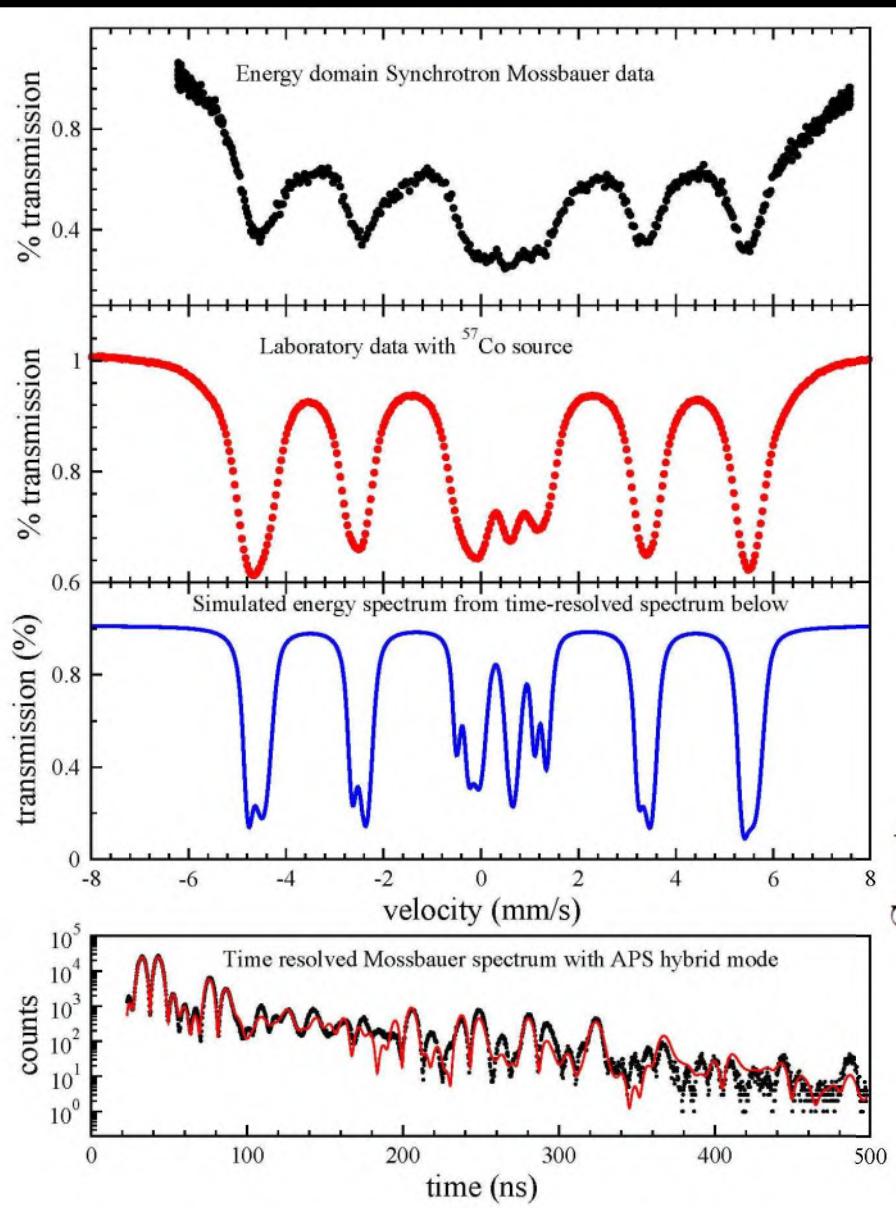


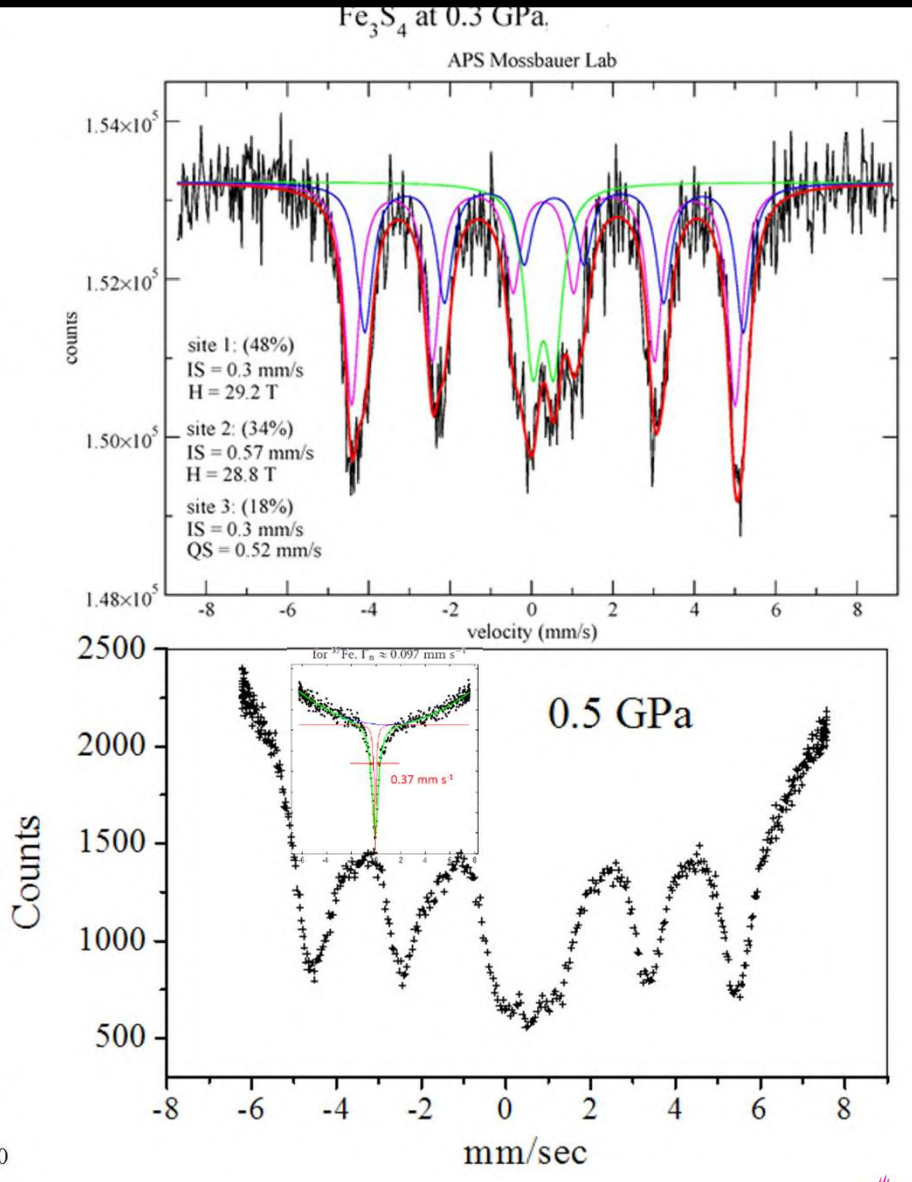
High to low spin and structural transitions at high pressure



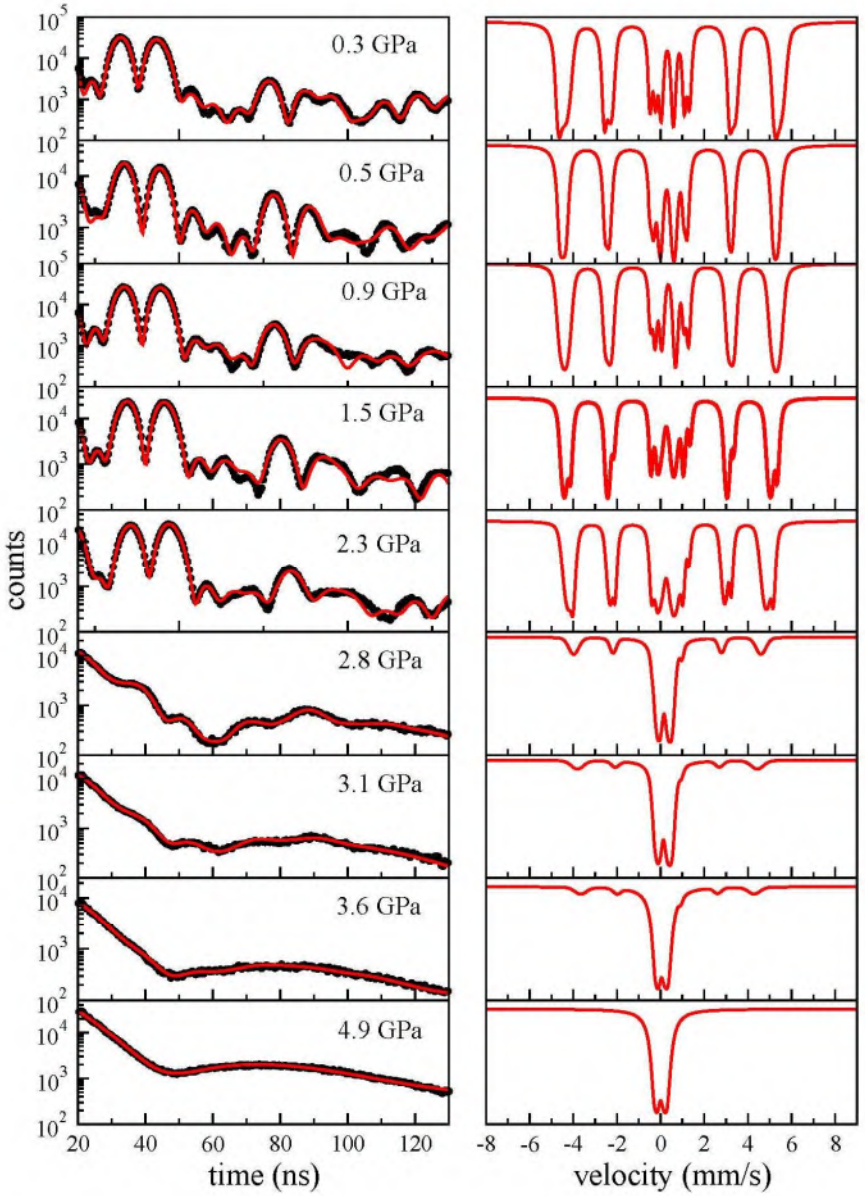


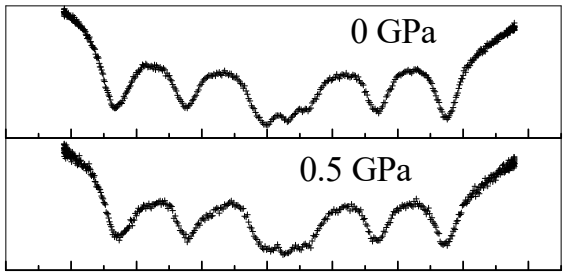
Comparison of Energy and Time domain Mossbauer spectra

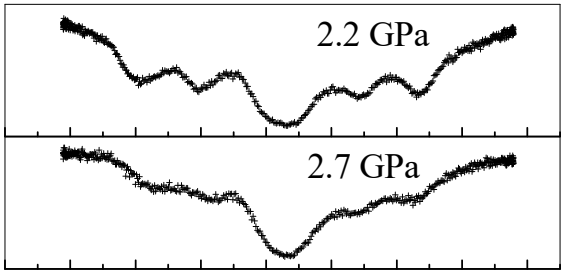


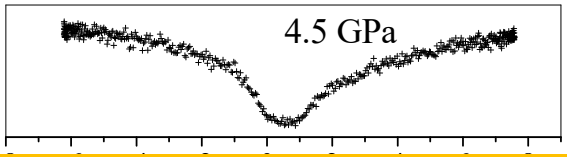


High pressure Energy and Time domain Mossbauer spectra

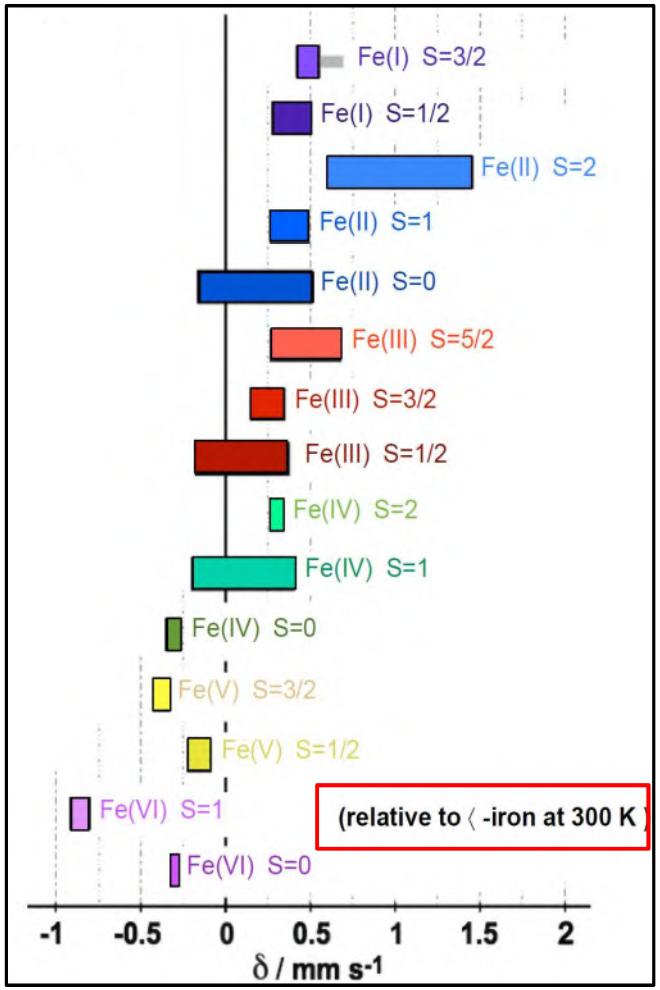








Isomer shift and Oxidation state of Fe and Fe-oxides under high pressure



$$IS_i = \alpha\{[\rho_e(\boldsymbol{r}_e)]_{\boldsymbol{r}_e \to \boldsymbol{R}_i} - [\rho_e(\boldsymbol{r}_e)]_{\boldsymbol{r}_e \to \boldsymbol{R}_{src}}\}$$

Isomer shift

electron density at nucleus — *properties of ^{57}Fe nucleus*

$$\delta = (|\psi_{sample}(0)|^2 - |\psi_{source}(0)|^2) \times 4/5\ \pi\ Ze^2\ R^2 \times (\Delta R/R)$$

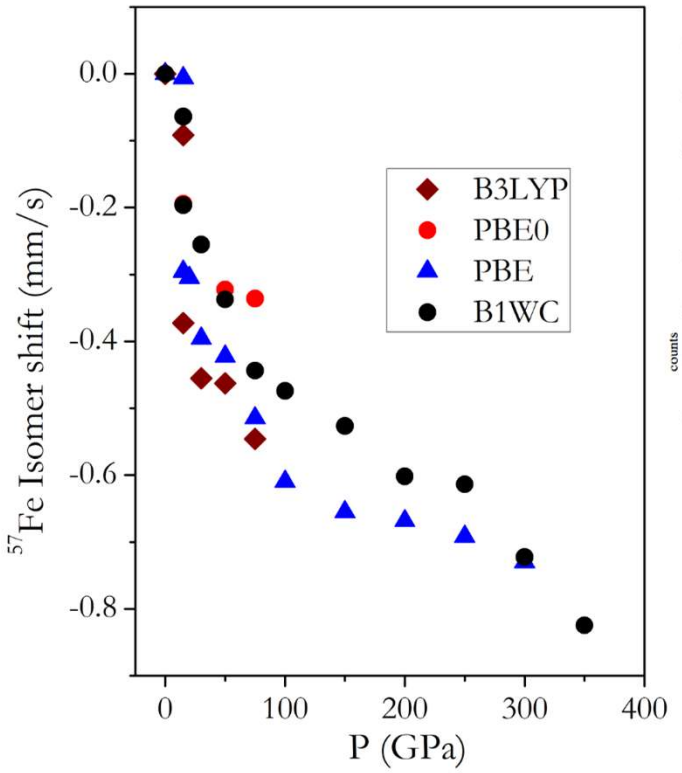
- $\Delta R/R$ is the change of radius in ground and excited state (negative for ^{57}Fe)
- $|\psi(0)|^2$ is the probability to find an electron at the ^{57}Fe nucleus
- only s-electrons have non-zero probability to be at nucleus
- d-electrons affect s-electron density by shielding

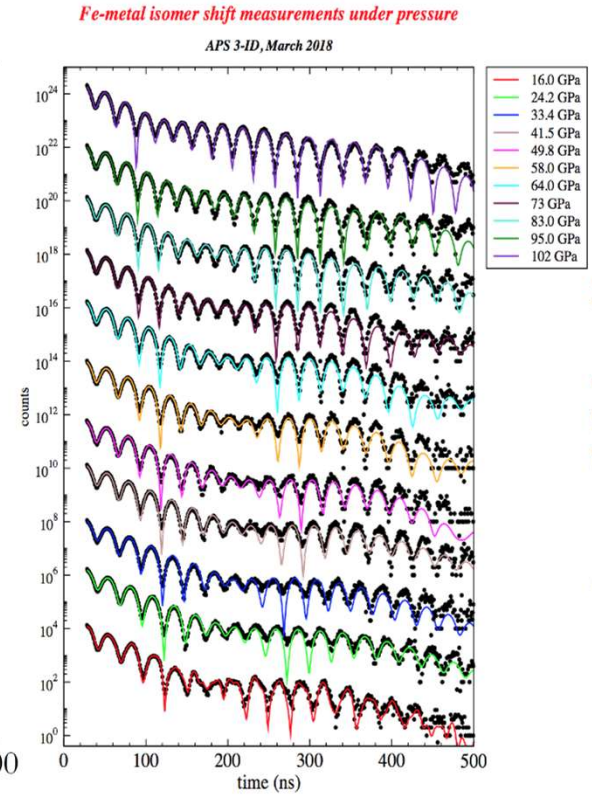
Gütlich, Bill, Trautwein, *Mössbauer Spectroscopy and Transition Metal Chemistry*, Springer 2011)

Isomer shift of pure Fe under high pressure

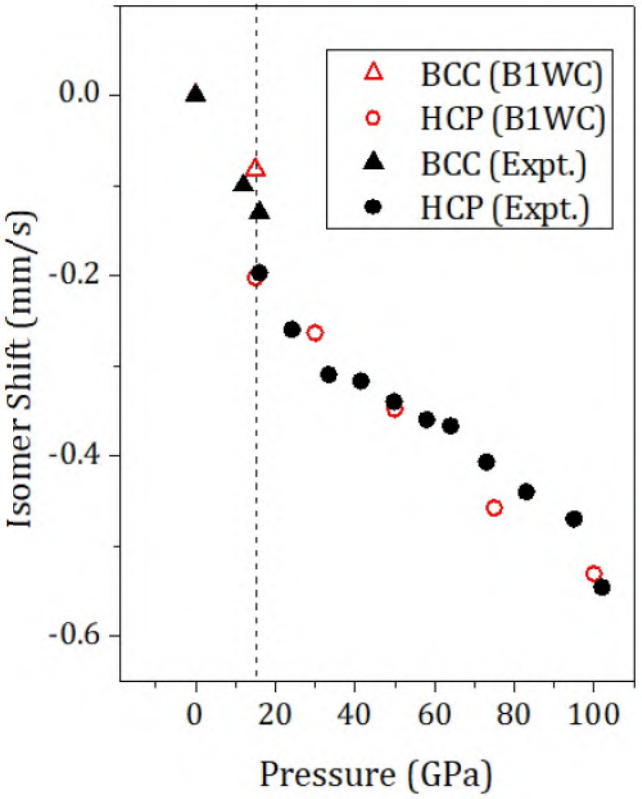
Fe localized basis set (uncontracted):
$(18s4sp10p6d3f1g)$

Theory





Theory *vs.* Expt.

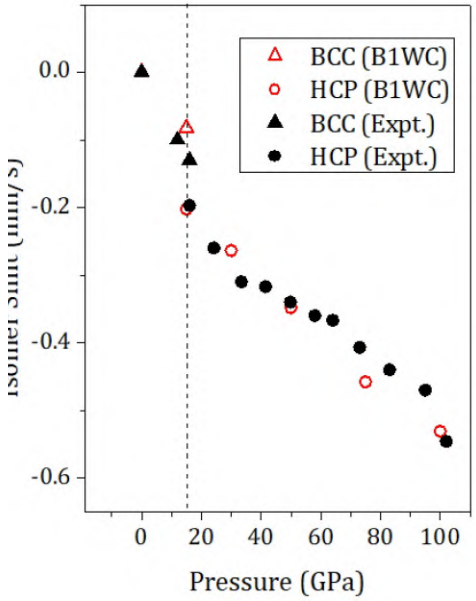


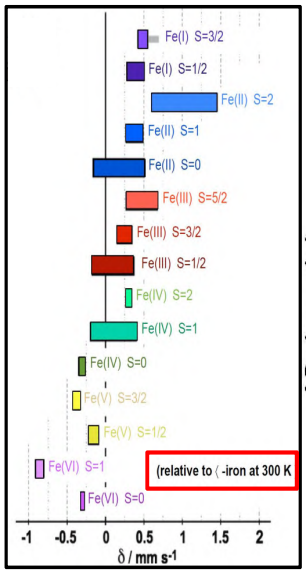
Isomer shift of Fe oxides under high pressure

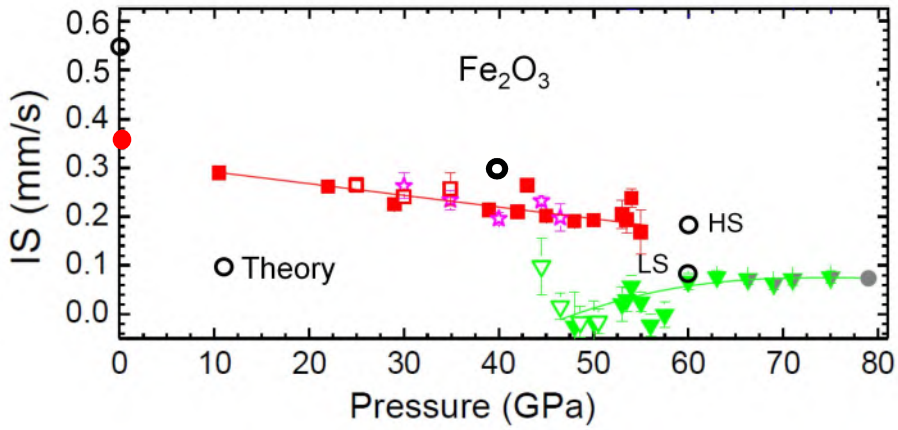
FeO_2 High Spin (B1WC)

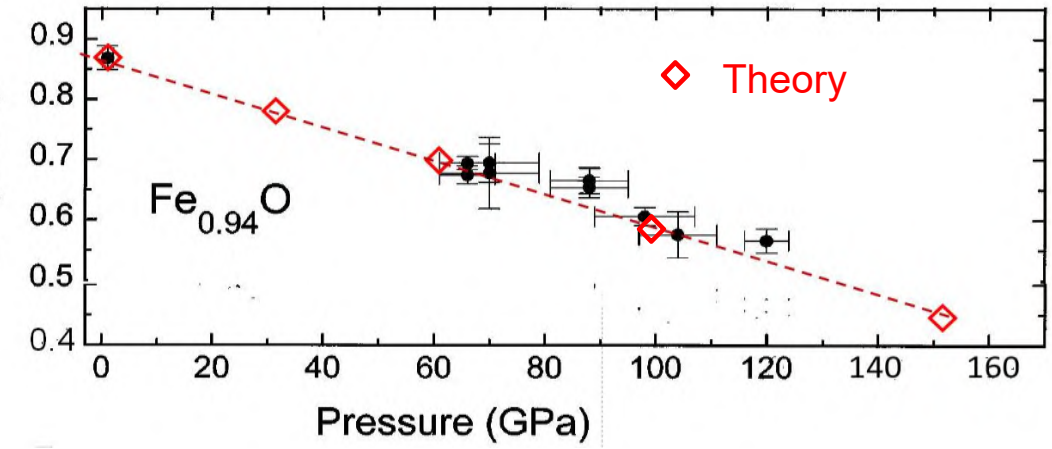
Fe : (18s4sp10p6d3f1g)/[3s4sp2p3d3f1g]
O : (8s6sp2d1f)/[1s3sp2d1f]

60 GPa : -0.17 mm/s
80 GPa : -0.11 mm/s









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