

Structure of Matter

The Solid State

WS 2013/14

Lectures (Tuesday & Friday)

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Last time:

Reciprocal lattice and
diffraction cont'd
Phonons

Today:

Phonons cont'd
Thermal properties

Phonons

Total lattice energy $U_{\text{total}} = \sum_{<\text{ij}>} U_{\text{ij}} (\vec{R}_j - \vec{R}_i)$

Stability: $\frac{\partial U_{\text{total}}}{\partial R_j} \Bigg|_{R_j=R_j^0} = 0 \Rightarrow$ Equilibrium coordinates

Harmonic approximation: $F_j = -\frac{\partial U_{\text{total}}}{\partial R_j}$

phonons

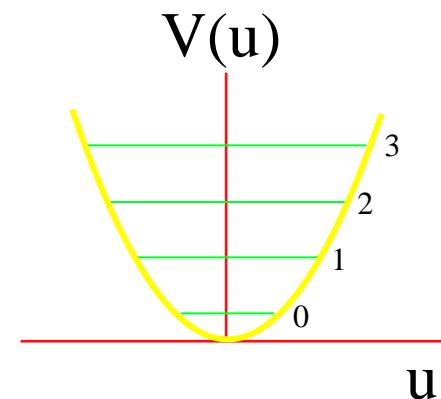
Classical: $u_s(t) = u_k(t) e^{i \omega_k t}$

EOM: $m\ddot{u}_k(t) = -C_k u_k(t)$ with $C_k = m\omega_k^2$

Quantum states of elastic waves:

$$\left\{ -\frac{\hbar}{2m} \frac{\partial^2}{\partial u_k^2} + \frac{1}{2} m \omega_k^2 u_k^2 \right\} \cdot \psi_k(u_k) = E_k \cdot \psi_k(u_k)$$

$$\psi_k(u_k, t) = e^{i(E_k/\hbar)t} \cdot \psi_k(u_k) \quad E_k = (n + \frac{1}{2}) \cdot \hbar \omega_k$$



See appendix C: quantization of elastic waves: phonons

Three dimensions

3-dimensional crystal:

s atoms per primitive cell:

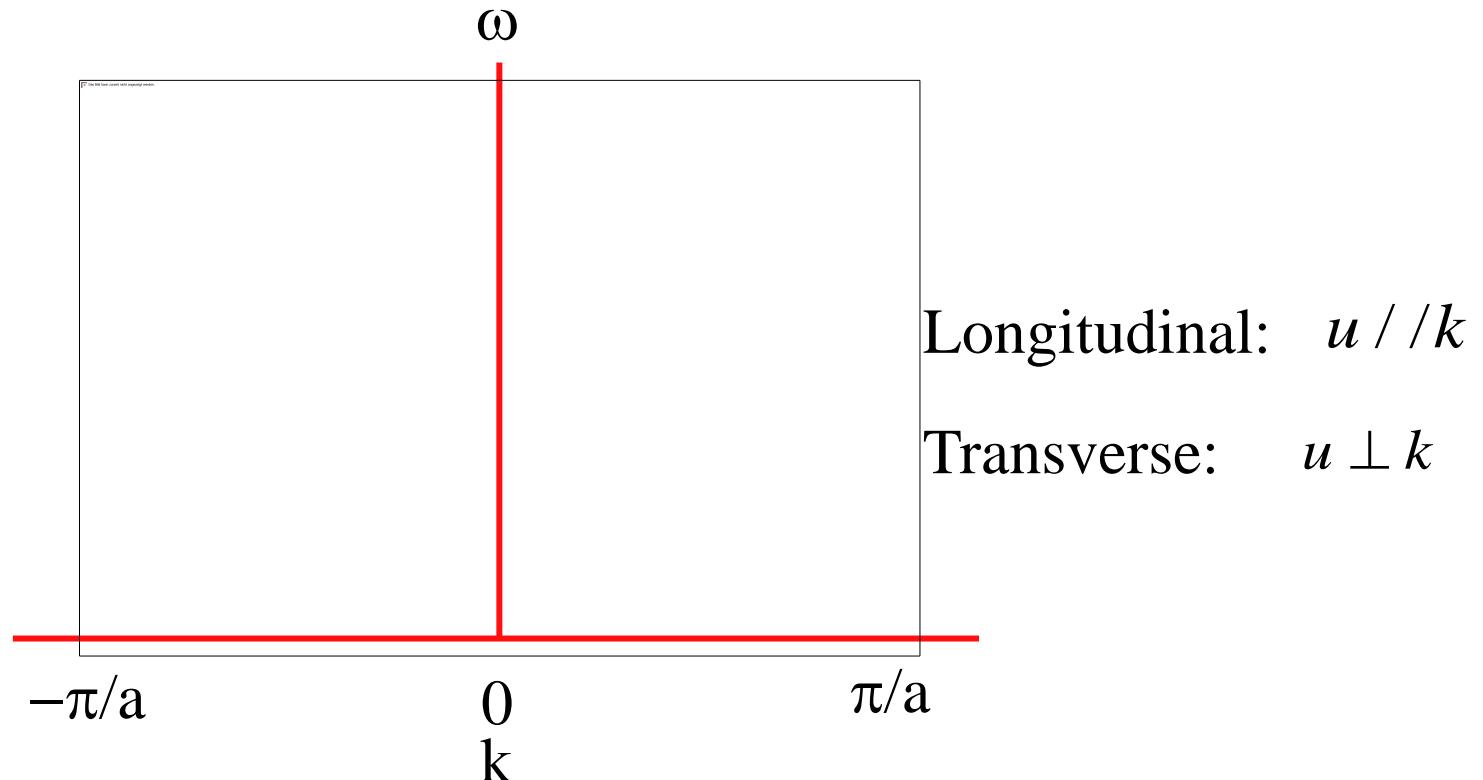
3 degrees of freedom per atom

3 acoustical branches

3s-3 optical branches

Optical modes

Acoustical modes



Properties of phonons

Any number can occupy the same vibrational mode u_k

Phonons are *bosons*

Thermal occupation given by Planck's distribution

$$\langle n_k \rangle = \frac{1}{e^{(\hbar\omega_k/k_bT)} - 1}$$

Zero-point energy: $E_0 = \sum_k \frac{1}{2} \hbar\omega_k$

Energy of 1 phonon: $\hbar\omega_k$

“Momentum” of 1 phonon: $\hbar k$

Phonons: Quantum excitations of solids

Measuring phonons

Inelastic neutron scattering

Inelastic light scattering (Raman/Brillouin)

(far) Infrared absorption

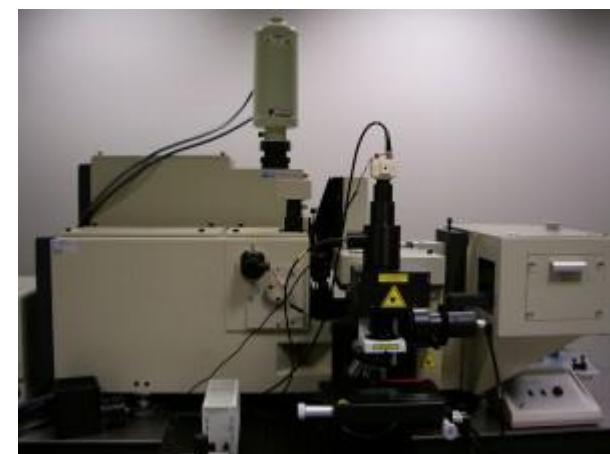
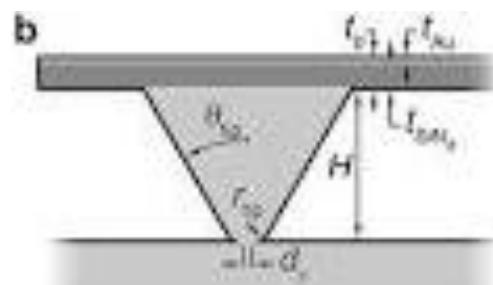
Electron energy loss spectroscopy

Inelastic X-ray scattering

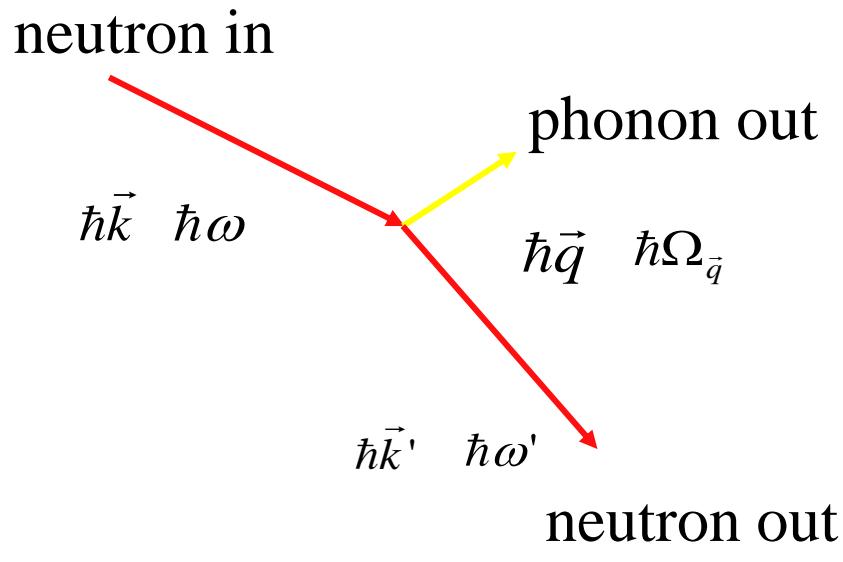
Ultrasound propagation

Point and tunnel spectroscopy

...



Inelastic scattering



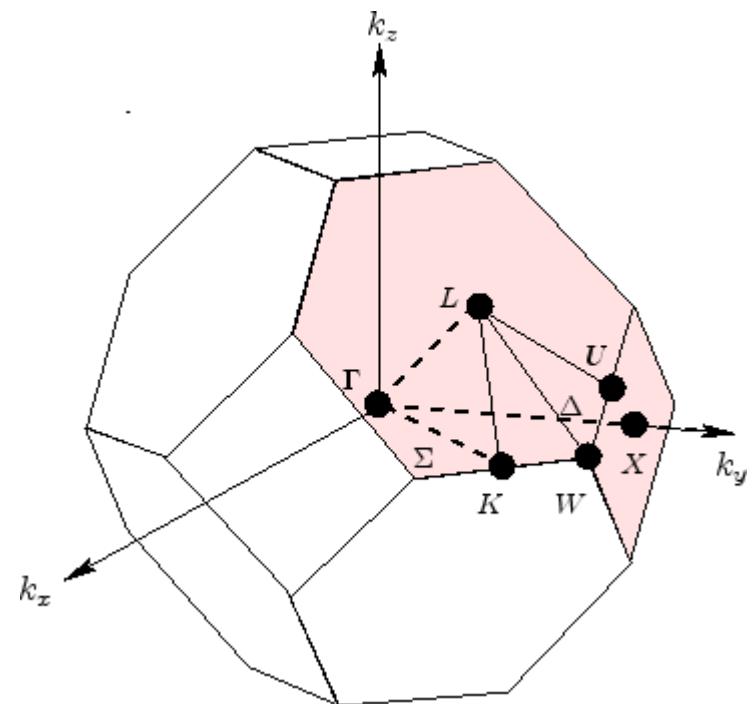
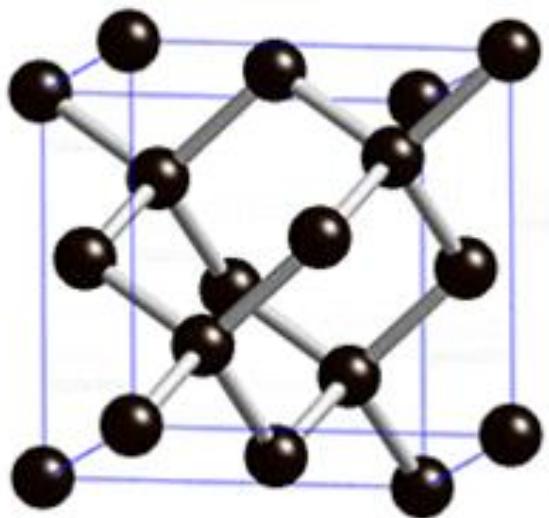
Energy conservation

$$\frac{\hbar^2 k^2}{2m_n} = \frac{\hbar^2 k'^2}{2m_n} \pm \hbar\Omega$$

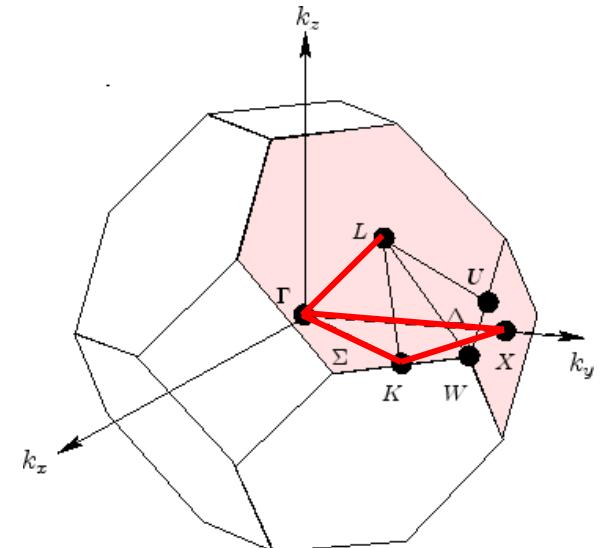
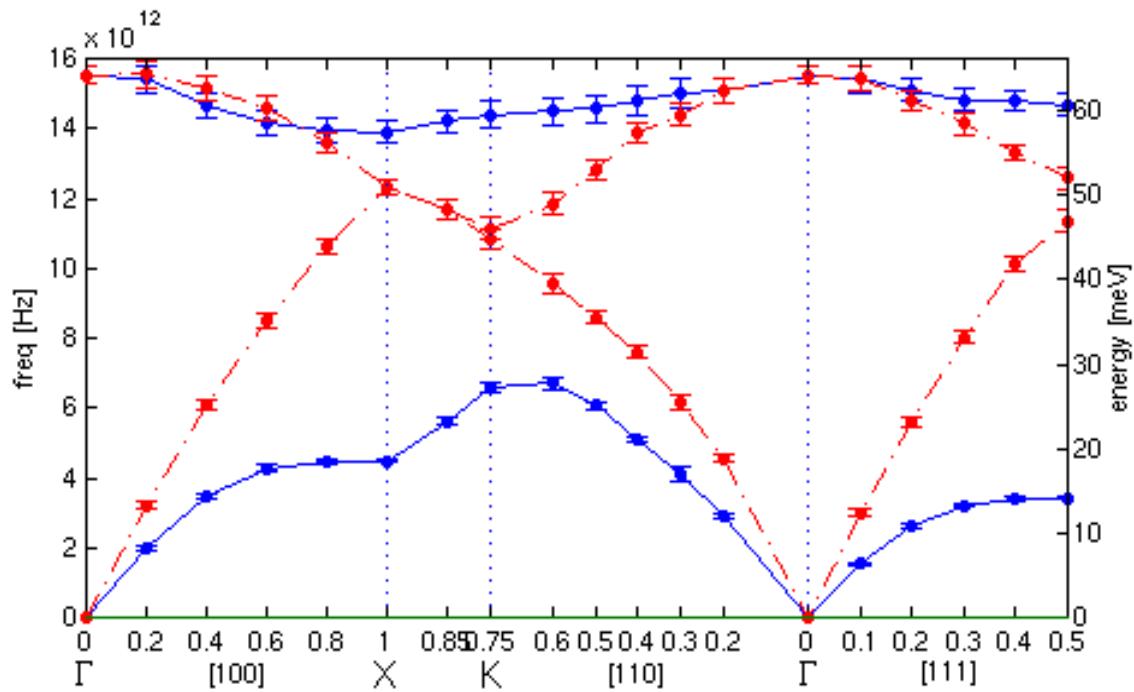
“Momentum” conservation

$$k = k' \pm q + G$$

Diamond lattice

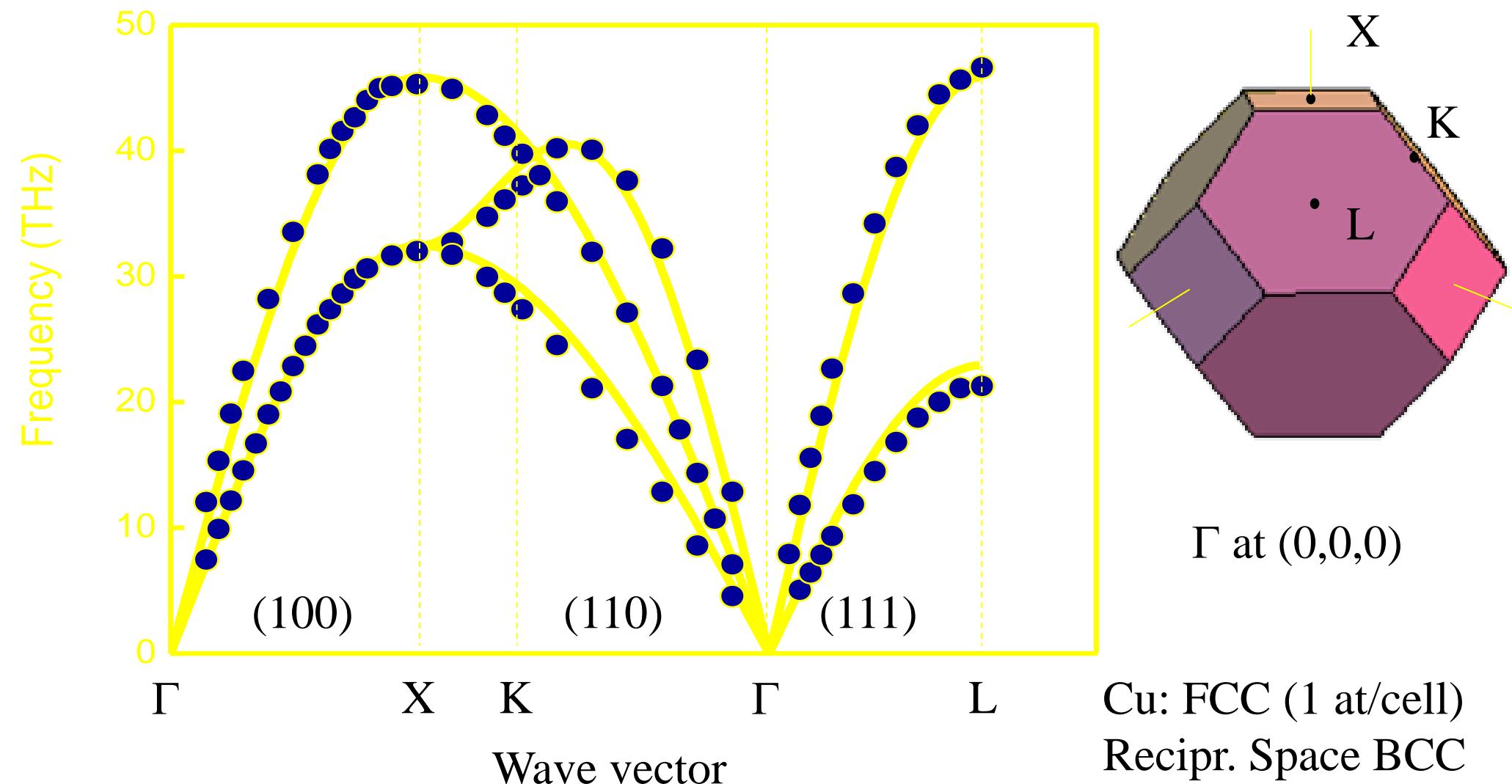


Phonon dispersion in Si



Si: FCC diamond structure (2 at. Prim. Cell)

Phonon dispersion in copper



Phonons

- Quantized lattice vibrations
- #modes: $3s$
- Optical & acoustical
- Transversal & longitudinal
- Relevant \mathbf{k} vectors in first BZ
- Thermal occupation: Planck
- Dispersion $\omega(\mathbf{k})$
- Energy $\hbar\omega(\mathbf{k})$
- ‘Momentum’ $\hbar\mathbf{k}$
- Sound velocity

Thermal properties

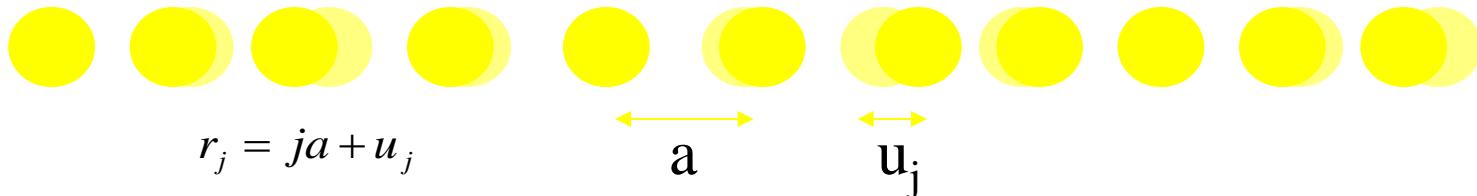
Thermal properties

- Thermal expansion (classical)
- Lattice specific heat
 - Density of States
 - Debye model
 - Einstein model
- Thermal conductivity
 - Phonon scattering, mean free path

Thermal expansion



Harmonic crystal: No thermal expansion!!



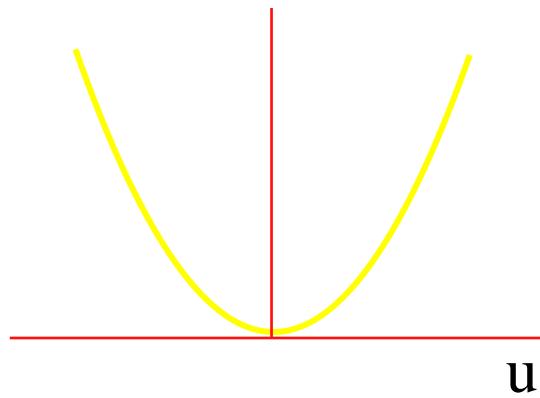
Harmonic

$$V(u_j) = \alpha \cdot u_j^2$$

$$a(T) = a + \langle u_j \rangle_T = a$$

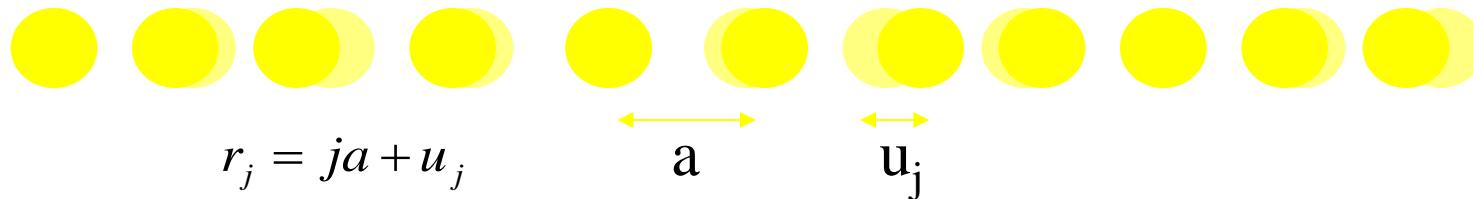
$$\langle u_j \rangle_T = \frac{\int du \cdot u e^{-V(u_j)/k_B T}}{\int du \cdot e^{-V(u_j)/k_B T}} = 0$$

$$V(u)$$



No lattice expansion !!

Anharmonicity: Thermal expansion (classical)

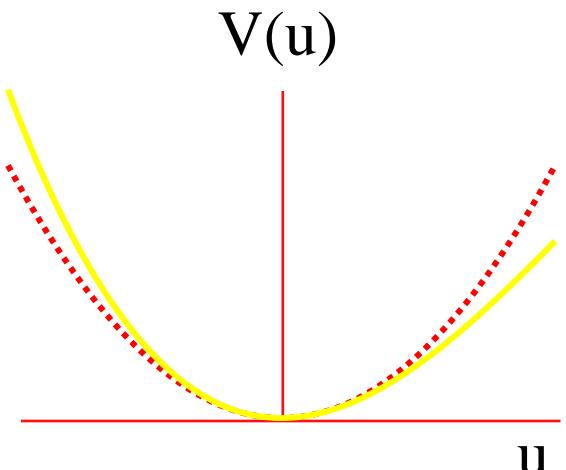


Weak anharmonicity

$$V(u_j) = \alpha \cdot u_j^2 - \gamma \cdot u_j^3$$

$$\langle u_j \rangle_T = \frac{\int du \cdot u e^{-V(u_j)/k_B T}}{\int du \cdot e^{-V(u_j)/k_B T}} \approx \frac{3/4 (k_B T)^{3/2} \sqrt{\pi} \gamma \alpha^{-5/2}}{\sqrt{k_B T} \sqrt{\pi} \alpha^{-1/2}}$$

$$a(T) = a_0 + \langle u_j \rangle_T = a_0 + \frac{3\gamma}{4\alpha^2} k_B T$$



Lattice expansion is caused by anharmonicity !

Specific heat

Heat capacity: $C_v = \frac{\partial U}{\partial T} \Big|_V$

Summation over modes k and branches p :

$$U = \sum_{k,p} U_{k,p} = \sum_{k,p} \langle n_{k,p} \rangle \hbar \omega_{k,p} = \sum_{k,p} \frac{\hbar \omega_{k,p}}{e^{\hbar \omega_{k,p} / k_B T} - 1}$$

Number of modes in range $\omega \rightarrow \omega + d\omega$: $d\omega D_p(\omega)$

D(ω): Density of states

$$\sum_k \rightarrow \int d\omega D_p(\omega)$$

$$U = \sum_p \int d\omega D_p(\omega) \frac{\hbar \omega}{e^{\hbar \omega / k_B T} - 1}$$

Lattice heat capacity

$$\sum_k \rightarrow \int d\omega D_p(\omega)$$



$$U = \sum_p \sum_k U_{k,p} = \sum_p \sum_k \langle n_{k,p} \rangle \hbar \omega_{k,p} = \sum_p \int d\omega D_p(\omega) \frac{\hbar \omega}{e^{\hbar \omega / k_B T} - 1}$$



$$C_{lattice} = \frac{\partial U}{\partial T} = k_B \sum_p \int d\omega D_p(\omega) \frac{x^2 e^x}{(e^x - 1)^2}$$

All lattice properties in $D(\omega)$:

Density of states: # modes per unit frequency

Density of states in 1D

1D crystal, N atoms, length L=Na

Vibrational mode: $u_k(j, t) = u_k e^{-i(\omega t - kaj)}$

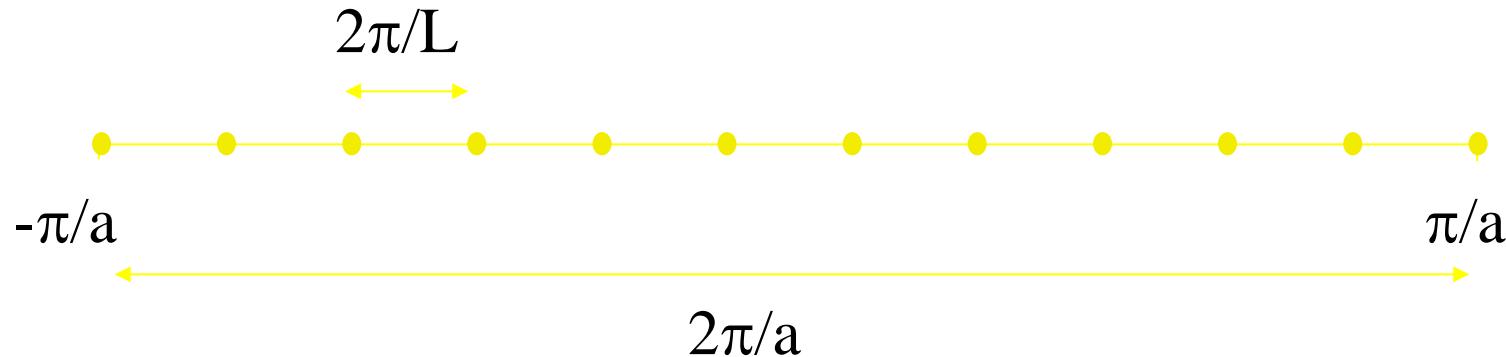
Periodicity over L=Na: $u_k \cdot e^{i kaj} = u_k \cdot e^{i ka(j+N)}$

$$\rightarrow e^{i kaN} = 1 \quad kaN = 2\pi s \quad k = \frac{2\pi s}{Na} = \frac{2\pi}{L} s$$

$$-\frac{\pi}{a} < k \leq \frac{\pi}{a} \Rightarrow s = -\frac{N-1}{2}, \dots, \frac{N-1}{2}, \frac{N}{2}$$

i.e. N modes in the first BZ

Density of states in 1D



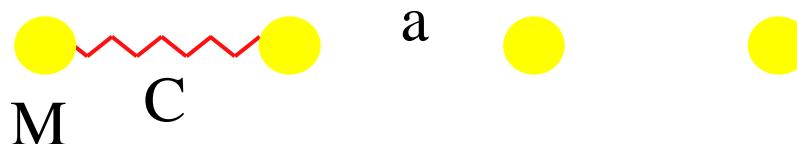
$$\text{\# modes/unit 'length'} = N / (2\pi/a) = L / 2\pi$$

In interval dk :

$$D(k)dk = \frac{N}{2\pi/a} dk = \frac{L}{2\pi} dk$$

$$D(\omega)d\omega = \frac{L}{2\pi} \frac{dk}{d\omega} d\omega$$

Density of states (1D)



$$D(\omega)d\omega = \frac{L}{2\pi} \frac{dk}{d\omega} d\omega$$

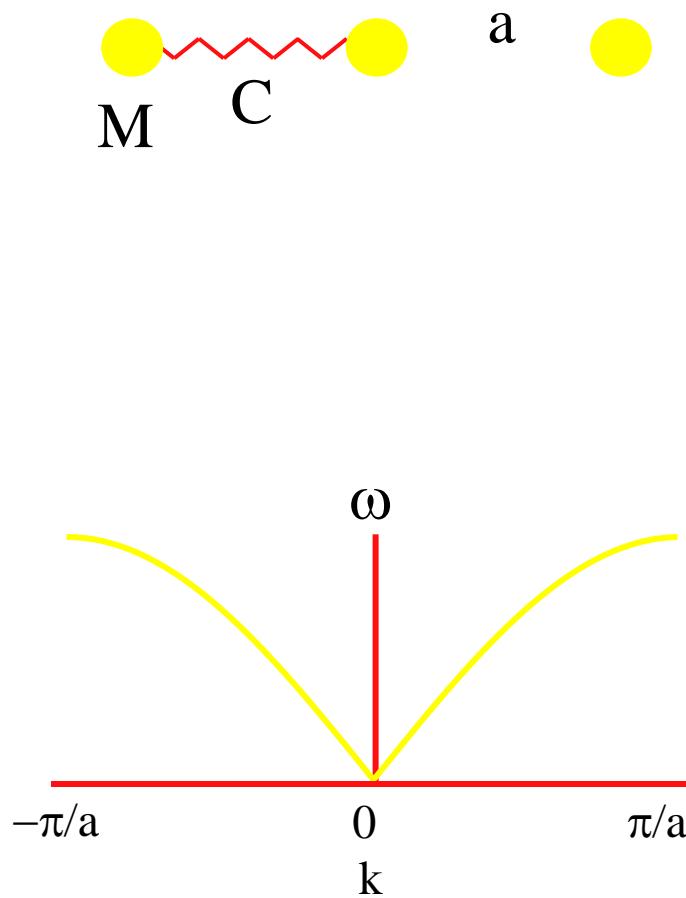
1D, 1 at./cell:

$$\omega(k) = \sqrt{\frac{4C}{m}} \left| \sin\left(\frac{ka}{2}\right) \right| \Rightarrow \omega(k) = \omega_m \left| \sin(ka/2) \right|$$

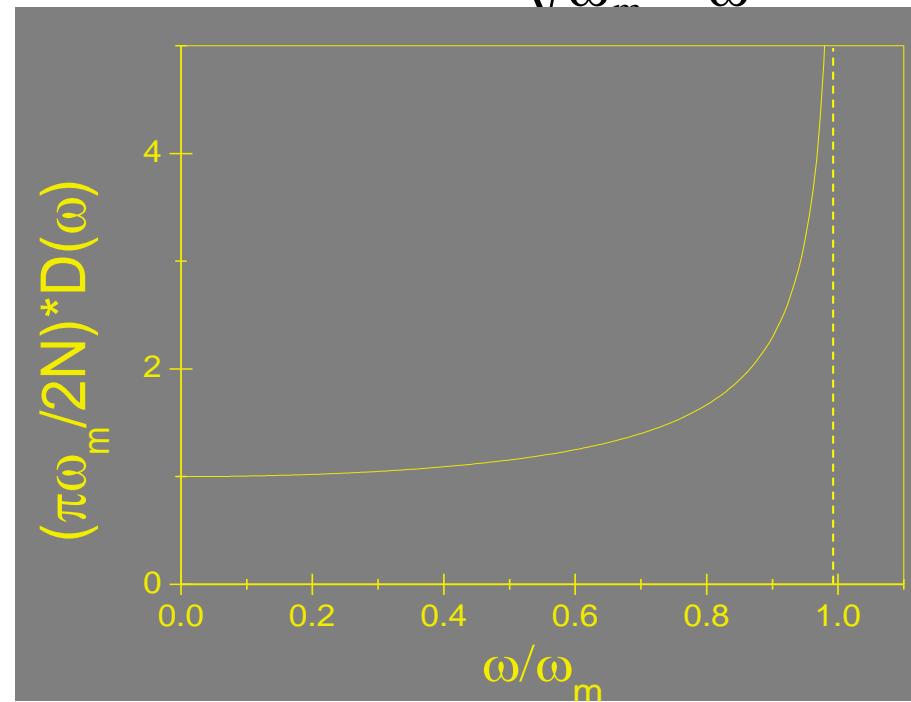
$$\left[\frac{\partial \omega(k)}{\partial k} \right]^{-1} = \frac{2}{a} \frac{1}{\omega_m |\cos(ka/2)|} = \frac{2}{a} \frac{1}{\sqrt{\omega_m^2 - \omega^2}}$$

$$\Rightarrow D(\omega) = 2 \frac{N}{\pi} \frac{1}{\sqrt{1 - \omega^2}}$$

Density of states (1D)



$$D(\omega) = 2 \frac{N}{\pi} \frac{1}{\sqrt{\omega_m^2 - \omega^2}}$$



Density of states in 3D

3D crystal, N^3 atoms, cube length L

Periodic boundary conditions: $e^{i(k_x x + k_y y + k_z z)} = e^{i(k_x(x+L) + k_y(y+L) + k_z(z+L))}$

$$\rightarrow k_x, k_y, k_z = s \cdot \frac{2\pi}{L}; \quad s = -\frac{N-1}{2}, \dots, \frac{N-1}{2}, \frac{N}{2}$$

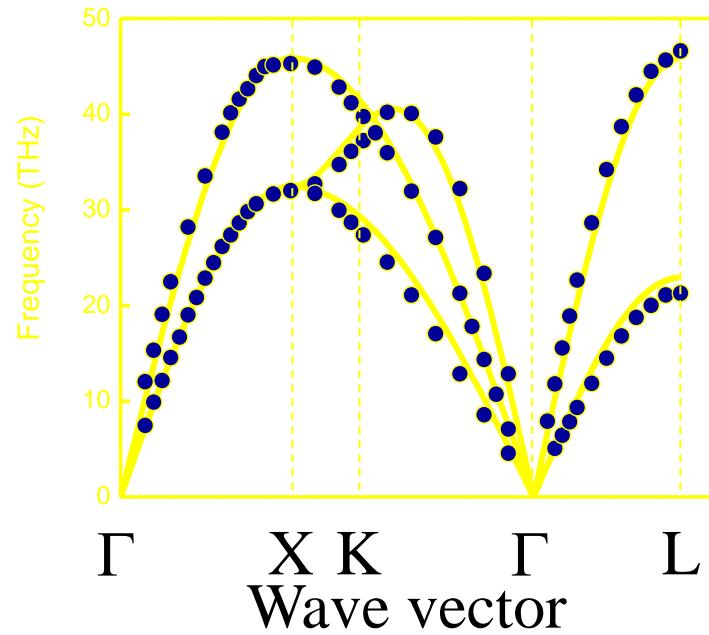
One value of k per volume $\left(\frac{2\pi}{L}\right)^3$

Total # k values in sphere with radius k: $N(k) = \frac{V_k}{(2\pi/L)^3} = \frac{4\pi k^3 / 3}{(2\pi)^3 / V}$

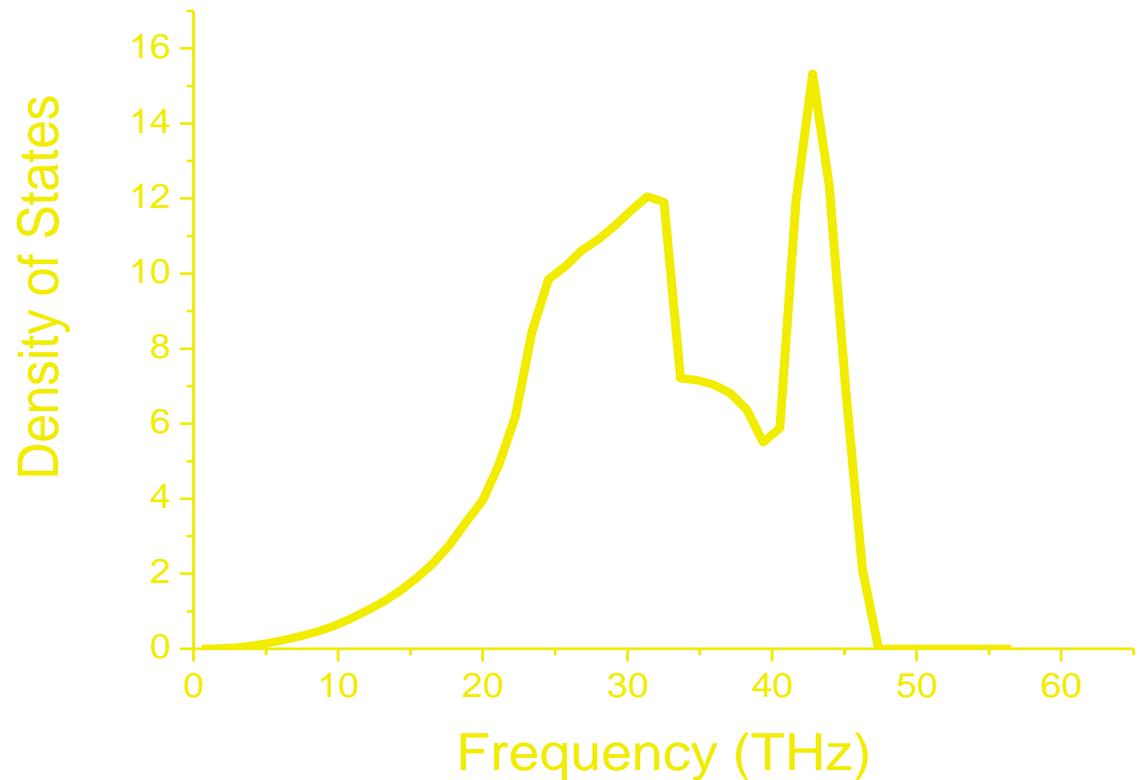
$$D(k) = \frac{dN(k)}{dk} = \frac{V k^2}{2\pi^2}$$

$$D(\omega) = \frac{V k^2}{2\pi^2} \frac{dk}{d\omega}$$

Density of states in 3D



COPPER



Density of States

	$D(k)$	$D(\omega)$
1D	$\frac{L}{2\pi}$	$\frac{L}{2\pi} \frac{dk}{d\omega}$
2D	$\frac{A}{2\pi^2} k$	$\frac{A}{2\pi^2} k \frac{dk}{d\omega}$
3D	$\frac{V}{2\pi^2} k^2$	$\frac{V}{2\pi^2} k^2 \frac{dk}{d\omega}$

Back to lattice heat capacity

$$C_{lattice} = \frac{\partial U}{\partial T} = k_B \sum_p \int d\omega D_p(\omega) \frac{x^2 e^x}{(e^x - 1)^2}$$

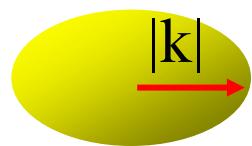
DOS in general complicated function
Simplifications:

- Debye model (take sound velocity constant)
- Einstein model (take phonon frequency constant)

Debye model for DOS

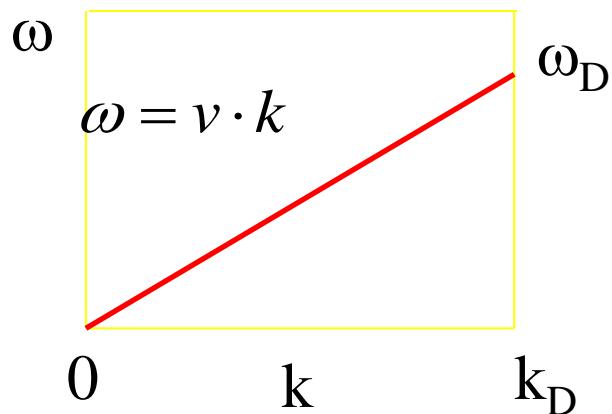
$\omega = v \cdot k$

Number of modes with $|k'| < |k|$ for each polarization (branch):



$$N(|\vec{k}|) = \frac{\frac{4}{3}\pi|\vec{k}|^3}{\left(\frac{2\pi}{V_{\text{cell}}}\right)^3}$$

Number of modes: $N(k_D) = N_{\text{atom}}$



$$\Rightarrow k_D = \left(\frac{6\pi^2 N_{\text{atom}}}{V_{\text{cell}}} \right)^{1/3}$$

$$\Rightarrow N(\omega < \omega_D) = \frac{V_{\text{cell}}}{(2\pi)^3} \frac{4\pi}{3} \left(\frac{\omega}{v} \right)^3$$

Debije model

Debije Frequency:

$$\omega_D = v \left(\frac{6\pi^2 N_{atom}}{V_{cell}} \right)^{1/3}$$

Debije Temperature:

$$\theta = \frac{\hbar \omega_D}{k_B} = \frac{\hbar v}{k_B} \left(\frac{6\pi^2 N_{atom}}{V_{cell}} \right)^{1/3}$$

Density of states:

$$D(\omega) = \frac{dN(\omega)}{d\omega} = V_{cell} \frac{\omega^2}{2\pi^2 v^3}$$

Total energy stored in phonons:

$$U = \sum_{k,p} \frac{\hbar \omega_{k,p}}{e^{\hbar \omega_{k,p}/k_B T} - 1} = 3 \int_0^{\omega_D} \frac{\hbar \omega}{e^{\hbar \omega/k_B T} - 1} D(\omega) d\omega$$

Debye specific heat

Total energy :

$$U = \frac{3V_{cell}\hbar}{2\pi^2 v^3} \int_0^{\omega_D} \frac{\omega^3}{\exp(\hbar\omega/k_B T) - 1} d\omega$$

Specific heat:

$$C_{lat} = \frac{dU}{dT} = \frac{3V_{cell}\hbar}{2\pi^2 v^3} \int_0^{\omega_D} \frac{\omega^3 \exp(\hbar\omega/k_B T)}{(\exp(\hbar\omega/k_B T) - 1)^2} \frac{\hbar\omega}{k_B T^2} d\omega$$

$$C_{lat} = \frac{dU}{dT} = 9N_{atom} \left(\frac{T}{\theta} \right)^3 \cdot \int_0^{\theta/T} \frac{x^4 e^x}{(e^x - 1)^2} dx \quad x = \frac{\hbar\omega}{k_B T}$$

Debije T³ law

Low temperature limit: $\theta / T \rightarrow \infty$

$$\int_0^{\infty} \frac{x^4 e^x}{(e^x - 1)^2} dx = \frac{\pi^4}{15}$$

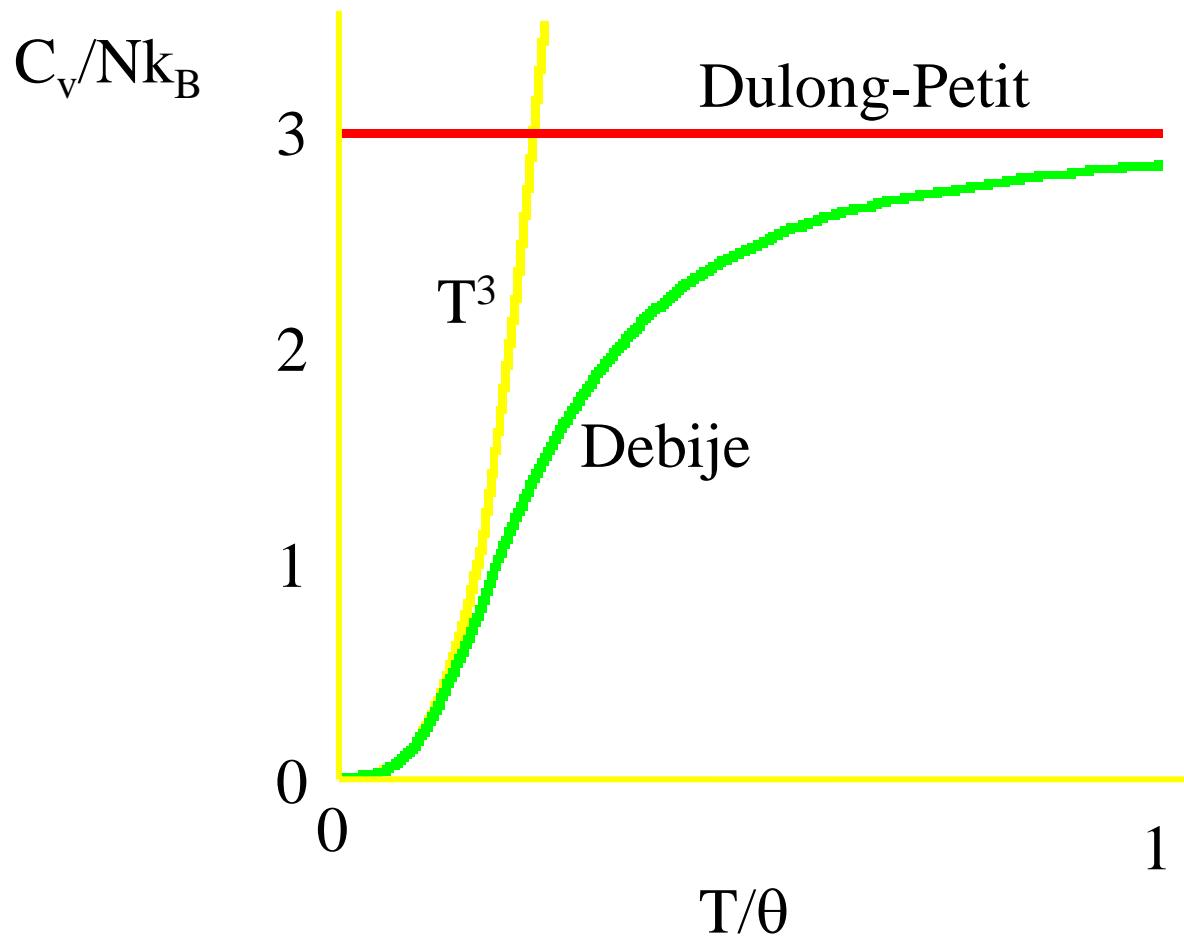
$$C_{lat} = \frac{12\pi^4}{5} N_{atom} k_B \left(\frac{T}{\theta}\right)^3$$

High temperature limit: $\theta / T \rightarrow 0$

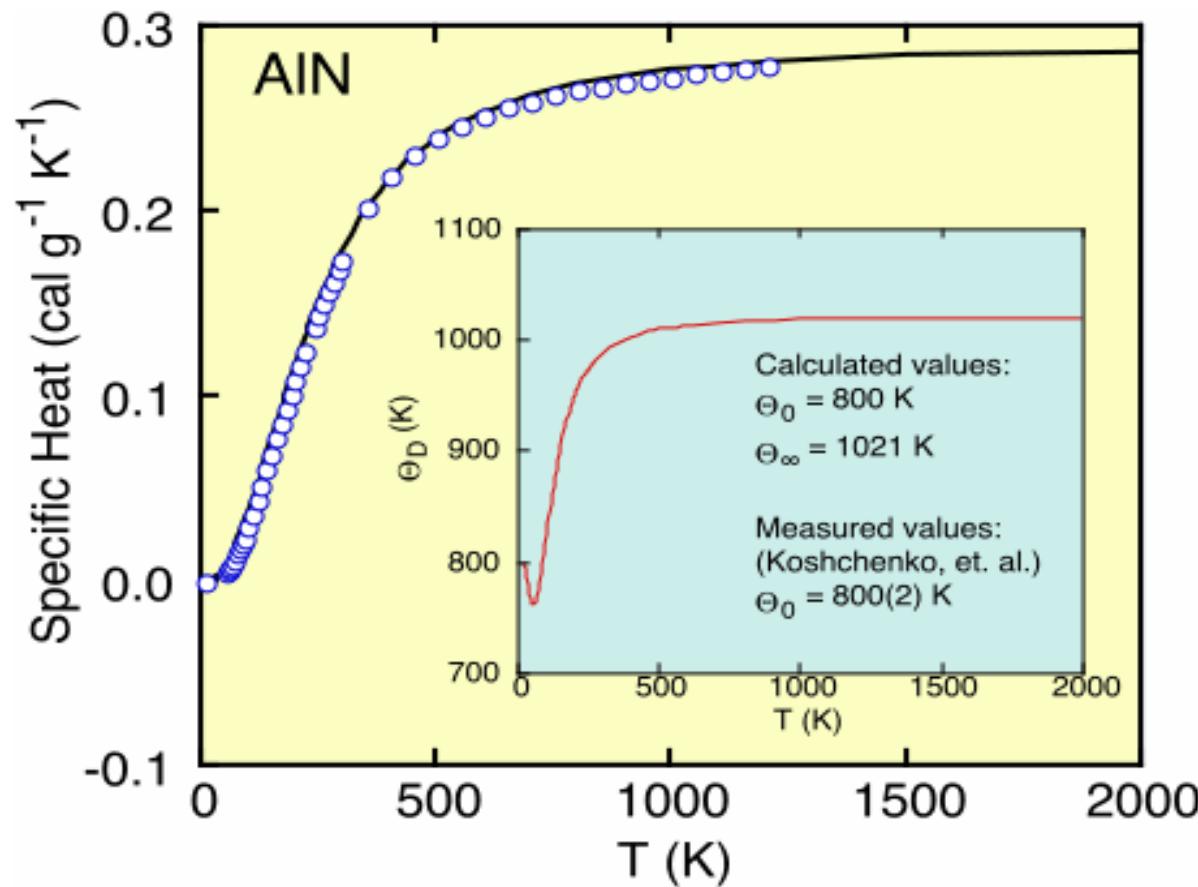
$$\int_0^{\theta/T} \frac{x^4 e^x}{(e^x - 1)^2} dx \approx \frac{1}{3} \left(\frac{\theta}{T}\right)^3$$

$$C_{lat} = 3N_{atom} k_B \quad (\text{Dulong-Petit, } U=3N \cdot k_B T)$$

Specific heat



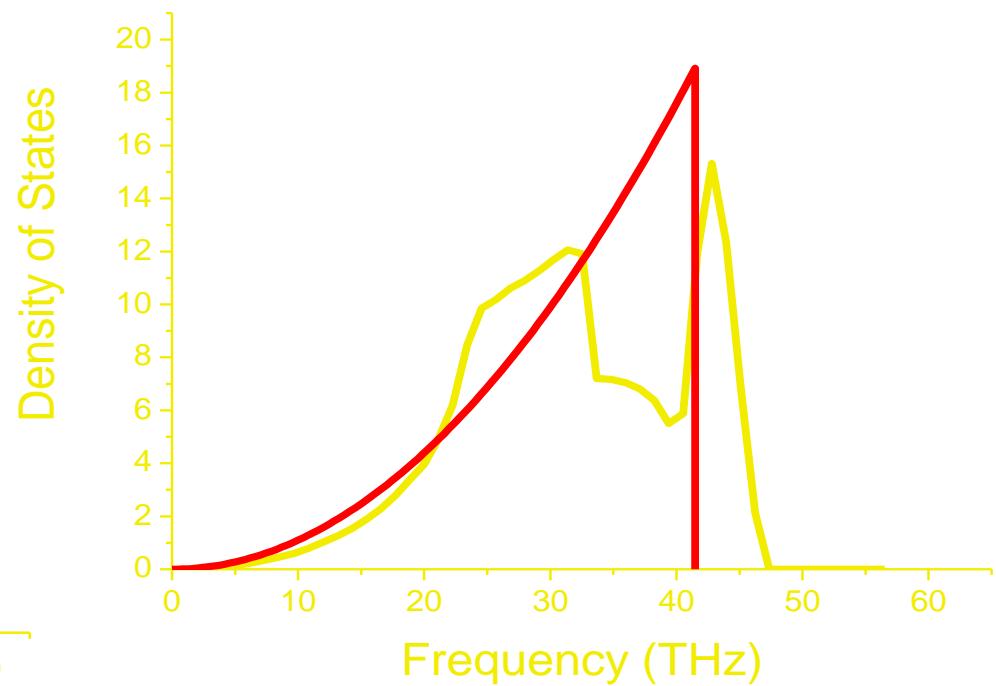
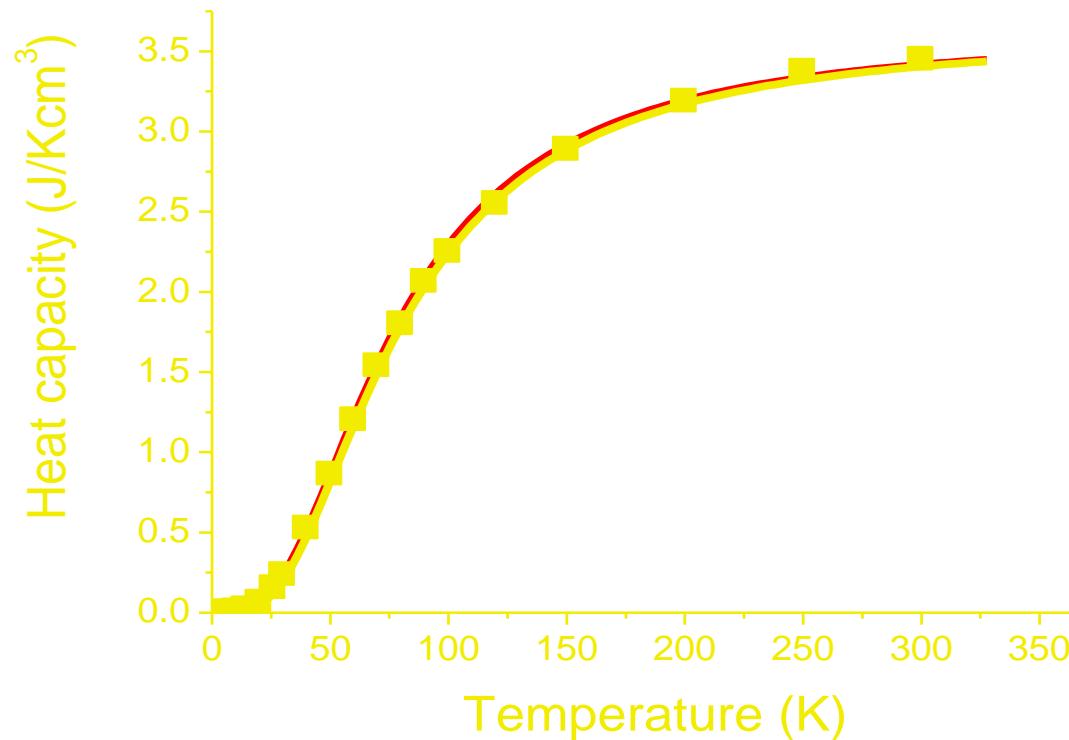
Specific heat AlN



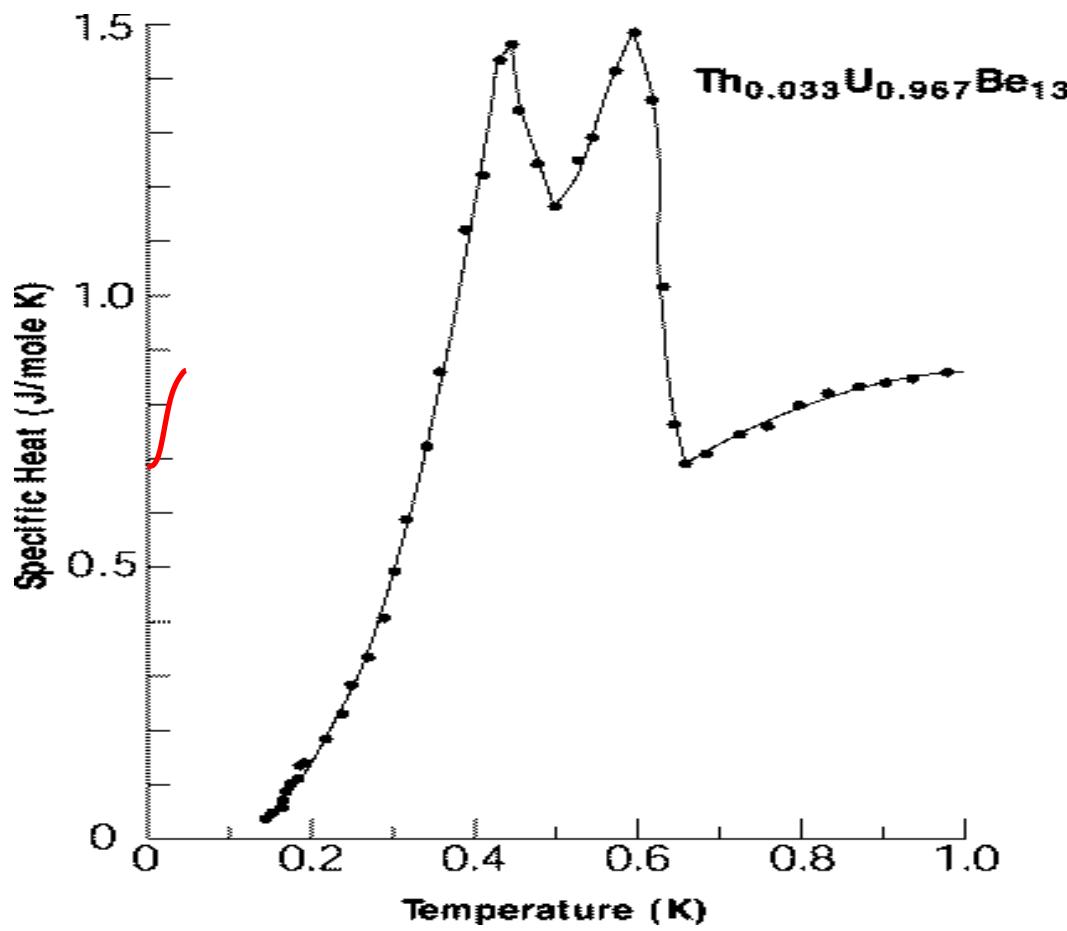
Specific heat Aluminum Nitride (Koshchenko et al., 1985)

Specific heat Cu

Copper again



Specific heat $\text{Th}_x\text{U}_{1-x}\text{Be}_{13}$



Heavy fermion system, 2 S.C. transitions (Z. Fisk et al., 2000)

Einstein model

Simpler model, approximation for optical phonons

$$D(\omega) = N_{atoms} \delta(\omega - \omega_e)$$

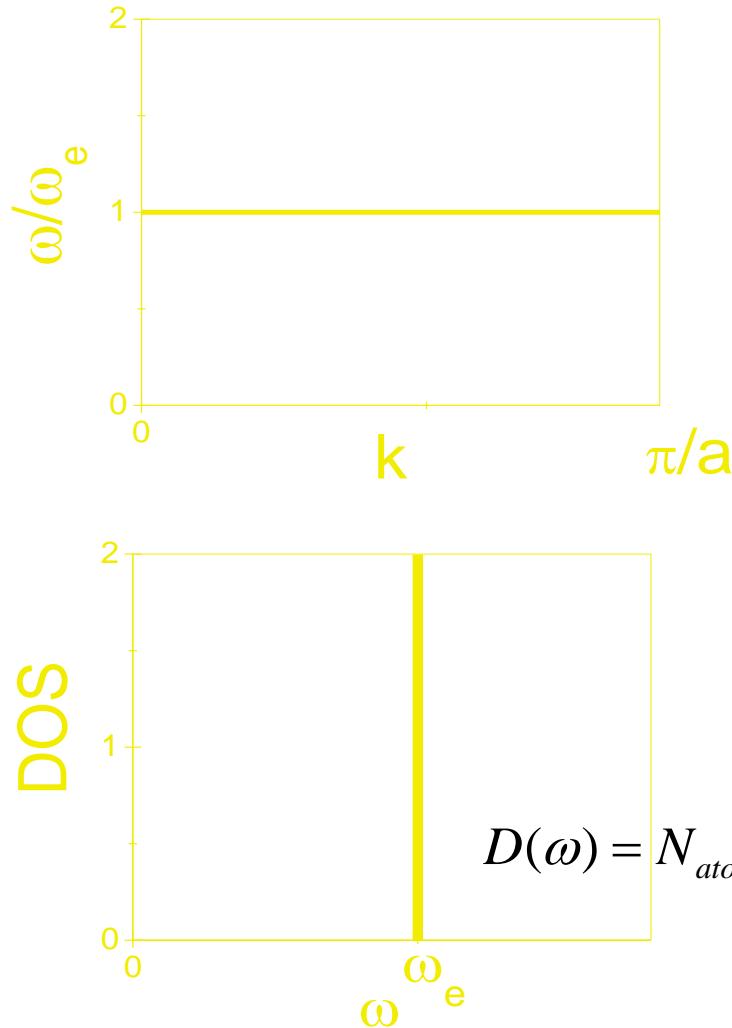
$$U = 3N_{atoms} \langle n(\omega_e) \rangle \hbar \omega_e = \frac{3N_{atoms} \hbar \omega_e}{e^{\hbar \omega_e / k_B T} - 1}$$

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V = 3N_{atoms} k_B \left(\frac{\hbar \omega_e}{k_B T} \right)^2 \frac{e^{\hbar \omega_e / k_B T}}{\left(e^{\hbar \omega_e / k_B T} - 1 \right)^2}$$

Limits $T \rightarrow 0: C_v \propto x^2 e^{-x} = 0$

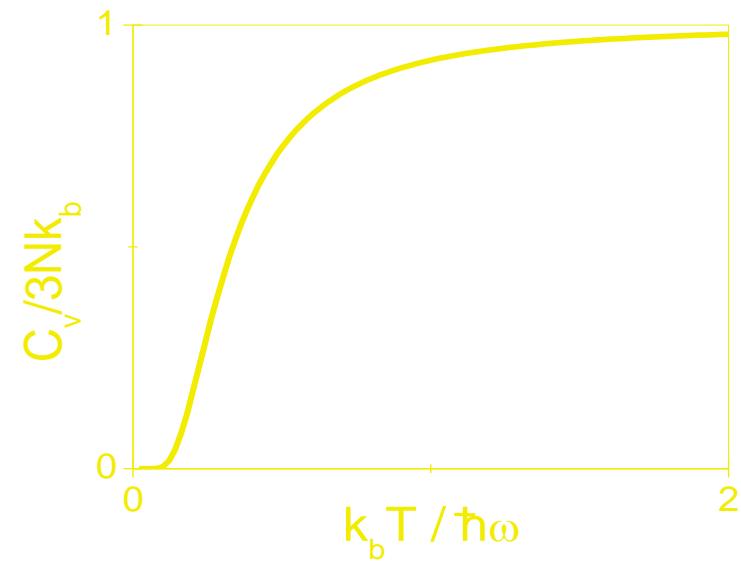
$$T \rightarrow \infty: C_v = 3N_{atoms} k_B$$

Einstein model, C_V

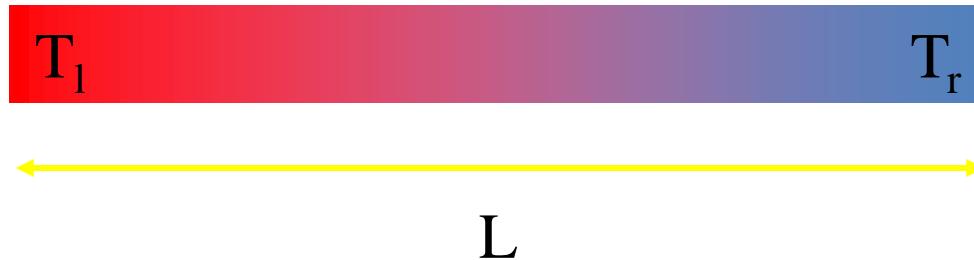


$$D(\omega) = N_{atoms} \delta(\omega - \omega_e)$$

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V = 3N_{atoms}k_B \left(\frac{\hbar\omega_e}{k_B T} \right)^2 \frac{e^{\hbar\omega_e/k_B T}}{(e^{\hbar\omega_e/k_B T} - 1)^2}$$



Thermal conductivity

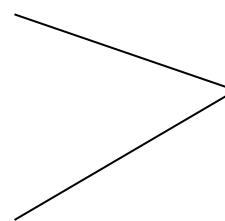


Thermal energy flux:

$$J_u = \frac{dw}{dt}$$

Thermal gradient:

$$\frac{dT}{dx} = \frac{T_r - T_l}{L}$$



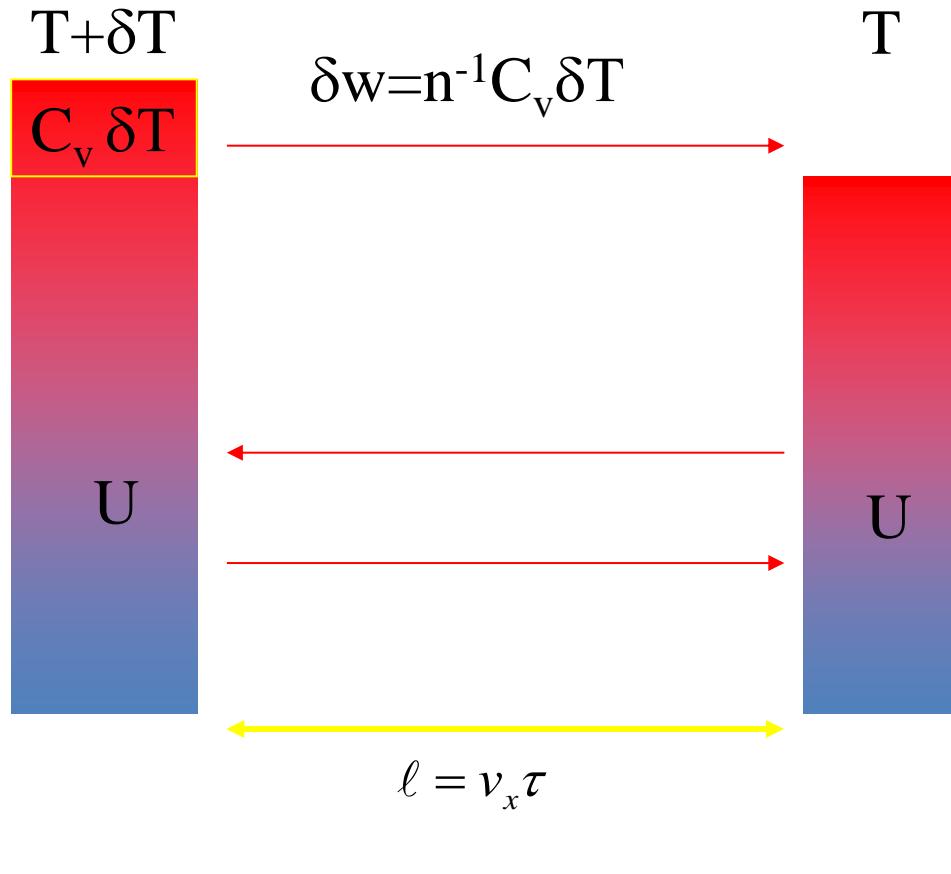
$$J_u = -\kappa \frac{dT}{dx}$$

κ : Thermal conductivity

Is due to diffusion of particles (here phonons)

Thermal conductivity

$$J_u = -\kappa \frac{dT}{dx}$$



$$J_u = \frac{dw}{dt} = n \langle v_x \cdot \delta w \rangle = C_v \langle v_x \delta T \rangle$$

$$\delta T = -v_x \tau \cdot \frac{dT}{dx}$$

$$J_u = -C_v \tau \frac{dT}{dx} \langle v_x^2 \rangle$$

$$\left. \begin{aligned} \langle v_x^2 \rangle &= \frac{1}{3} v^2 \\ \tau &= \ell / v \end{aligned} \right\} \Rightarrow J_u = -\frac{1}{3} C_v v \ell \frac{dT}{dx}$$



$$\kappa = \frac{1}{3} C_v v \ell$$

Scattering of phonons

Phonon mean free path ℓ limited by

- Imperfections, crystal boundaries, isotopes
- Phonon-phonon scattering (normal processes)
- Phonon-phonon scattering (Umklapp processes)

Harmonic approximation: NO phonon-phonon scattering

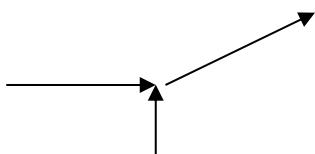
Scattering of phonons

Imperfections etc.: $\ell = T$ independent: $\kappa \propto v\ell C_v(T) \propto T^3$

Normal processes:

$$\hbar\omega_{k_1} + \hbar\omega_{k_2} = \hbar\omega_{k_3}$$

$$\vec{k}_1 + \vec{k}_2 = \vec{k}_3$$



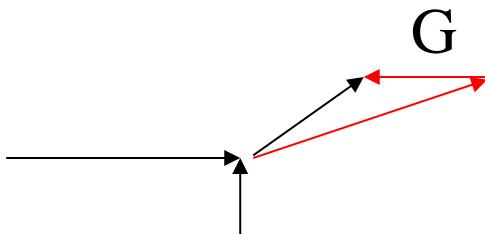
No net change of phonon momentum

Umklapp processes:

$$\hbar\omega_{k_1} + \hbar\omega_{k_2} = \hbar\omega_{k_3}$$

$$\vec{k}_1 + \vec{k}_2 = \vec{k}_3 + \vec{G}$$

Momentum transferred to crystal:



$$\hbar\vec{G}$$

Thermal conductivity

$$\kappa = \frac{1}{3} C_v v \ell$$

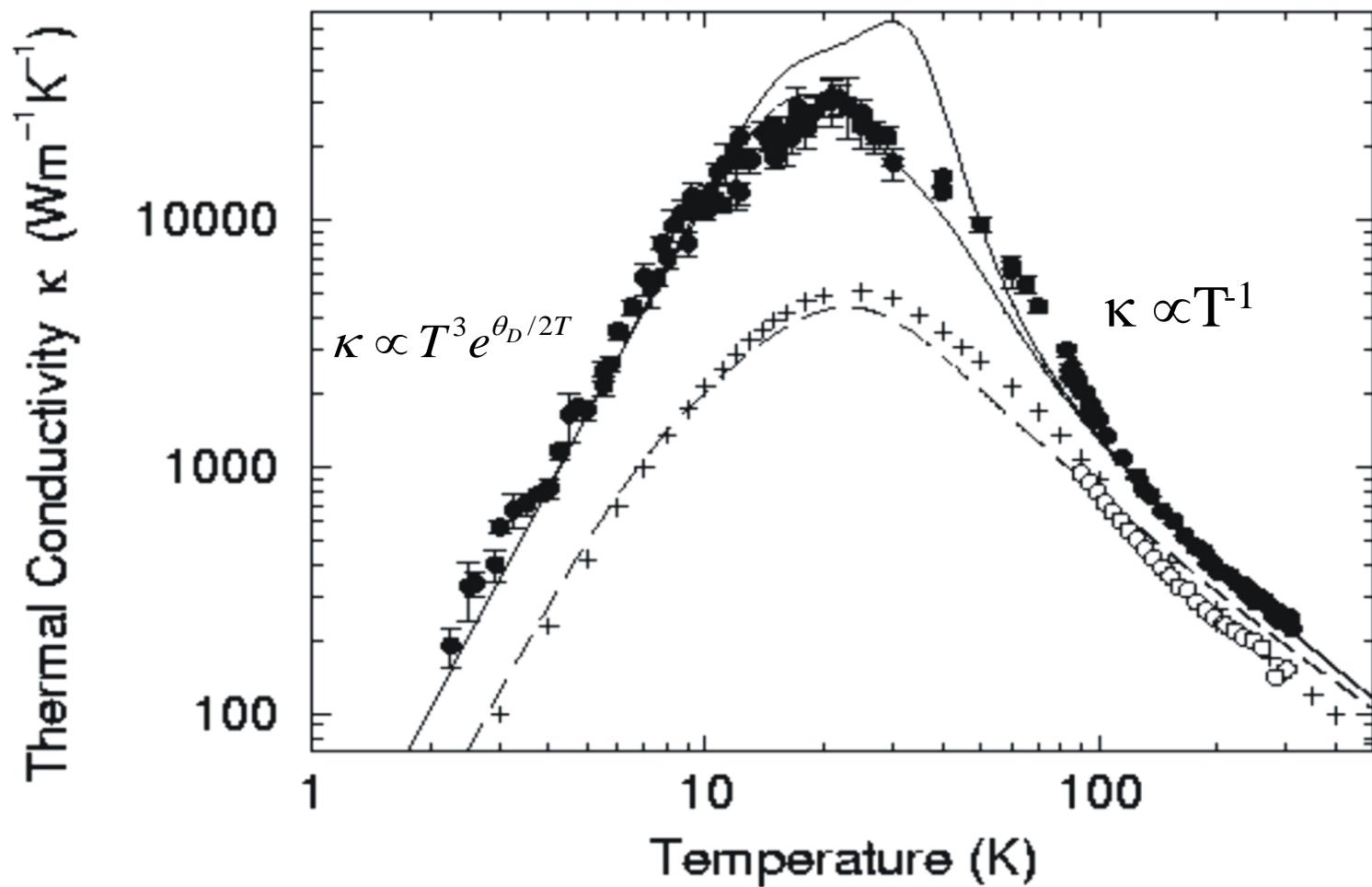
High T: C_v constant, $\ell \propto n(\omega) \propto T^1 \quad \rightarrow \quad \kappa \propto T^1$

Low T: imperfections give $\kappa \propto T^3$

Umklapp: $\ell^{-1} \propto n(\hbar\omega_D / 2) = \frac{1}{e^{\theta_D/2T} - 1} \approx e^{-\theta_D/2T}$

$$\kappa \propto T^3 e^{\theta_D/2T}$$

Thermal conductivity



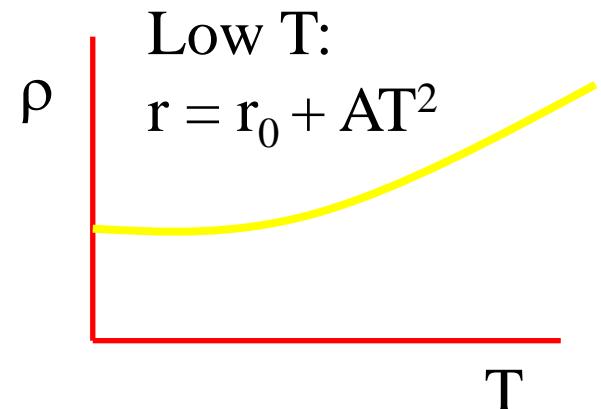
Isotope pure Silicon (T. Ruf et al. Sol. St. Comm. 2000)

METALS

What is a metal ?

Electrical conductivity:

$$\rho_{300\text{ K}} \sim 1.7 \text{ (Cu)} - 153 \text{ } \mu\Omega\cdot\text{cm (Pu)}$$



Thermal conductivity:

$$\text{Cu: } K_{300\text{ K}} \sim 3.9 \text{ W/Kcm} \quad \text{Pu: } K_{300\text{ K}} \sim 0.049 \text{ W/Kcm}$$

$$\text{Wiedemann-Franz: } K/\sigma = \alpha T$$

$$\text{Quartz: } K \sim 0.13 \text{ W/Kcm} \quad \text{NaCl: } K \sim 0.27 \text{ W/Kcm}$$

Reflectivity:

Highly reflecting upto plasma-frequency

$$\omega < \omega_p \quad \omega_p^2 = 4 \pi n e^2 / m$$