

Introduction to Lattice Dynamics

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The Dulong Pettit's Law

The **heat capacity** of a material is used to indicate that it takes different amount of heat to raise the temperature of different materials by a given amount.

Dulong and Petit's Law was discovered by these experimenters in 1819. The law states that for most elements the specific heat multiplied by the **atomic weight gives a constant number**.

Neumann and Regnault found that all compound bodies of similar **atomic** composition follow the same law. At **room temperature**, the difference for solids is about 5%.

<u>Element</u>	<u>Specific Heat</u>	<u>Atomic Weight</u>	<u>Atomic Heat</u>
Zinc	.0955	65	25.95
Iron	.1138	56	26.64
Tin	.0562	118	27.72
Copper	.0951	63.5	25.24
Lead	.0314	207	27.17
Silver	.0570	108	25.73
Gold	.0324	196	26.54

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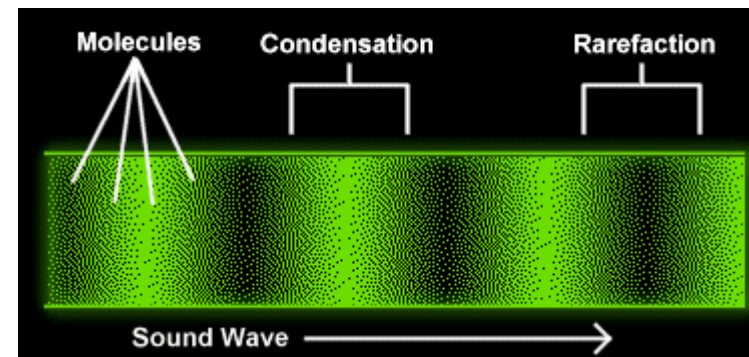
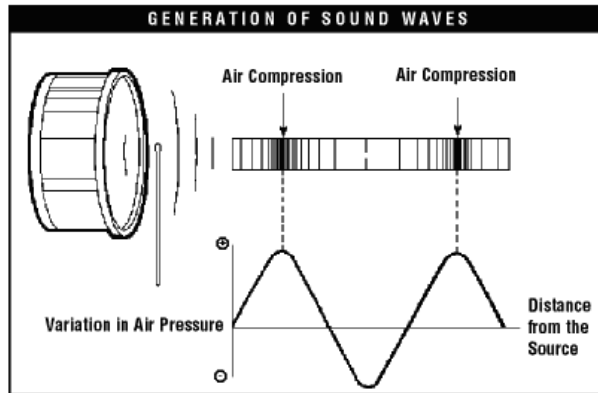
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Heat is a form of ENERGY!!

Sound and vibration

Where the energy gone?

How do we know there are vibrations in matters (gas, liquid and solid)?



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

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

Heat Capacity

Heat capacity

is a measure of how much materials can store up heat as they change temperature.

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, about six calories per gram atom.

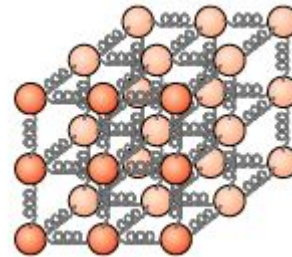
Where the heat had gone? Or
How heat can be stored in a solid ?

The molar specific heat of a solid at high temperatures can be explained using the equipartition theorem. The energy associated with vibrational motion (*e.g.* in the x direction)

$$U = \frac{1}{2}mv^2 + \frac{1}{2}k\Delta x^2$$

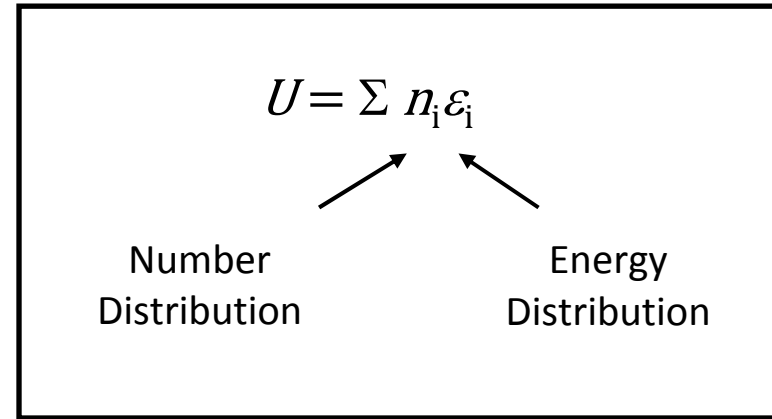
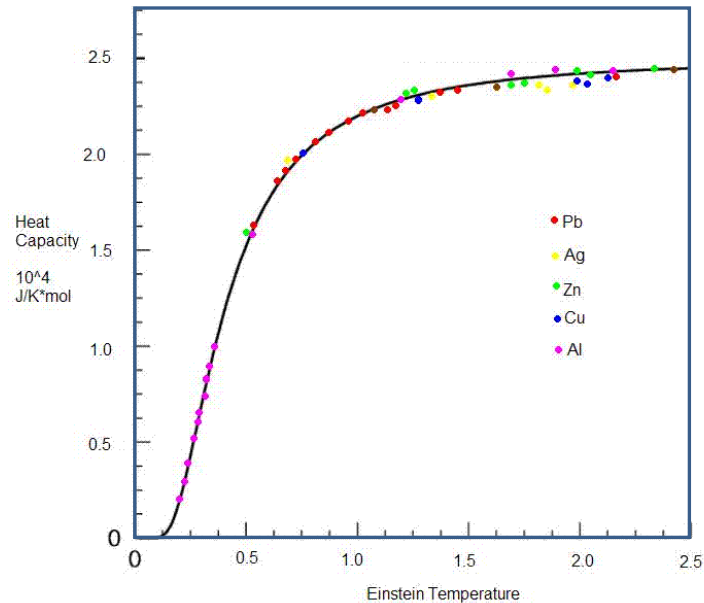
this corresponds to an average vibrational energy of $6(1/2 k_B T) = 3k_B T$ per atom. Therefore, the total internal energy (E) of a solid consisting of N atoms is $3Nk_B T = 3nRT$. The molar specific heat of a solid at constant volume is

$$C_v = \frac{1}{n} \frac{dU}{dT} = 3R (= 24.94 \text{ JK}^{-1})$$



	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

Heat Capacity – Einstein model



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

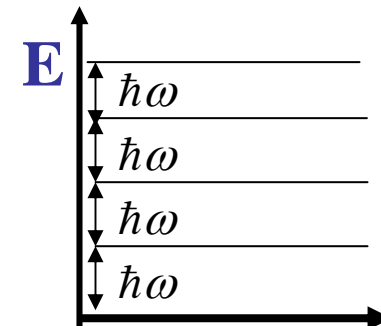
$$\bar{n} = \frac{1}{e^{\hbar\omega/k_B T} - 1}$$

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

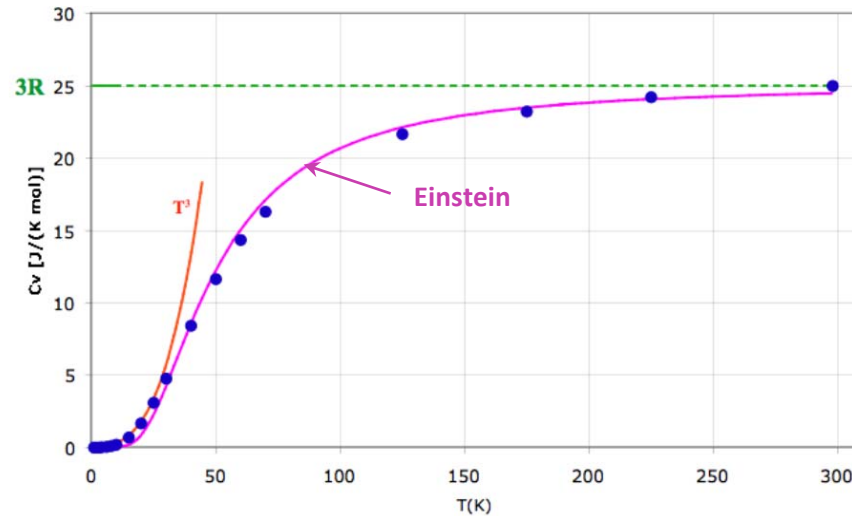
$$C_v = \left(\frac{\partial U}{\partial T}\right)_v = 3Nk_B F_E \left(\frac{\hbar\omega}{k_B T}\right)$$

$$F_E(x) = \frac{x^2}{(e^x - 1)(1 - e^{-x})}$$

Energy levels are equally spaced!



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 !

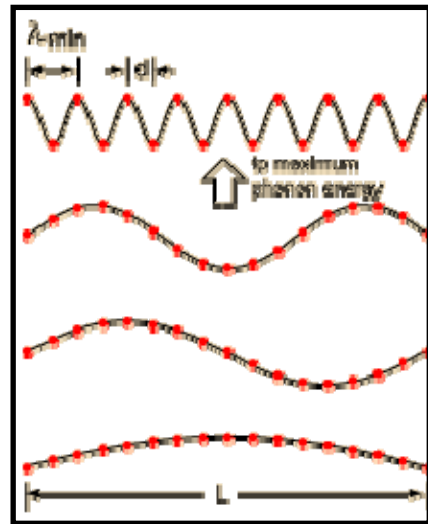
Therefore the total internal energy should be,

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

Annotations:

- $\frac{\hbar\omega}{\exp(\hbar\omega/kT) - 1}$: Einstein statistic
- $g(\omega)d\omega$: No. of phonons in $d\omega$ at ω

Phonon in a box



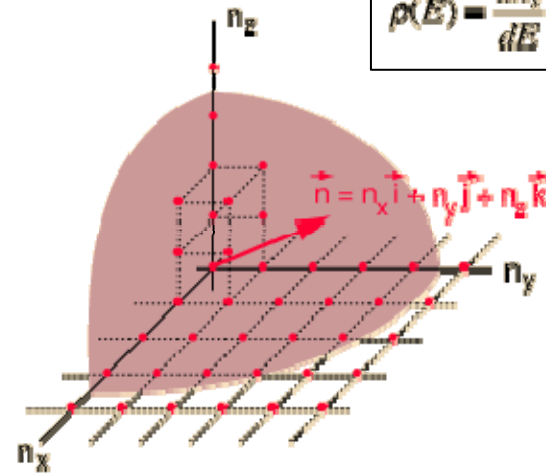
$$h\nu = \frac{h\nu_s}{\lambda} = \frac{h\nu_s n}{2L}$$

$$\lambda_{\min} = 2d$$

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

$$\lambda_{\max} = 2L$$

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



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.

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

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

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

Heat Capacity - Debye model

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,

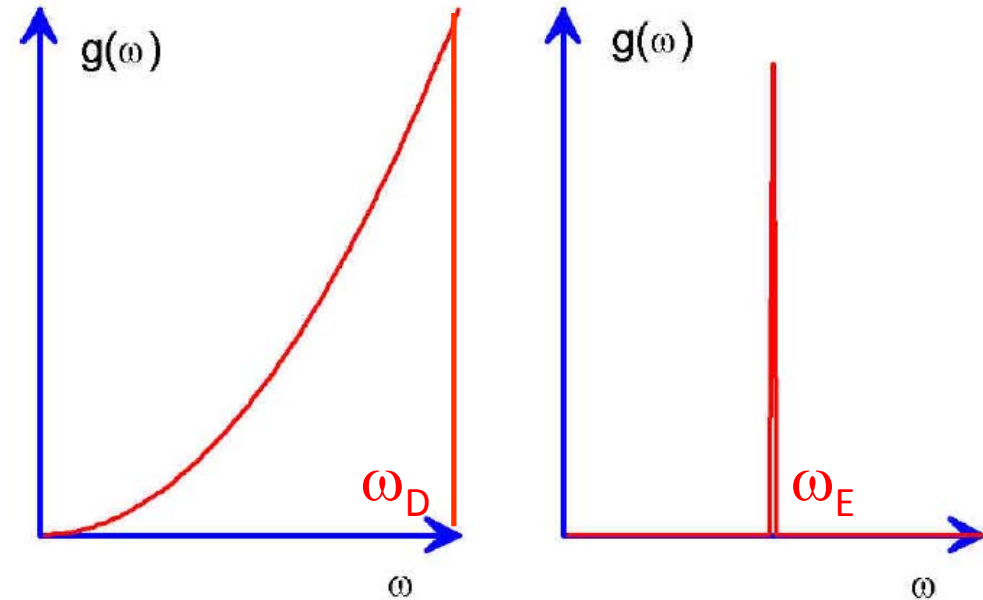
$$g(\omega) = D\omega^2$$

with a cutoff frequency, ω_D

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

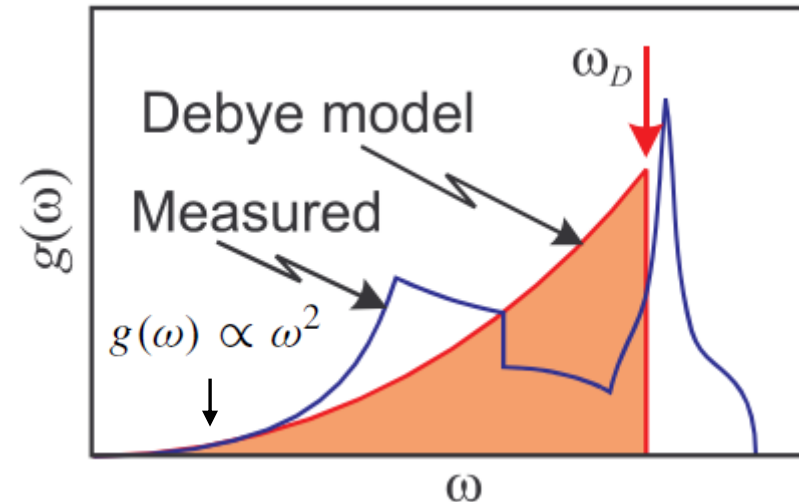
$$U = \frac{3V\hbar}{2\pi^2 v_s^3} \int_0^{\omega_D} \omega^3 \frac{1}{\exp(\hbar\omega/kT) - 1} d\omega$$

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



Debye model

Einstein model



What can we learn from Debye temperature?

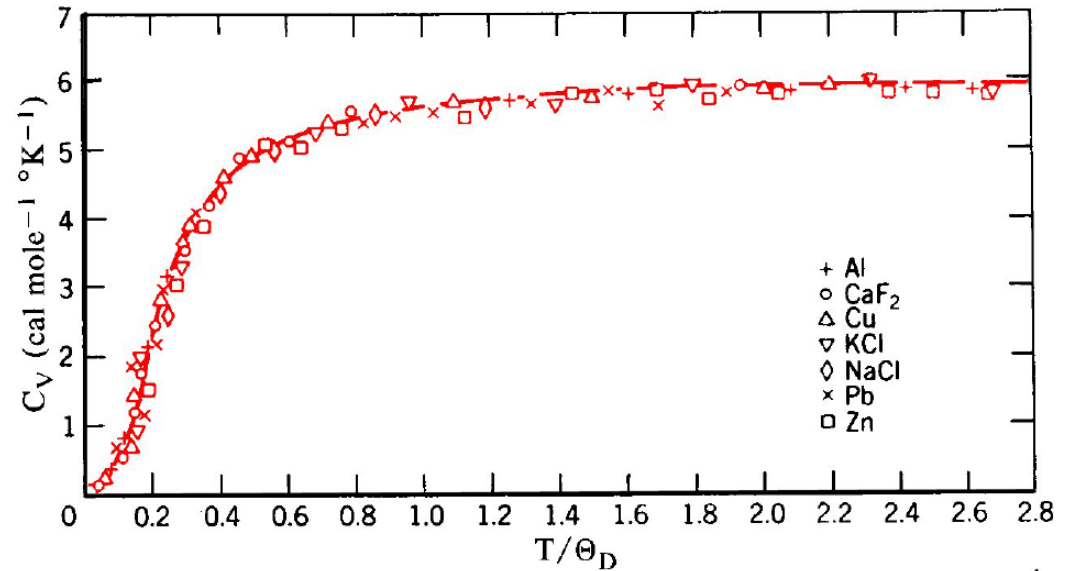
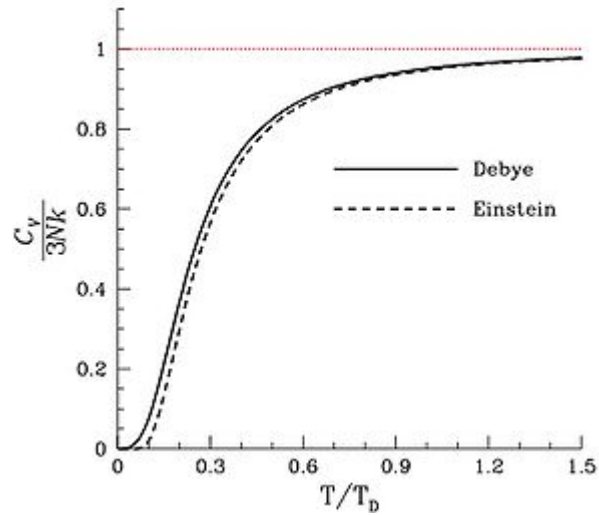
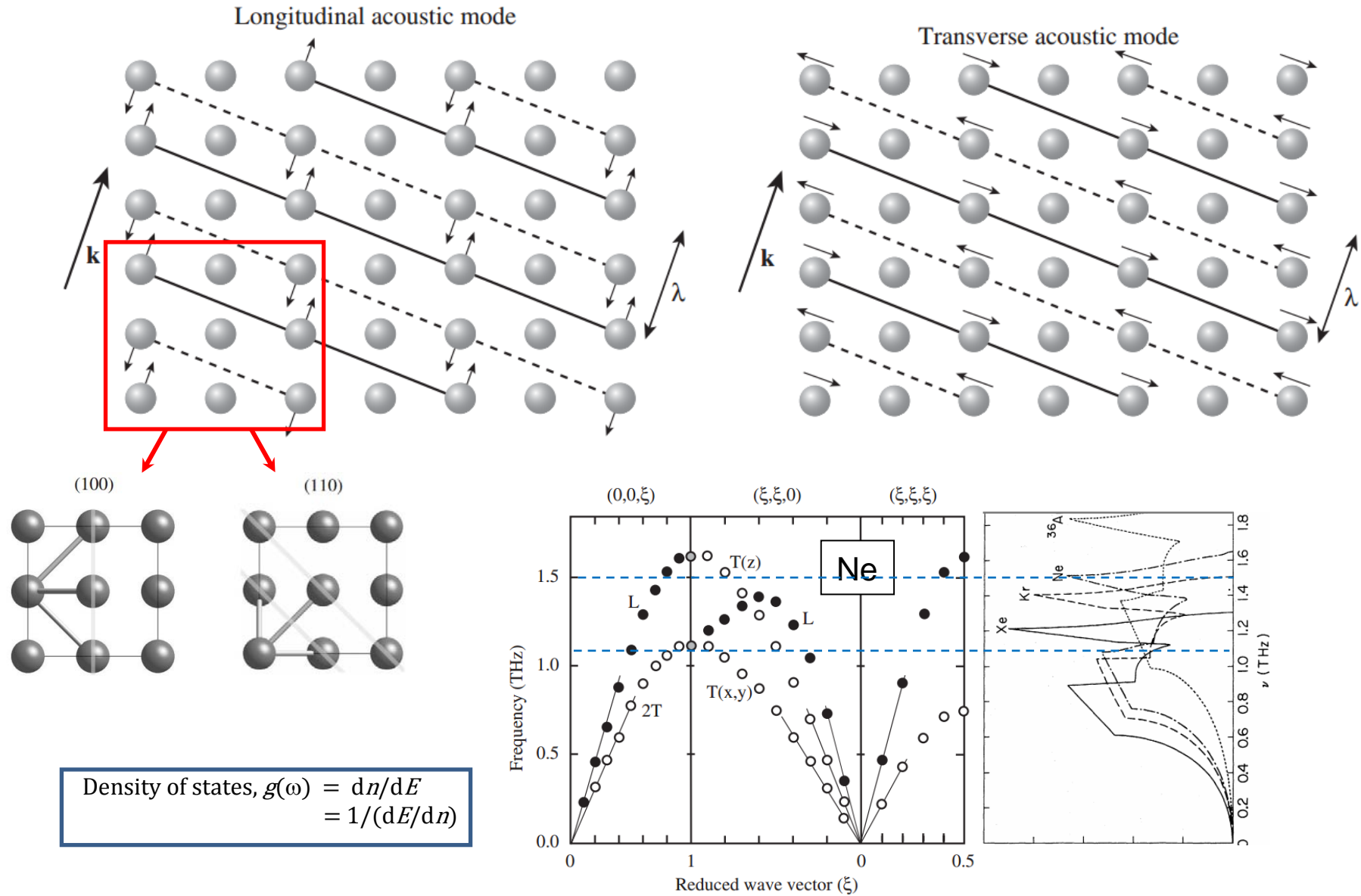


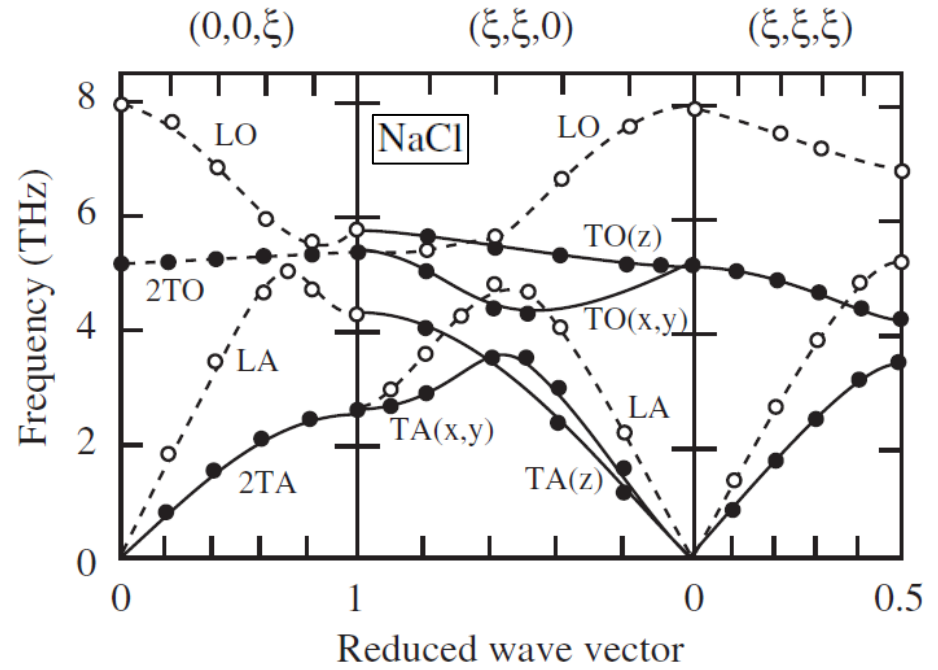
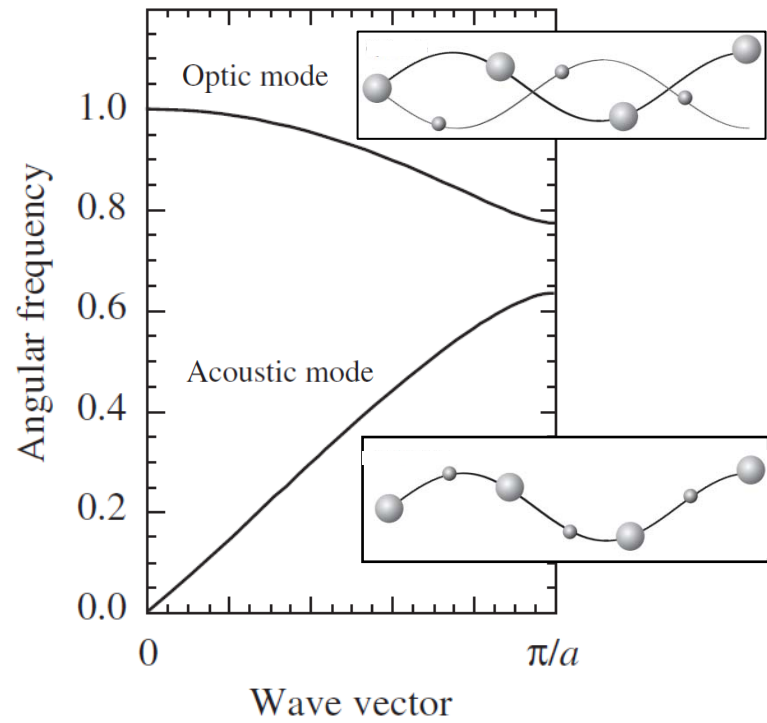
Table 4.5 Debye temperatures T_D , heat capacities, and thermal conductivities of selected elements

	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

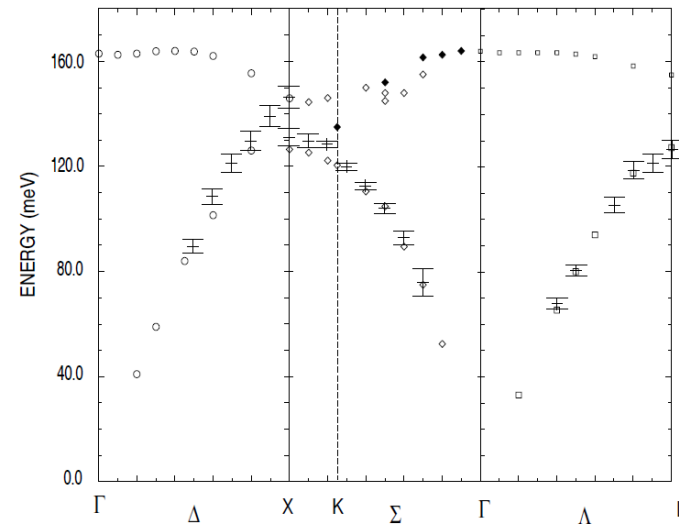
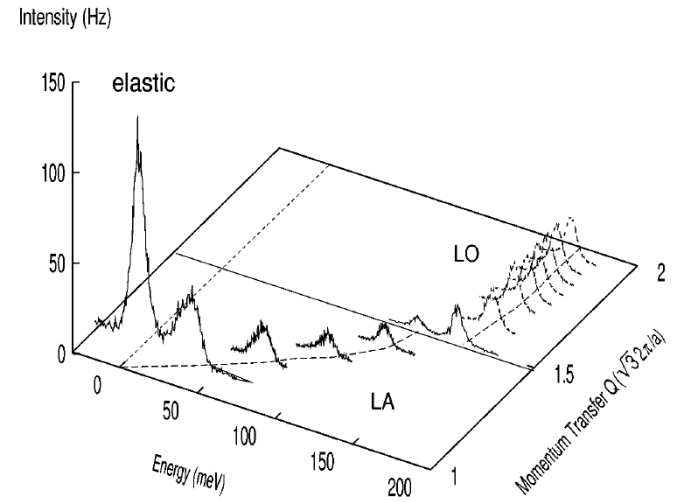
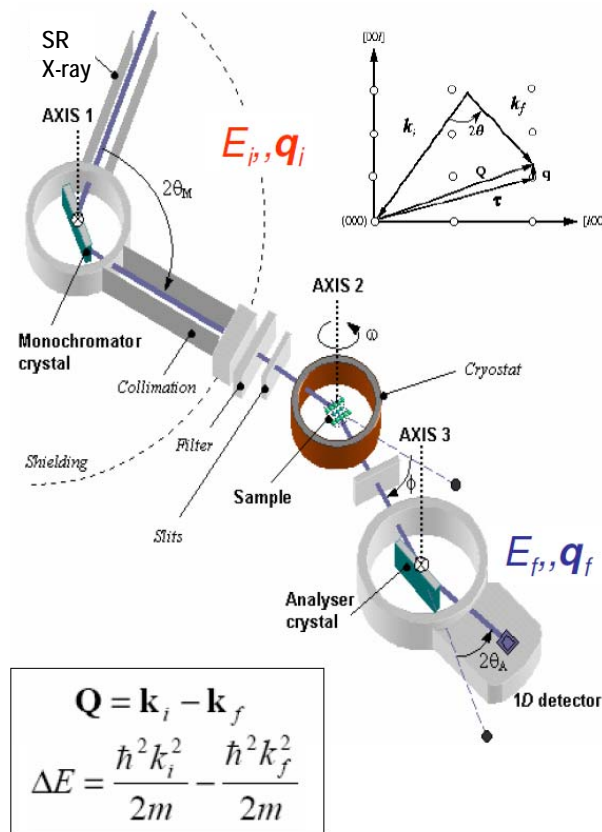
Phonon band structure



Phonon band structure



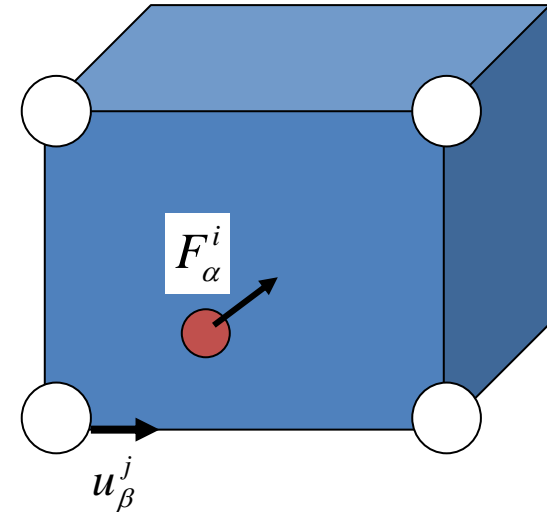
Phonon Dispersion of Diamond Measured by Inelastic X-Ray Scattering



Theoretical lattice dynamics

Force constant, Hooke's Law

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

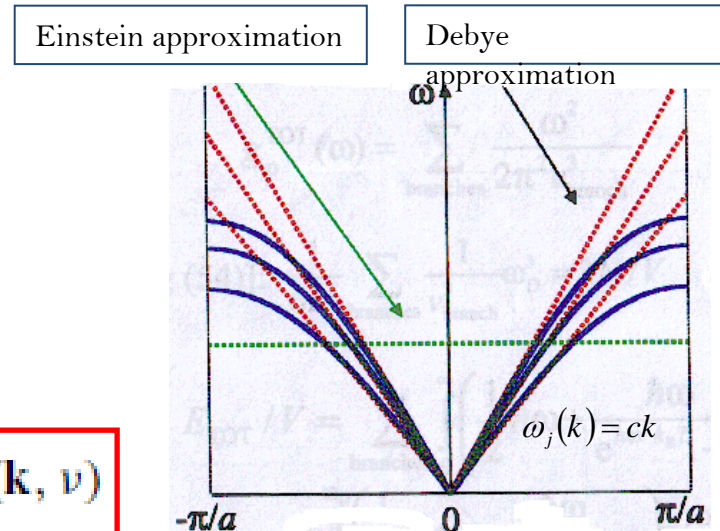


Dynamic matrix is the Fourier transformation of force constants

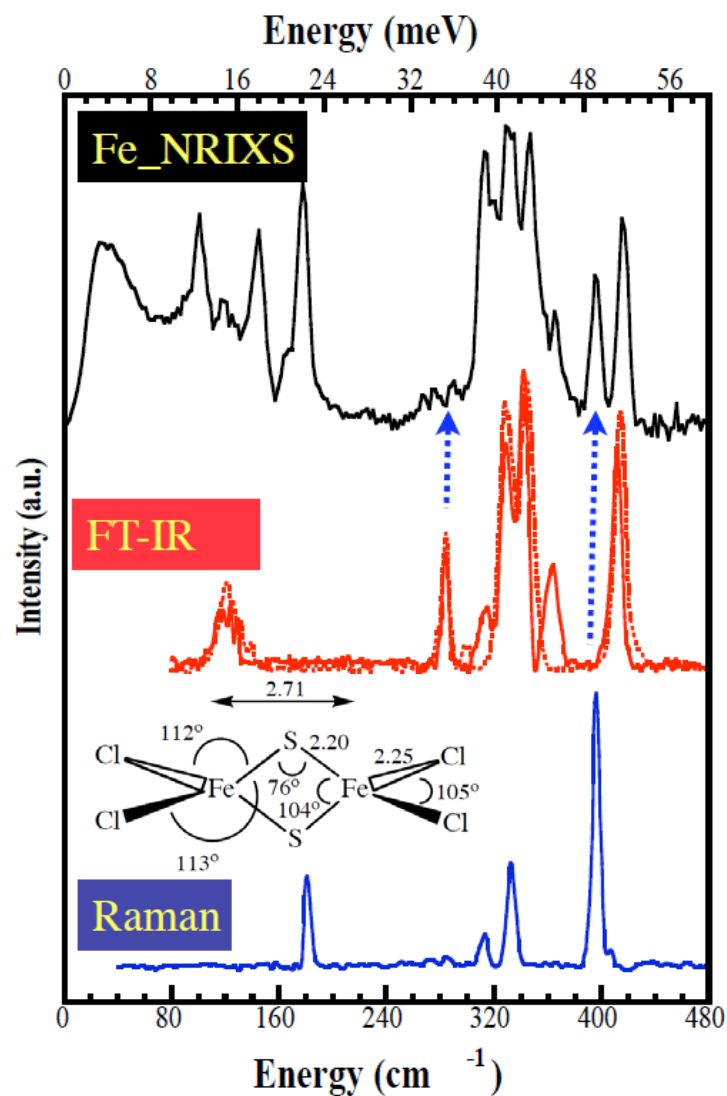
$$D_{\alpha\beta}^{ij}(q) = \frac{1}{\sqrt{M_i M_j}} \sum_L \Phi_{\alpha\beta}^{i, j+L} e^{-iq \cdot (R^{j+L} - R^i)}$$

Diagonalize Dynamic matrix to get phonon dispersions, and DOS

$$\mathbf{u}(jl) = \frac{1}{\sqrt{Nm_j}} \sum_{\mathbf{k}, \nu} \mathbf{e}(j, \mathbf{k}, \nu) \exp(i\mathbf{k} \cdot \mathbf{r}(jl)) Q(\mathbf{k}, \nu)$$



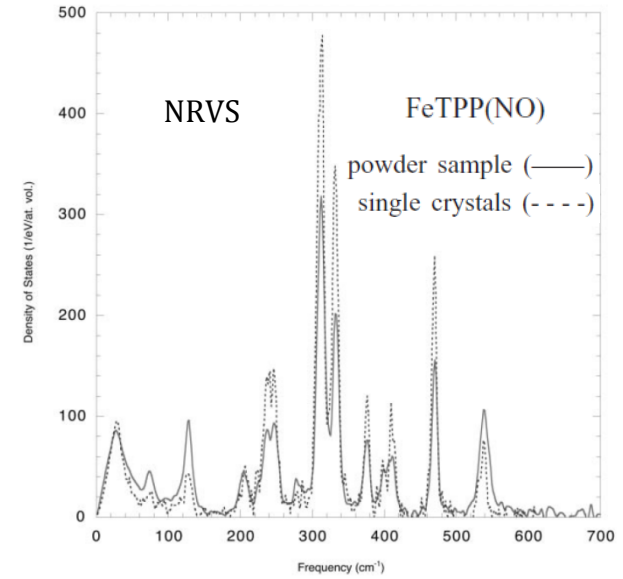
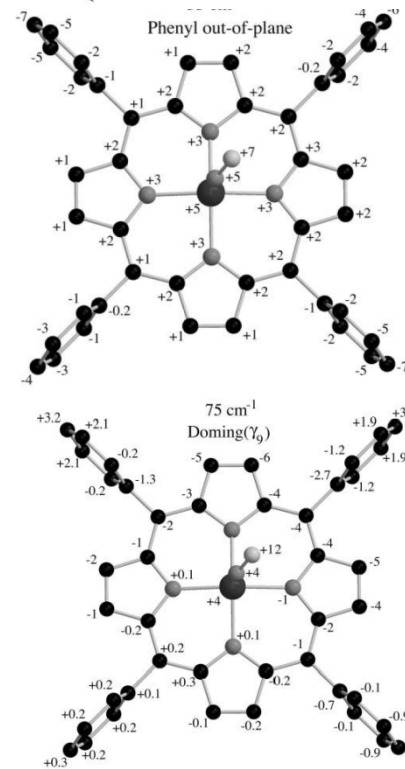
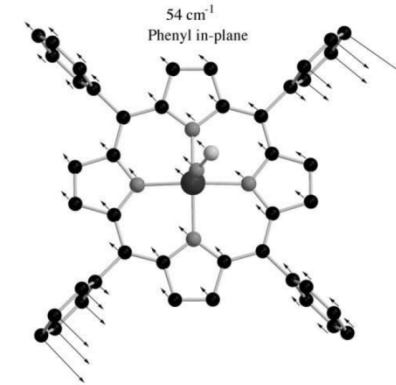
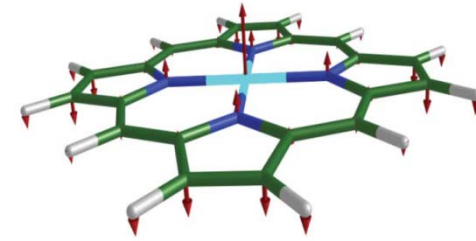
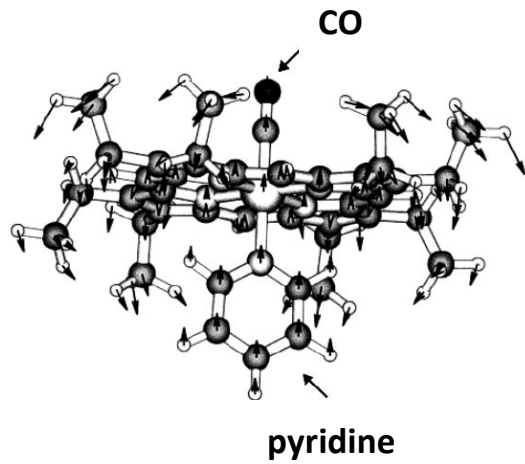
Selection rules



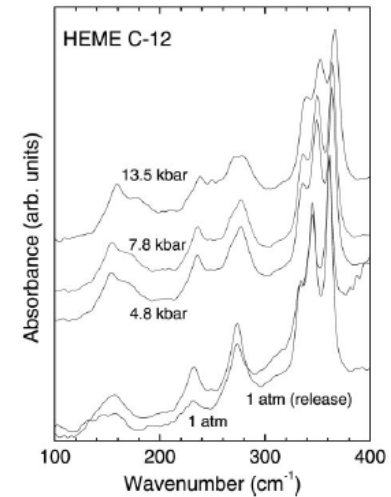
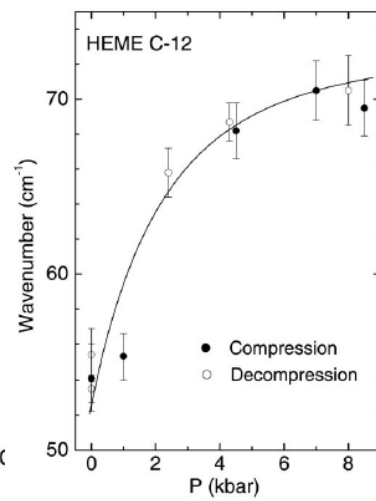
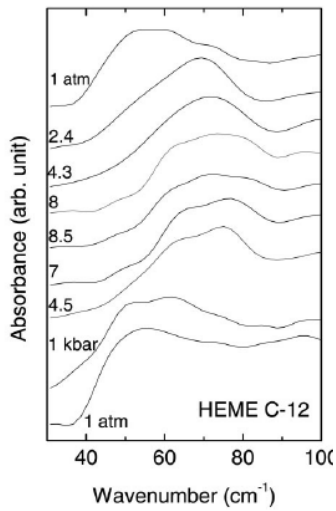
Selection rules:

- 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
 $I \propto \text{VDOS}$

Doming modes



Infrared COFe(OEP)Py



D.D. Klug, J.S. Tse, et.al., PNAS, 99, 12526 (2002)

B.K. Rai, et.al., Biophys. J., 82, 2951 (2002)

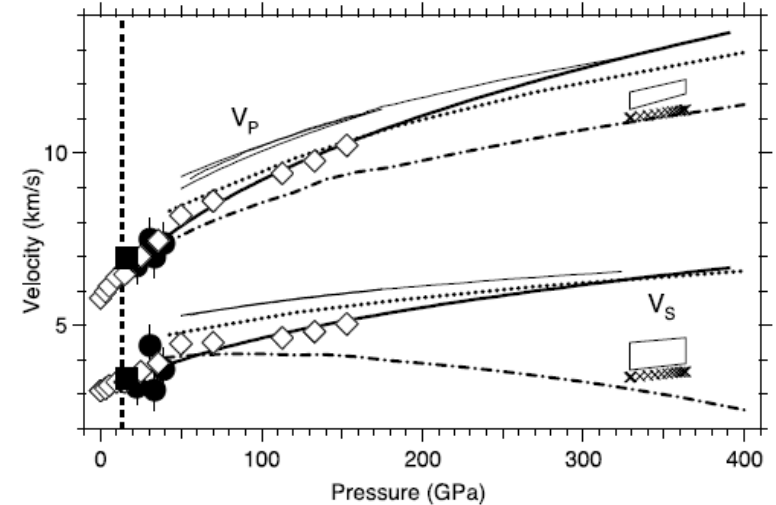
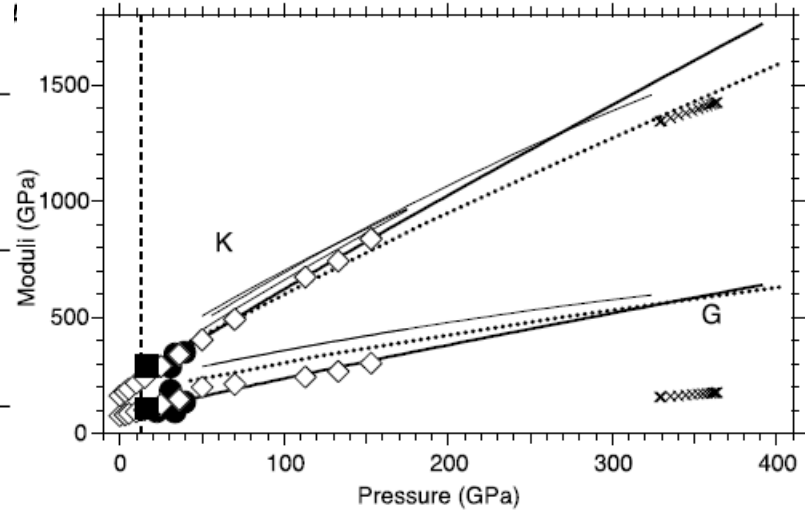
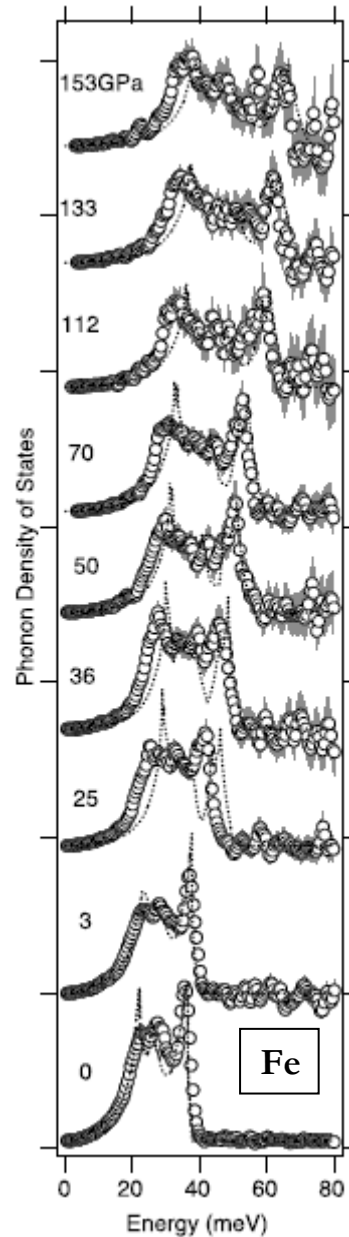
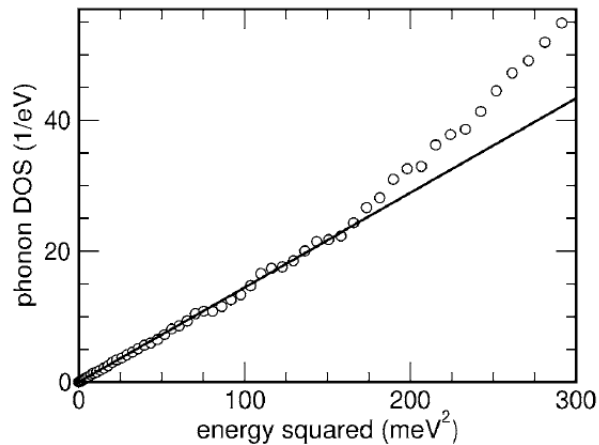
Properties derived from sound velocity

$$g(\omega) = \frac{V\omega^2}{2\pi^2 v_s^3} \Rightarrow g(\omega) = \frac{V\omega^2}{2\pi^2} \left(\frac{1}{v_L^3} + \frac{2}{v_T^3} \right)$$

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

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

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



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

Properties derived from vibrational density of states

The partition function for the harmonic lattice is given by

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

the vibrational energy per atom

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

vibrational entropy per atom S

$$S = k_B \beta U + k_B \ln Z$$

the free energy per atom F

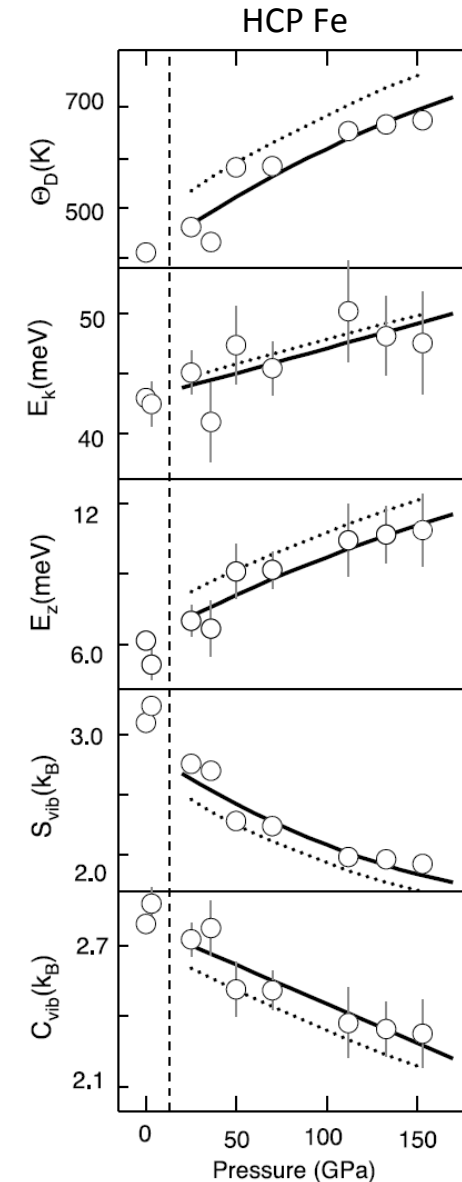
$$F = -\frac{1}{\beta} \ln Z$$

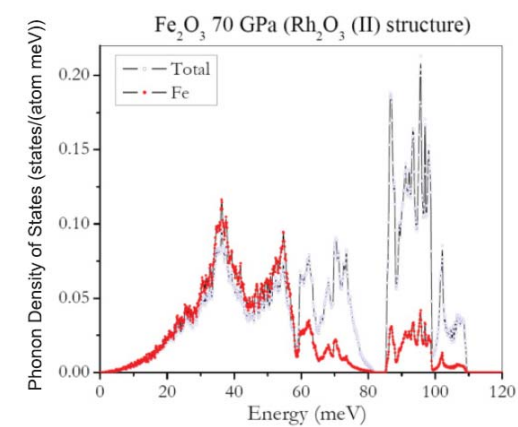
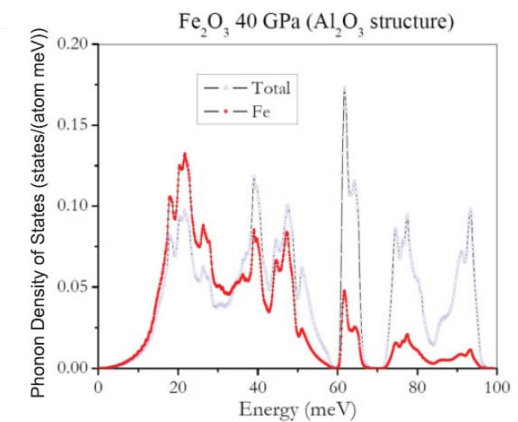
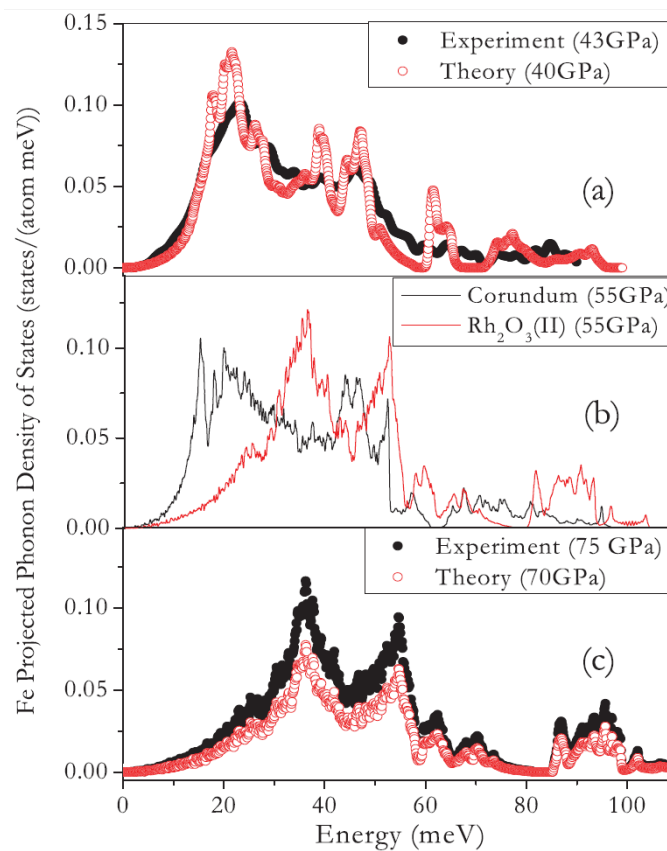
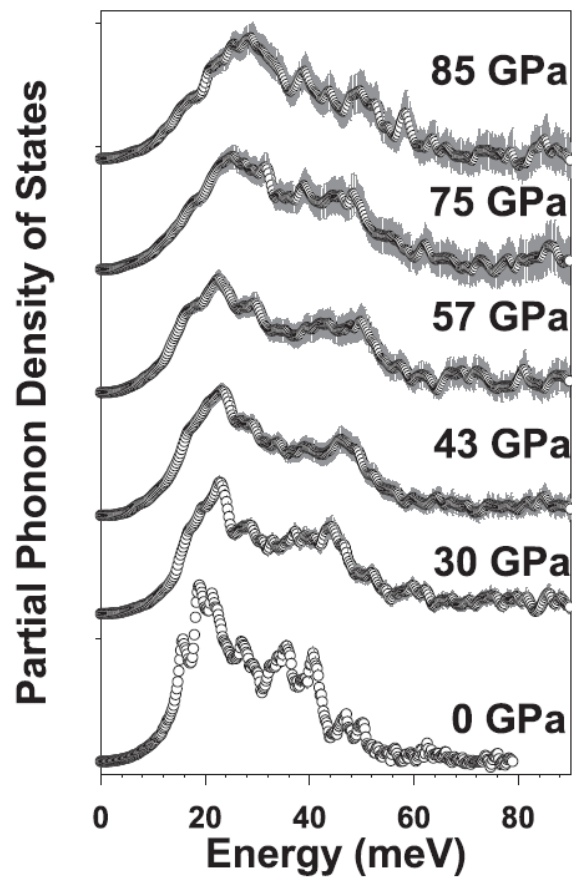
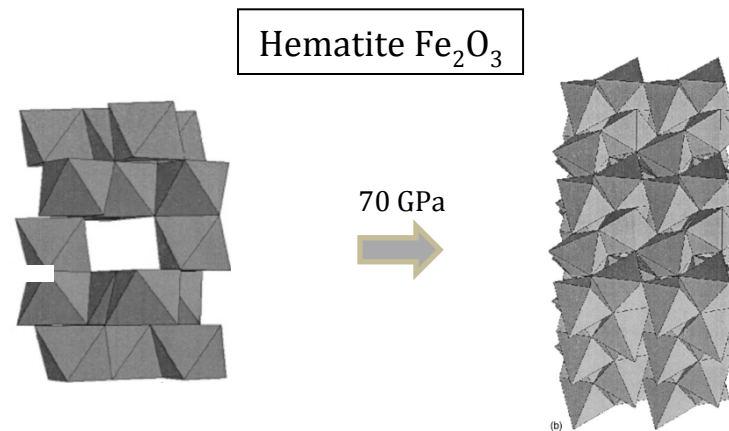
the specific heat per atom at constant volume

$$c_V = \frac{\partial U}{\partial T} = k_B \beta^2 \frac{\partial^2 \ln Z}{\partial \beta^2} = 3k_B \int \left(\frac{\beta E}{2 \sinh(\beta E/2)} \right)^2 g(E) dE$$

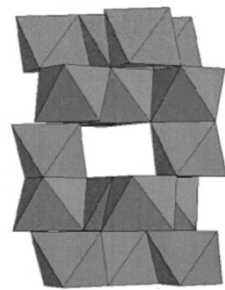
mean force constant

$$F_m = \frac{9}{10} \frac{k^2}{E_r} k_B^2 \theta_D^2$$

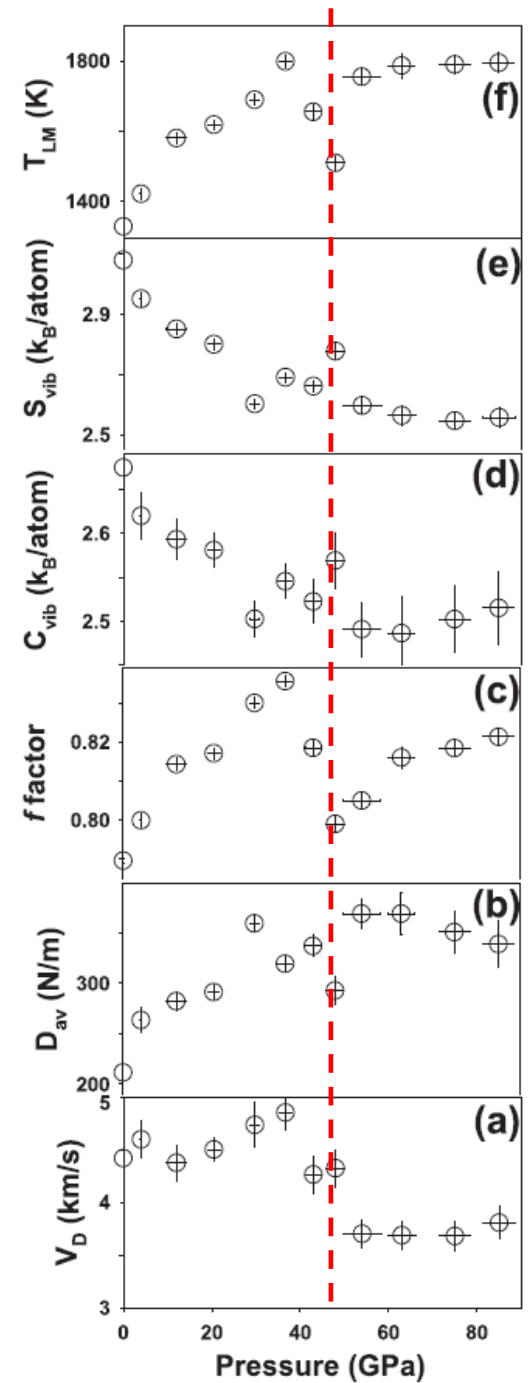
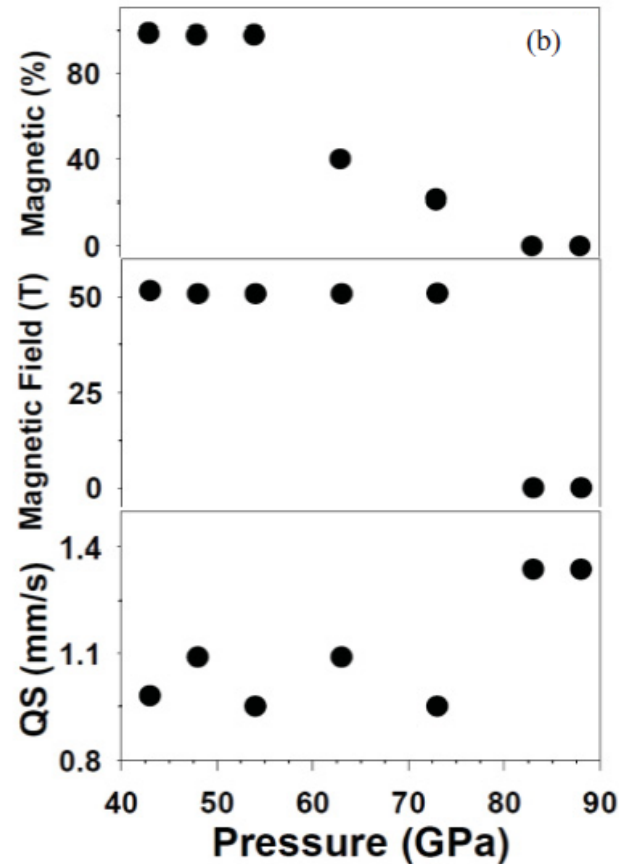
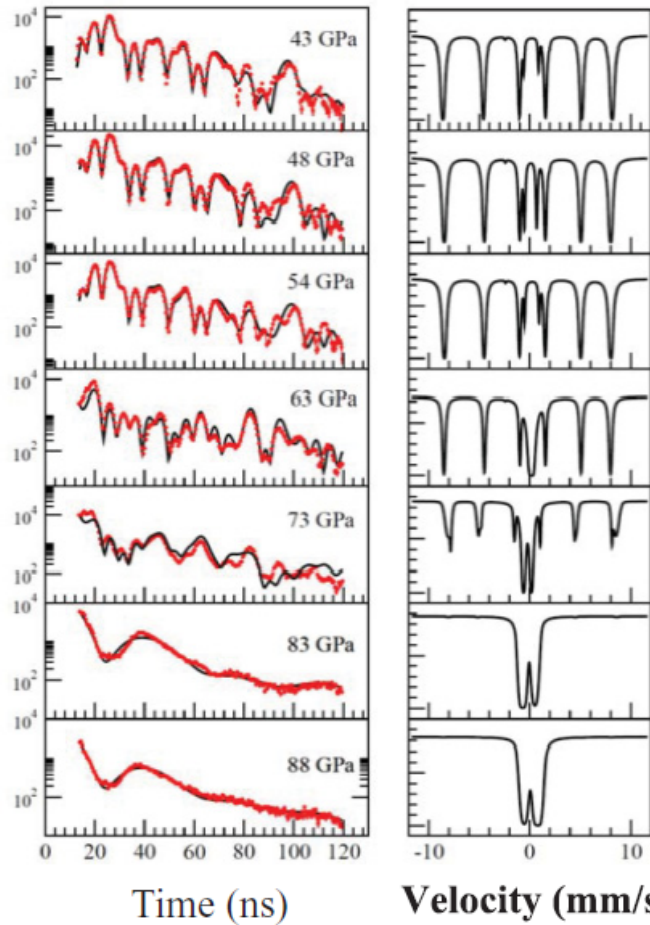
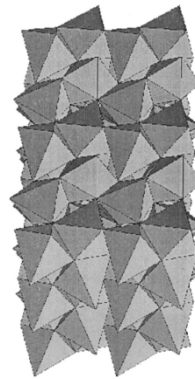




Hematite Fe_2O_3

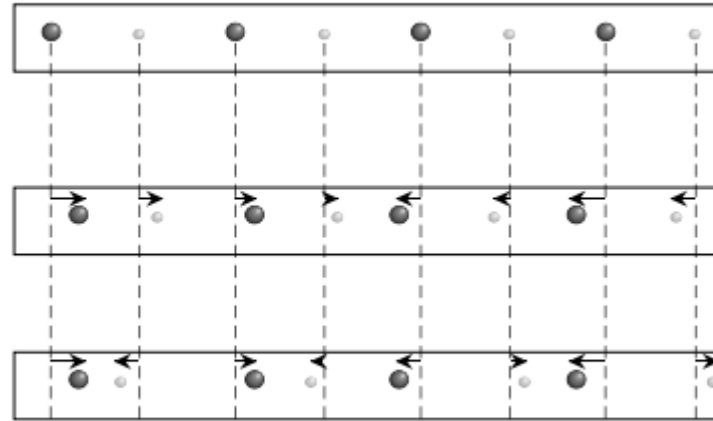


70 GPa



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

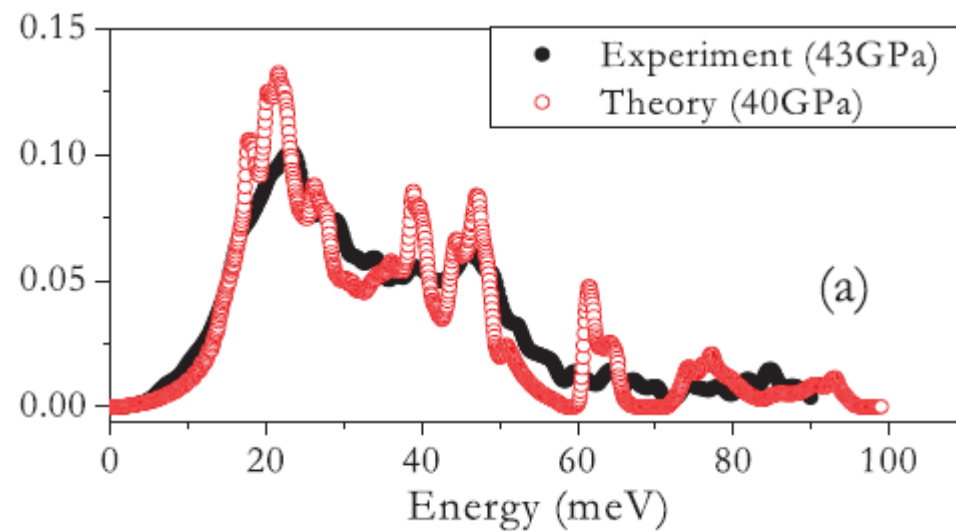
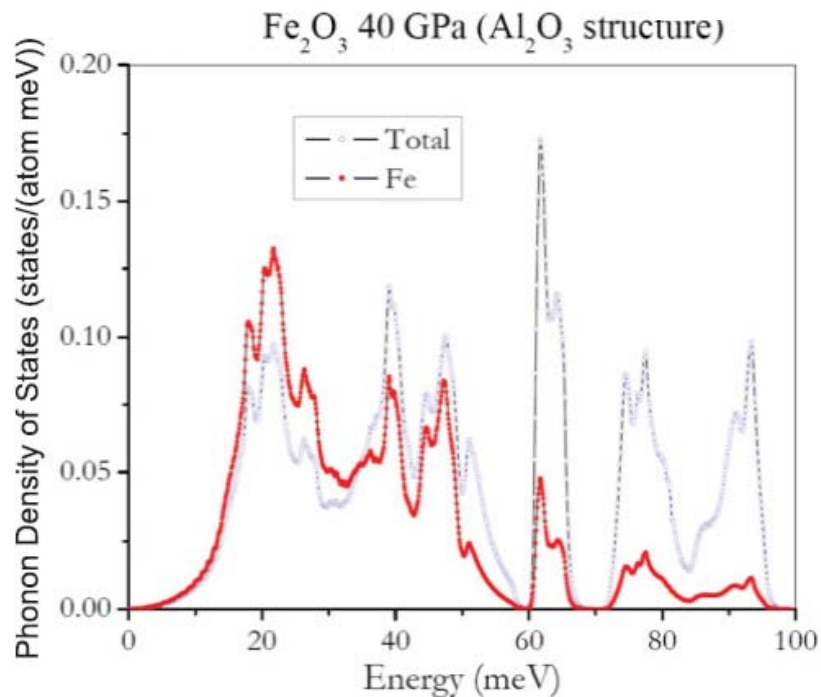
Why it works for multi-component systems?



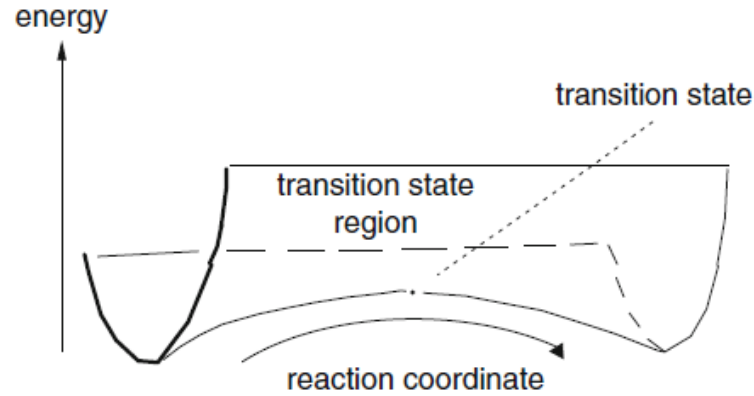
EQUILIBRIUM POSITIONS OF ATOMS

ACOUSTICAL VIBRATION:
The two atoms on the unit cell vibrate along the same direction

OPTICAL VIBRATION:
The two atoms on the unit cell vibrate in opposing motion.



Soft mode and Gruneisen parameter



$$\gamma_i(\mathbf{q}) = - \frac{\partial \ln \omega(\mathbf{q})_i}{\partial \ln V}$$

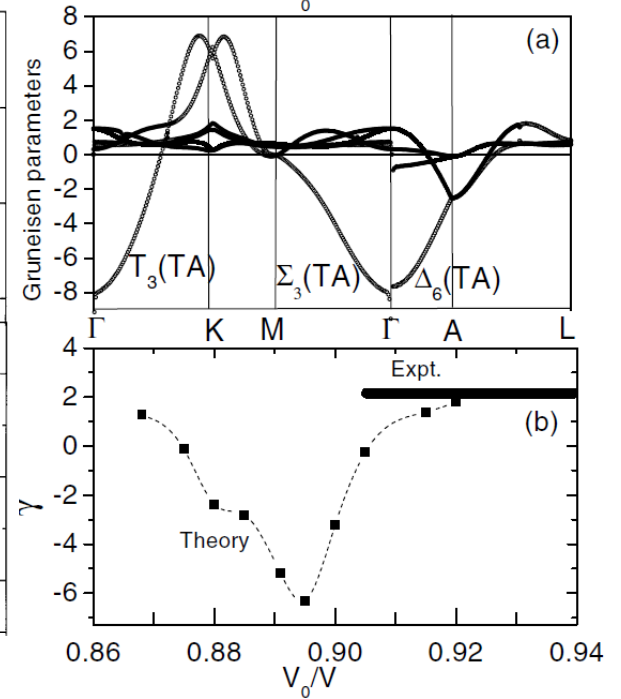
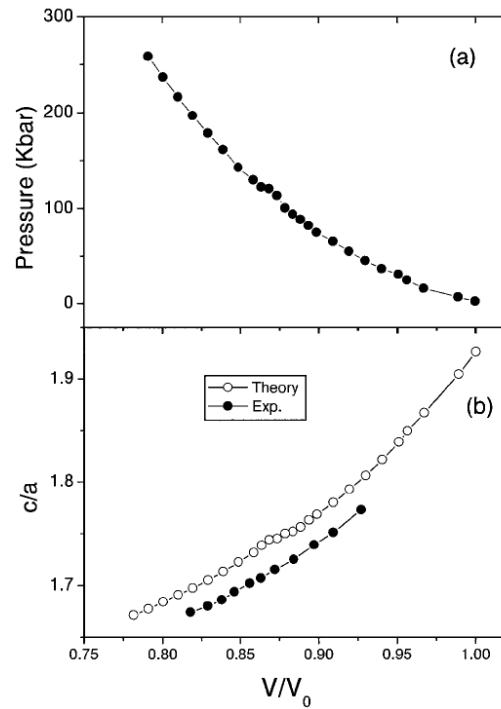
$V_0/V=0.88$

$$\tilde{\nu} = \frac{1}{2\pi c} \left(\frac{k}{\mu} \right)^{1/2}$$

$$F = -kq \quad \Rightarrow \quad -k = \frac{\partial F}{\partial q} = \frac{\partial^2 E}{\partial q^2}$$

For a transition state $\frac{\partial^2 E}{\partial q^2} > 0$

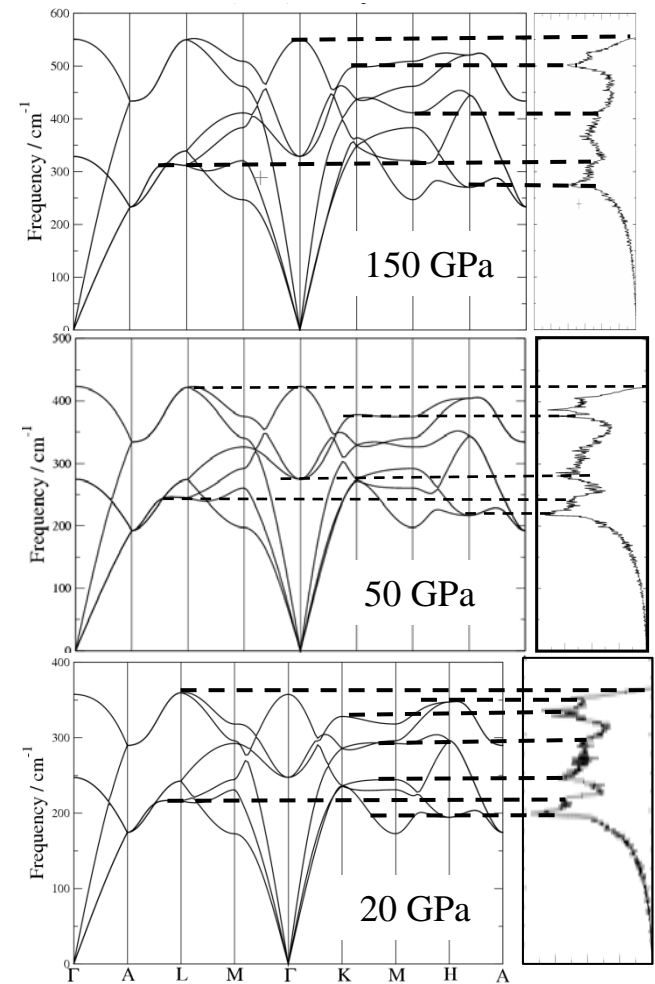
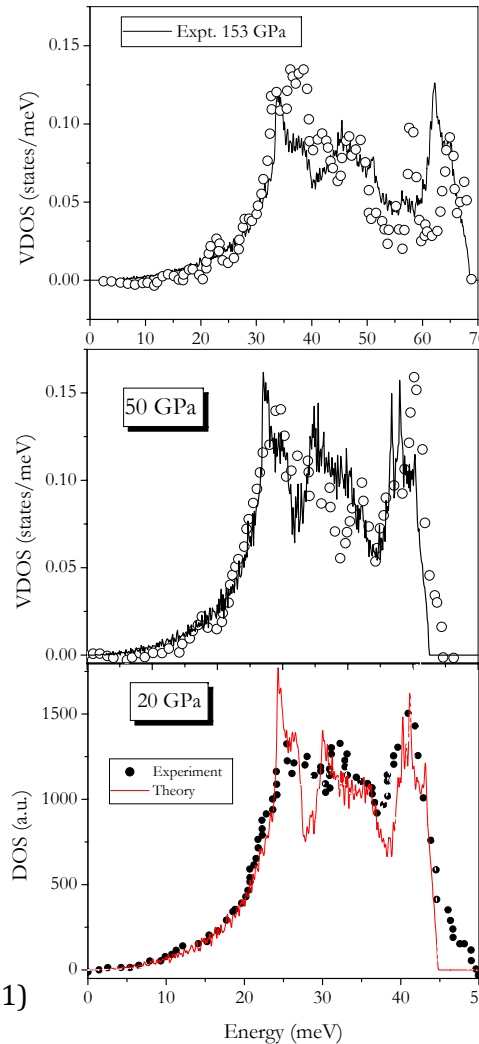
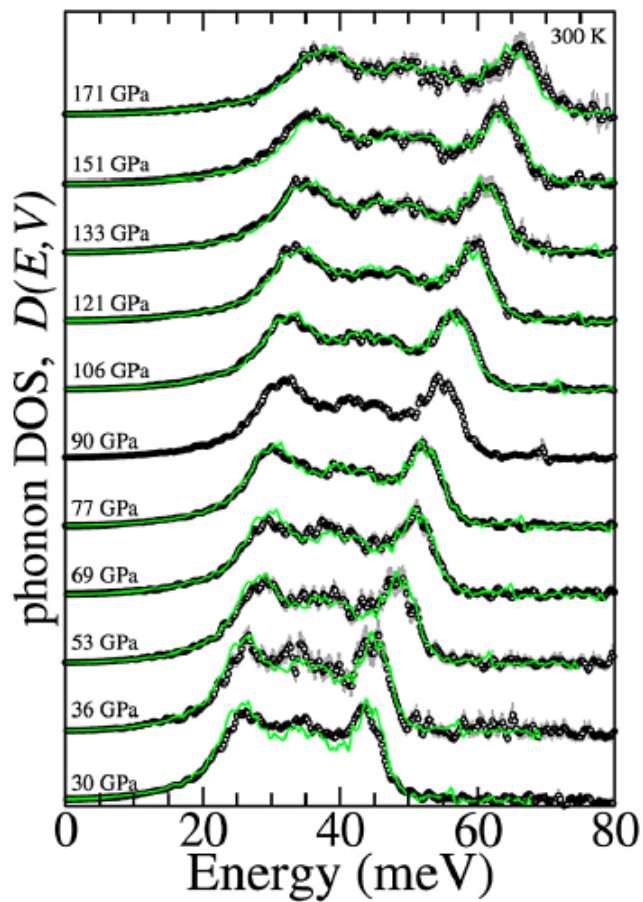
$k < 0$ and $\tilde{\nu}$ is imaginary



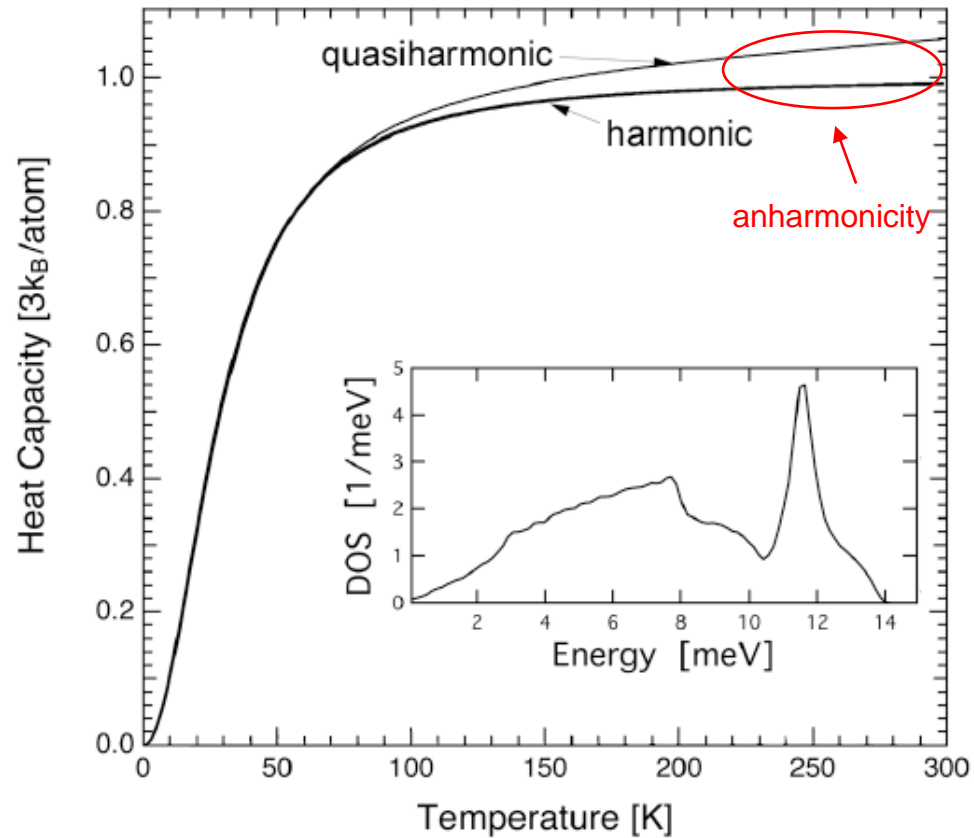
$$\gamma_{vib} = \gamma_{vib,i} \left(\frac{V}{V_i}\right)^q \quad \gamma_D = \frac{1}{3} - \frac{V}{v_D} \left(\frac{\partial v_D}{\partial V}\right)_T \quad \boxed{\epsilon\text{-Fe}} \quad T_M(V) = T_M^{ref} \left(\frac{V}{V_M^{ref}}\right)^{2/3} \exp\left\{\frac{2\gamma_{vib}^{ref}}{q} \left[1 - \left(\frac{V}{V_M^{ref}}\right)^q\right]\right\}$$

$$v_D = v_{D,0} \left(\frac{V}{V_i}\right)^{1/3} \exp\left\{-\frac{\gamma_{D,0}}{q} \left[\left(\frac{V}{V_0}\right)^q - 1\right]\right\} \quad T_M(4.70 \text{ cm}^3/\text{mol}) = 4100 \pm 100 \text{ K}$$

$$T_M(4.58 \text{ cm}^3/\text{mol}) = 4300 \pm 100 \text{ K}$$



Anharmonicity in Phonons

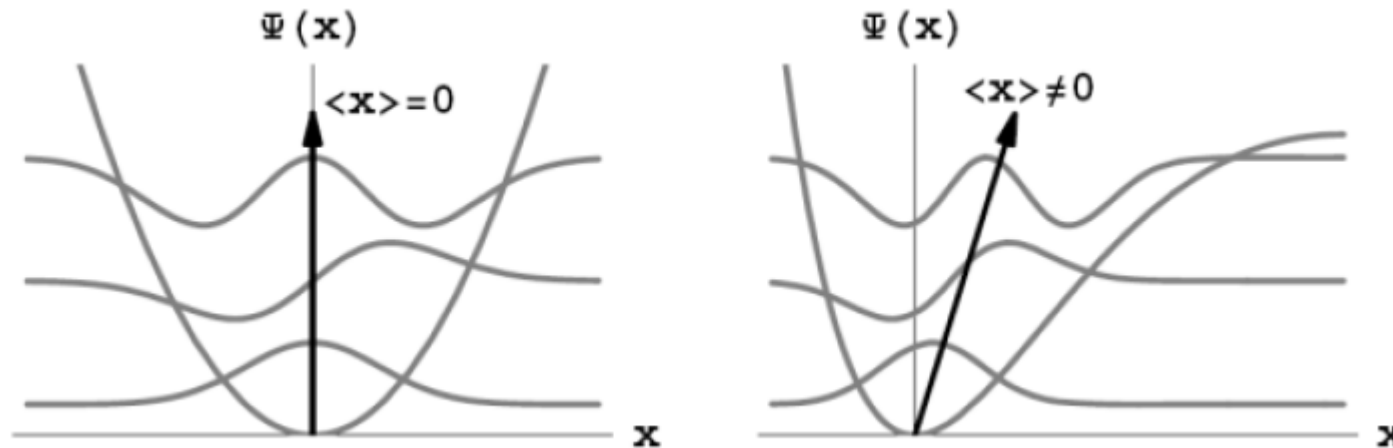


1. The heat capacity becomes T independent for $T > T_D$.
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3. Thermal conductivity of solids is infinite

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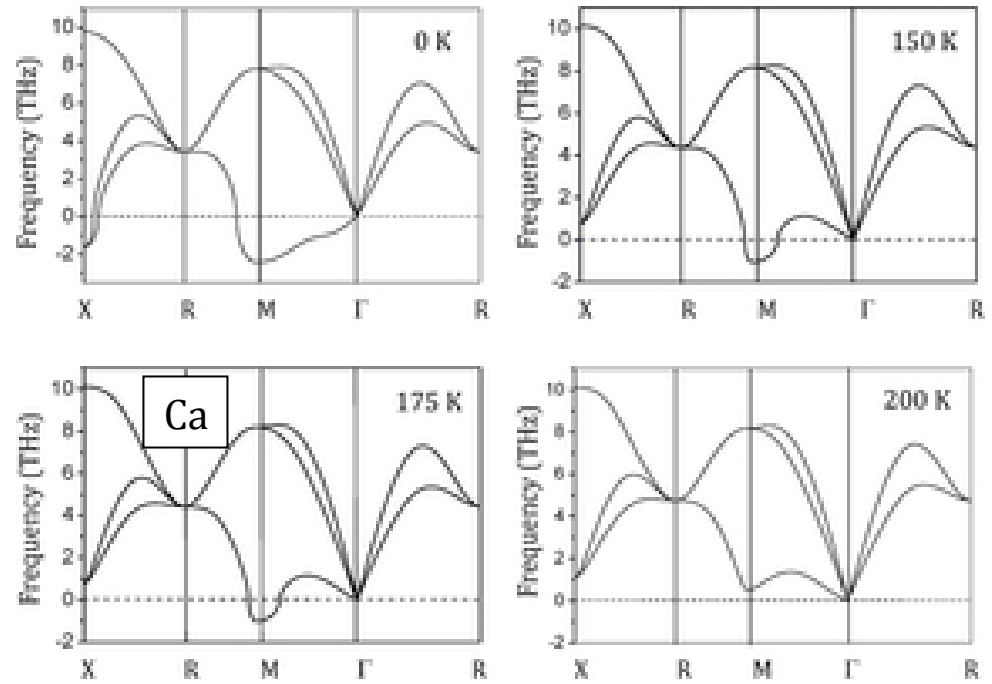
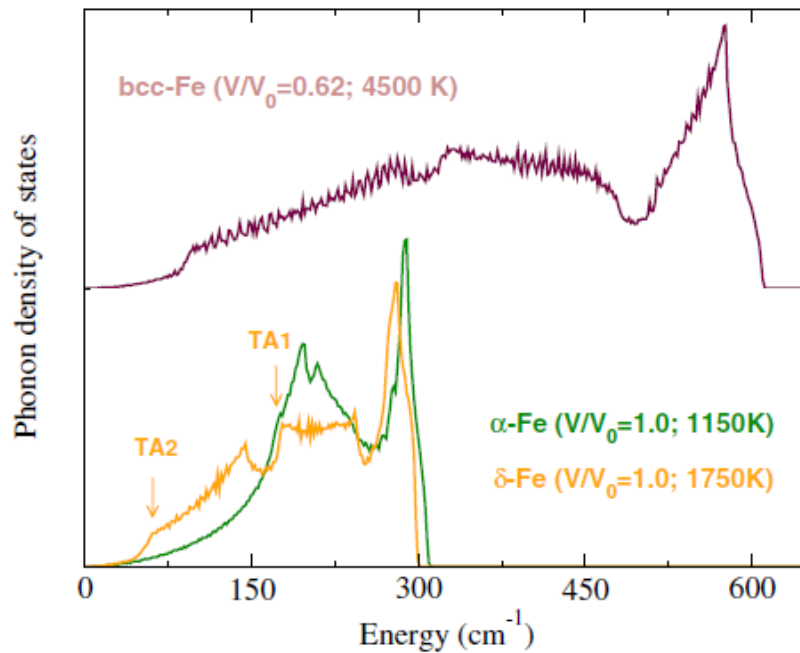
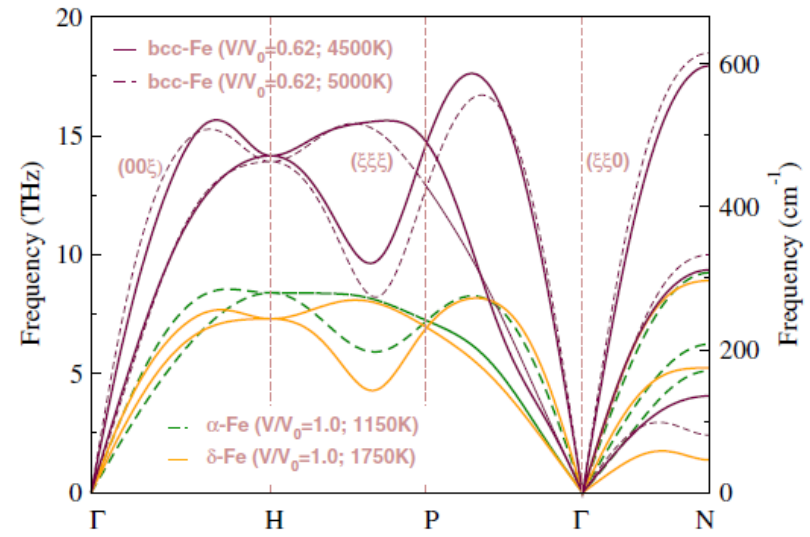
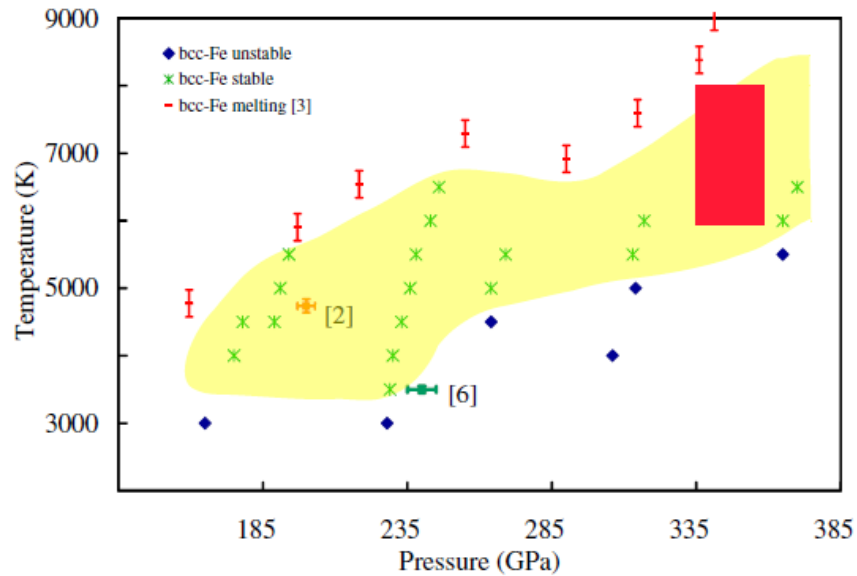
$$U(x) = U_{\text{harm}}(x) + U_{\text{anharm}}(x) = cx^2 - gx^3 - fx^4$$



Phonon wavefunctions for (Left) harmonic potential (Right) anharmonic potential

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

Finite temperature lattice dynamics

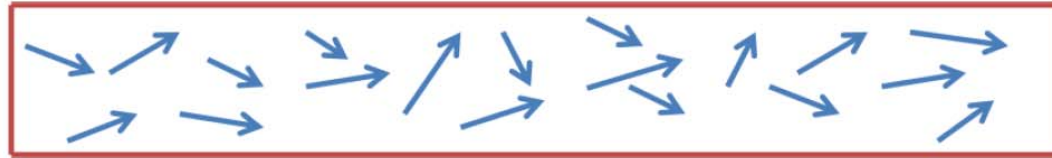


W. Luo, et al., *PNAS*, **107**, 9962 (2010)

JS Tse, et al., *Nature Sci. rep.*, **2**, 372 (2012).

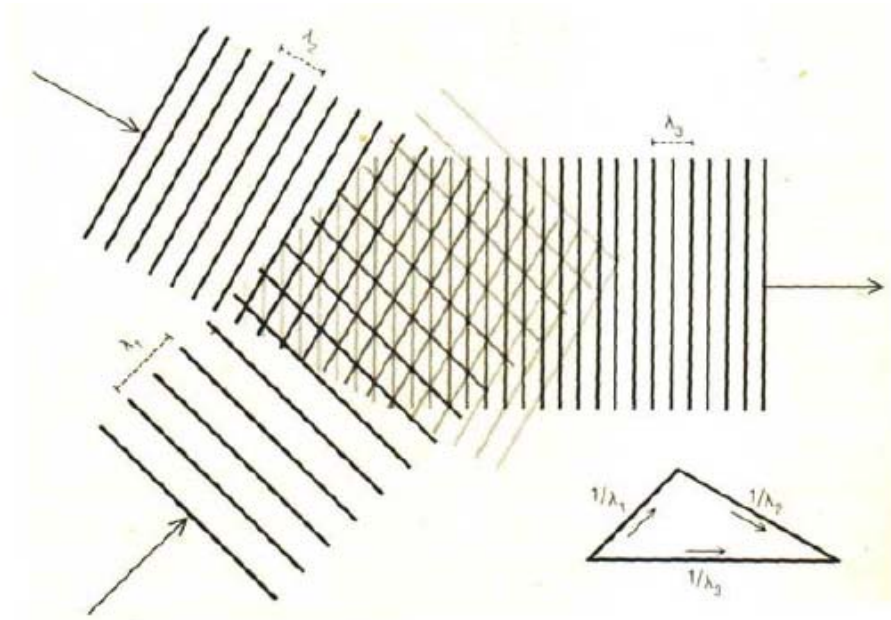
Thermal conductivity

hot end

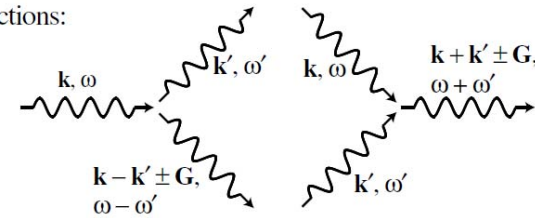


cold end

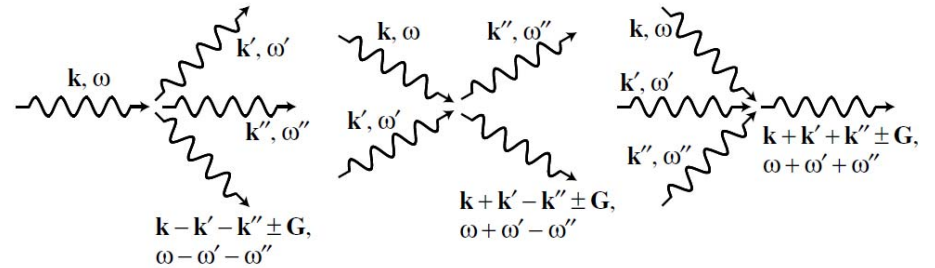
$$U(x) = U_{\text{harm}}(x) + U_{\text{anharm}}(x) = cx^2 - gx^3 - fx^4$$



Cubic interactions:



Quartic interactions:



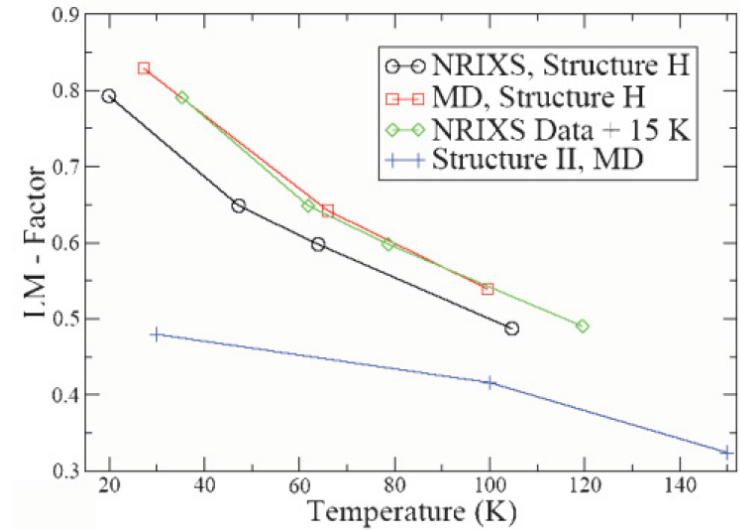
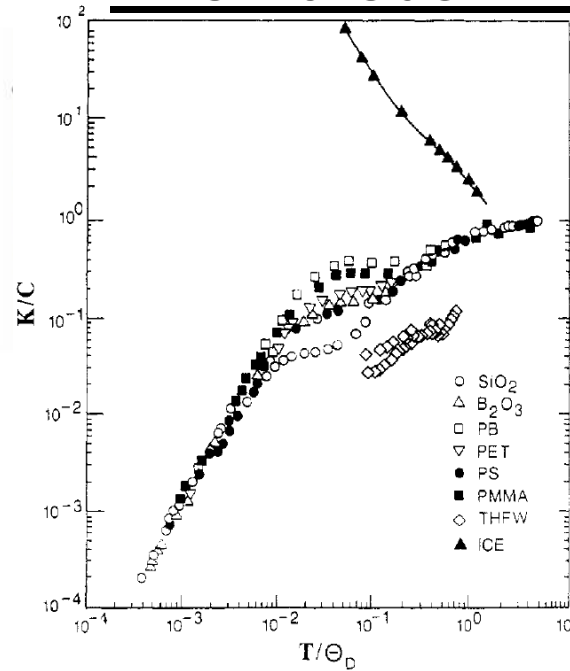
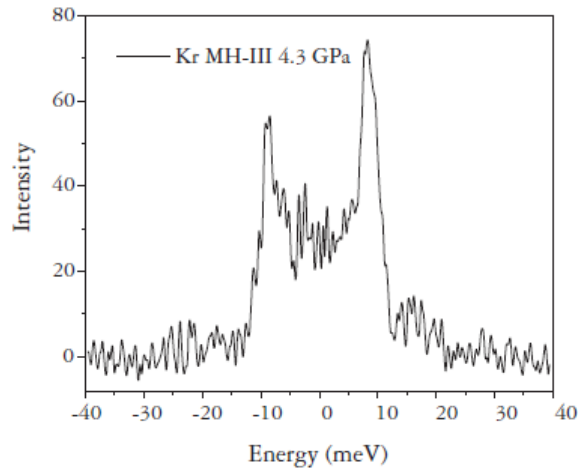
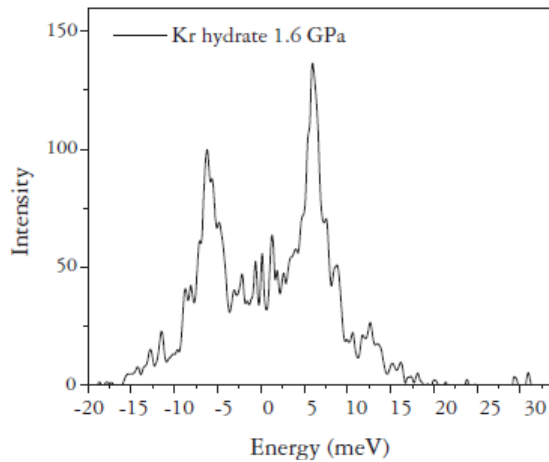
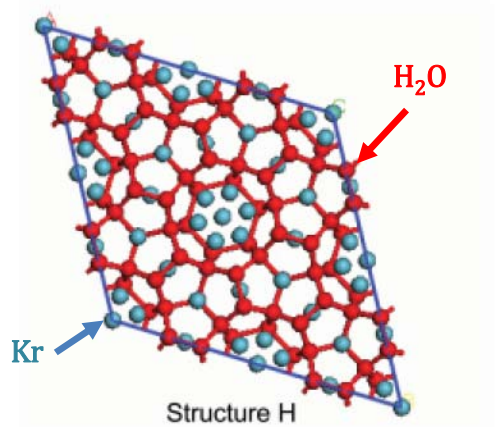
Mossbauer Nuclei

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	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn	
Fr	Ra	Ac																
			Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu		
			Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr		

Elements of the periodic table which have known Mössbauer isotopes (shown in red font).

Isotope	E_0 (keV)	τ (ns)	Strength
^{181}Ta	6.214	8730	0.0007
^{169}Tm	8.410	5.8	0.38
^{83}Kr	9.404	212	0.2
^{73}Ge	13.263	4260	0.00003
^{57}Fe	14.4125	141	1
^{151}Eu	21.541	14	0.63
^{149}Sm	22.496	10.2	1.3
^{119}Sn	23.88	25.7	6.7
^{161}Dy	25.651	40.5	1.2
^{40}K	29.83	6.1	391

Anomalous Thermal Conductivity



The Lamb-Mössbauer factor

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

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

The Debye-Waller factor is

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

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