Solid state physics for Nano

Lecture 5: Specific heat and anharmonicity

Prof. Dr. U. Pietsch

Safety instructions: 13.5.19 10 am

Additional excercise: 10.5. 12:30

B019

Pseudo-momentum of phonons

C. Kittel p 101: A phonon of wavector K will interact with particles such as photons, neutrons, and electrons as if it had a momentum $\hbar$K. However, a phonon does not carry physical momentum. [...] The true momentum of the whole system always is rigorously conserved.

Phonons have no physical momentum , p= $\hbar$K, because the the atomic displacement is on relative coordinates and the sum over all these atomic displacements is always zero

$$p = M\frac{du}{dt}\sum u_s = M\frac{du}{dt}\sum e^{iSKa} = M\frac{du}{dt}\frac{1-\exp(iNka)}{1-\exp(ika)}$$

Crystal length L=Na → k=2πl/Na; with l – integer; $\exp(iNka) = \exp(i2\pi l) = 1$

Because of $1-\exp(iNka) = 0$ → $p = M\frac{du}{dt}\sum u_s = 0$

BUT: **Phonon can exchange momentum by interaction with other quasi particles : electron – phonon intercation, phonon-phonon interaction**

Methods to measure phonons: neutron scattering

$$\boxed{E = \frac{\hbar^2 k^2}{2m} = 2.07214\ \mathrm{meV\,\mathring{A}}^2 \times k^2}$$

$$m_n = 1.675 \times 10^{-24}\,\mathrm{g}$$

$$\boxed{\lambda = \frac{2\pi}{k} = \frac{9.044605\ \mathrm{\mathring{A}}}{\sqrt{E[\mathrm{meV}]}}}$$

$$\lambda = \frac{h}{p} = \frac{h}{\sqrt{2m_n E_{kin}}}$$

$$1\,\mathrm{meV} = 1.6\times10^{-9}\,\mathrm{erg} = 11.6\,\mathrm{K} = 0.24\,\mathrm{THz}$$

$\boxed{E = Ue}$ $\boxed{E = \kappa T}$ $\boxed{E = h\nu}$

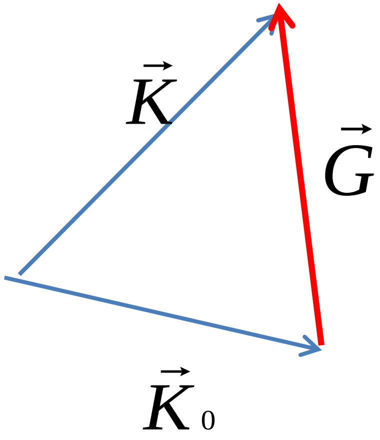
$\boxed{\lambda = 5\ \mathrm{A} = 3.3\,\mathrm{meV}}$

De Broglie
1892- 1987

elastic scattering

$$E = E_0$$

$$\vec{K} - \vec{K}_0 = \vec{G}$$

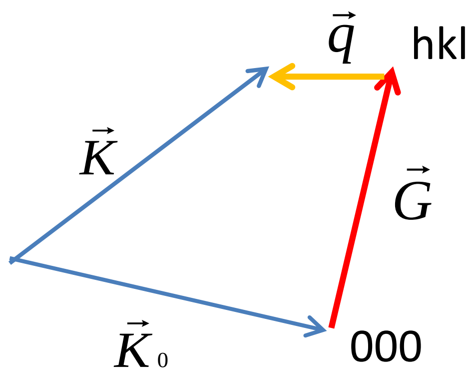


Methods to measure phonons: neutron scattering

Inelastic neutron scattering

$E <> E_0$

$$\vec{K} = \vec{K}' - \vec{K}_0 = \vec{G} \mp \vec{q}$$

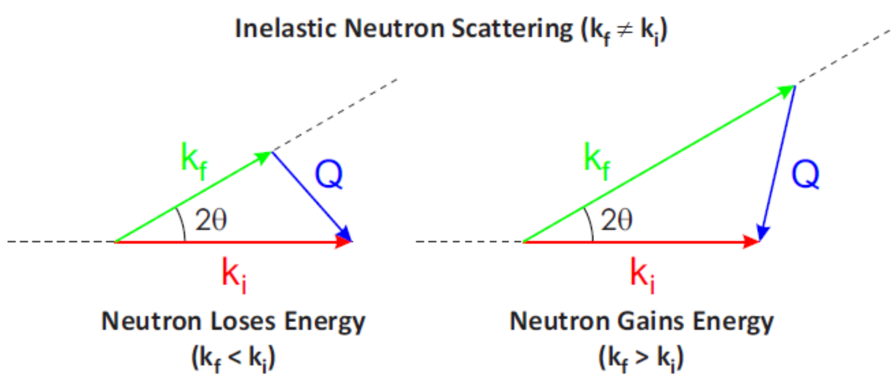


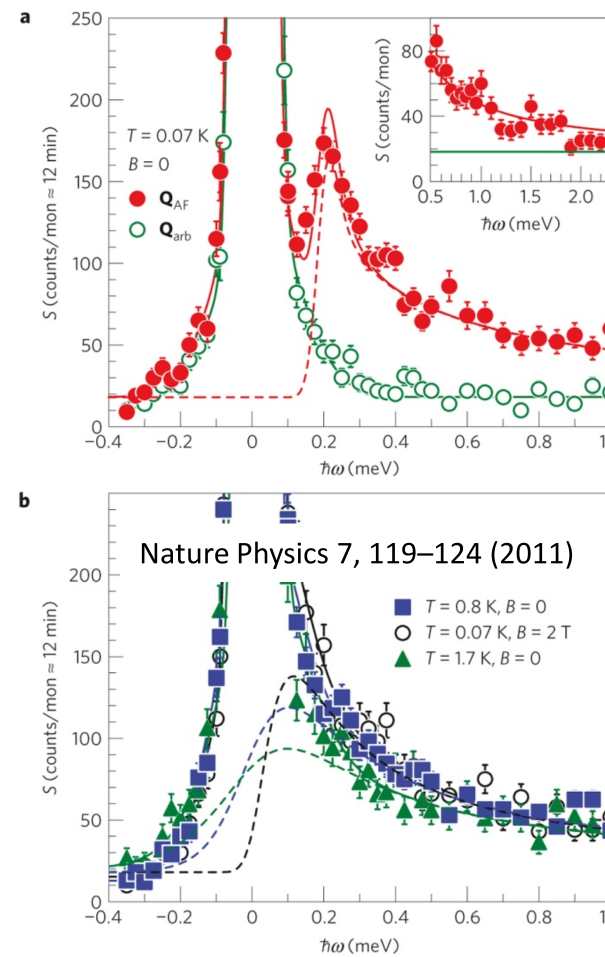
Phonon is created (+) or annihilated (-)

$$E_0 = E' \pm \hbar\omega$$

Energy conservation

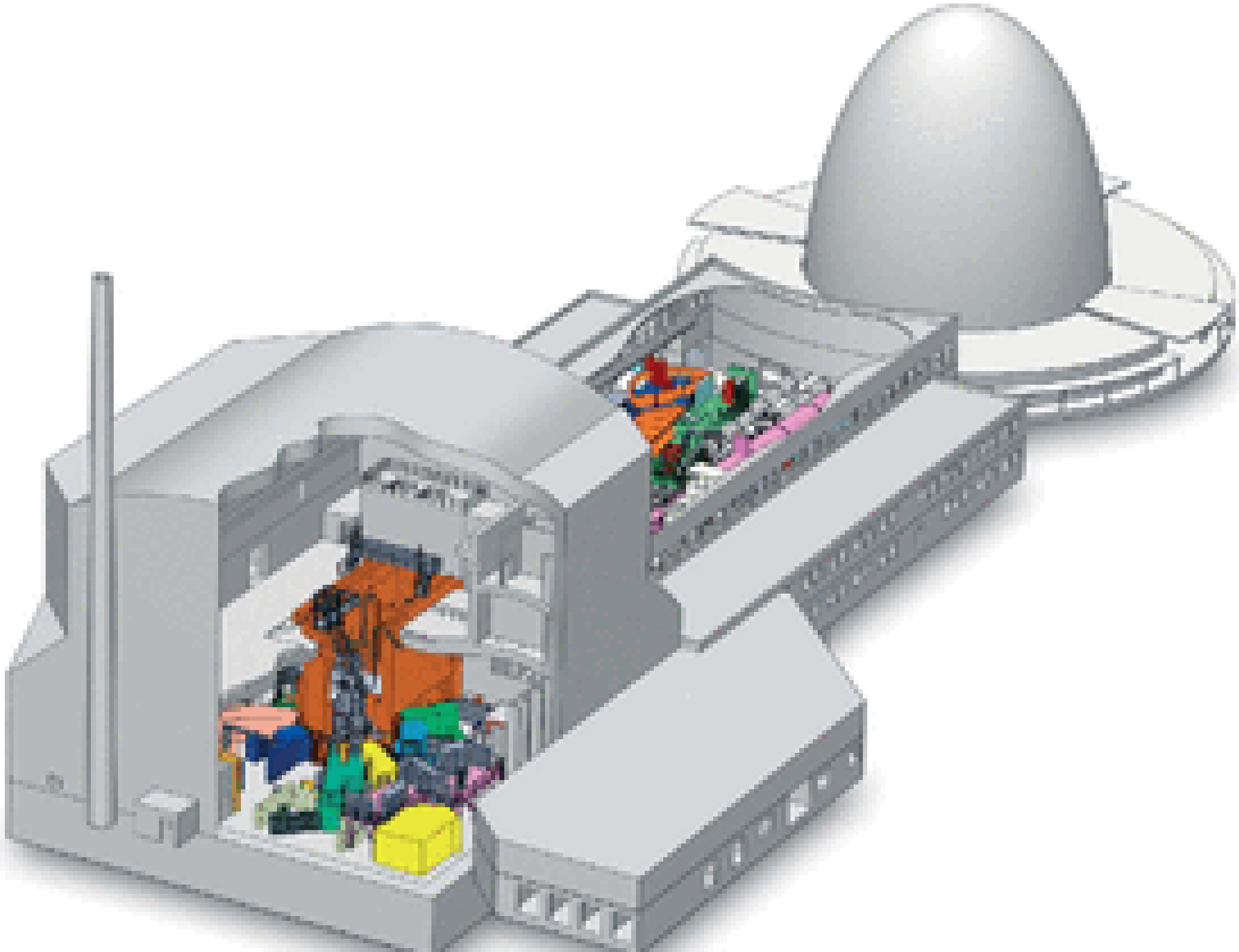
$$\frac{\hbar^2 K_0^2}{2m} = \frac{\hbar^2 K'^2}{2m} \pm \hbar\omega(q)$$





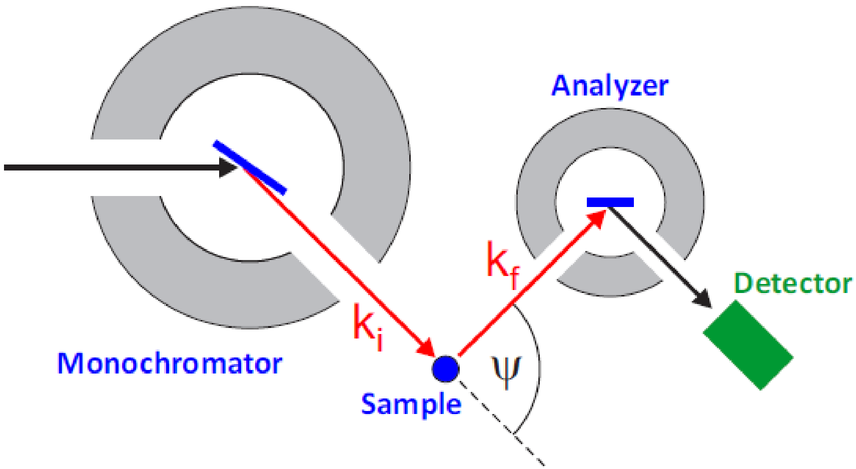
Nature Physics 7, 119–124 (2011)

Research Reactor FRM II in Garching



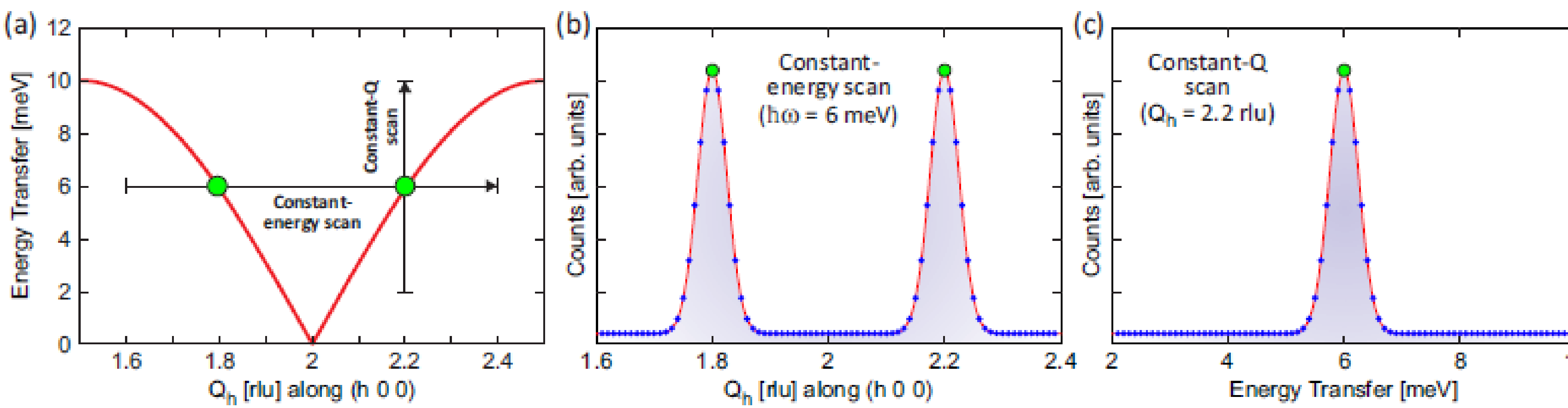
https://www.frm2.tum.de/

Triple-axis Spectrometer (TAS)



TRISP at FRM-II

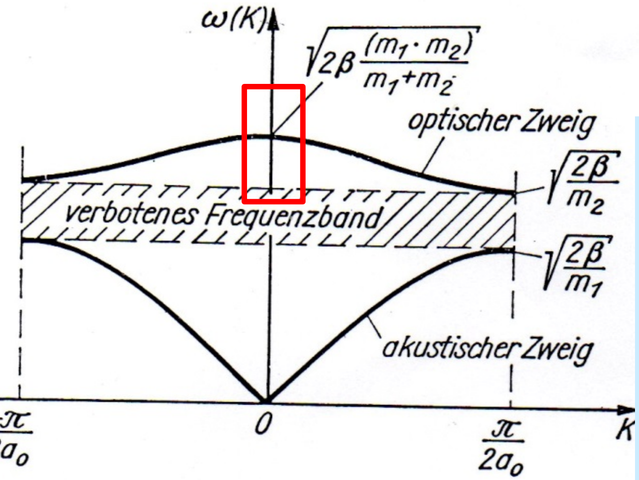
http://www.fkf.mpg.de/keimer/groups/frm/index.html



Methods to measure phonons: Raman and IR

Boriana Mihailova

Sir C. V. Raman
1888 - 1970



- only optical phonons near the FBZ centre are involved

$\mathbf{k}_i - \mathbf{k}_s = \mathbf{K}$ ⇨ $K_{\max} = \Delta k \approx 2k_i$ (e.g. Raman, 180°-scattering geometry)

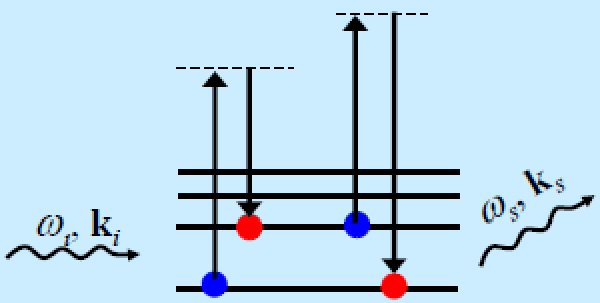
λ_i (IR, vis, UV) ~ $10^3 - 10^5$ Å ⇨ $k_i \sim 10^{-5} - 10^{-3}$ Å $\approx K_{\max}$ ⇨ $K_{\max} << \frac{\pi}{a}$ ($a \sim 10$ Å)

⇨ photon-phonon interaction only for $K \approx 0$

- spectroscopic units: cm^{-1} ⇔ $E = \hbar ck = \hbar c(2\pi/\lambda) = hc(1/\lambda)$

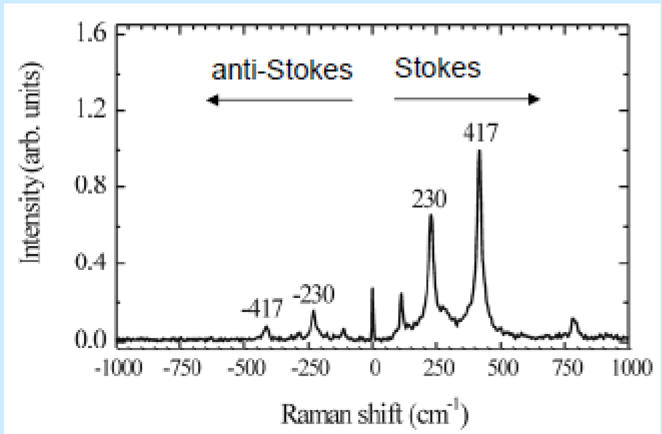
10 [cm^{-1}] ⇔ 1.24 [meV] 10 [cm^{-1}] ⇔ 0.30 [THz] [Å].[cm^{-1}] = 10^8

Raman scattering ≡ inelastic light scattering from optical phonons



Stokes
$\omega_s = \omega_i - \Omega$
$\mathbf{k}_s = \mathbf{k}_i - \mathbf{K}$

anti-Stokes
$\omega_s = \omega_i + \Omega$
$\mathbf{k}_s = \mathbf{k}_i + \mathbf{K}$



$$m = \alpha E = \alpha E_0 \cos(\omega_0 t)$$

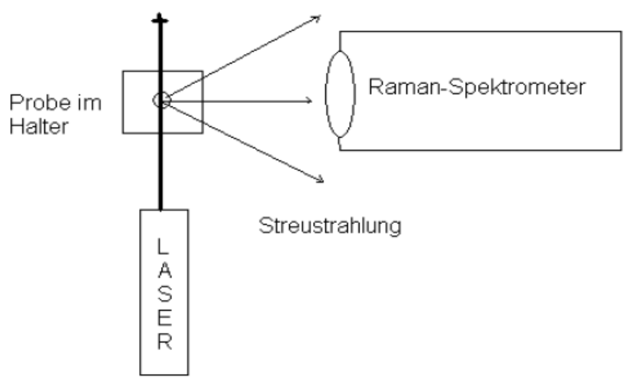
electr. dipole moment, m
polarizability, α

$$\alpha = \alpha_0 + \alpha_1 \cos(\omega_M t)$$

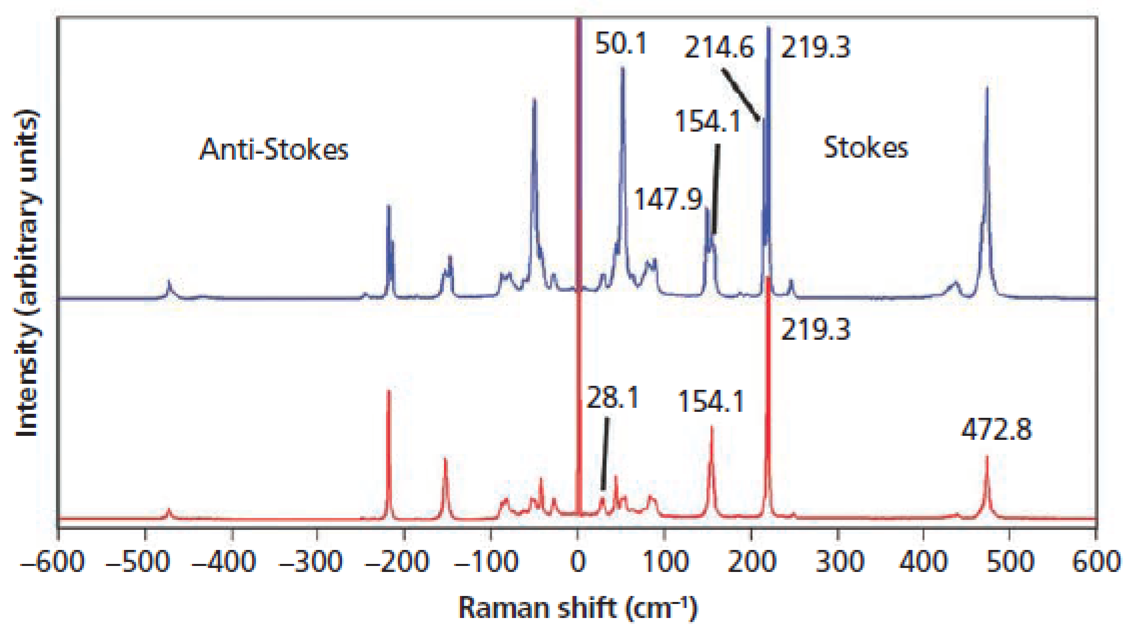
$$m = (\alpha_0 + \alpha_1 \cos(\omega_M t)) E_0 \cos(\omega_0 t)$$

$$= \alpha_0 E_0 \cos(\omega_0 t) + \tfrac{1}{2} \alpha_1 E_0 [\cos(\omega_0 - \omega_M) t + \cos(\omega_0 + \omega_M) t]$$

Rayleigh line Stokes line Anti- Stokes line



Raman spectrum from sulfur



www.spectroscopyonline.com/

Energy of lattice vibration : Phonons

Energy of lattice vibration is quantized, quantum = phonon = bosons, thermally excited lattice vibrations are „thermal phonons“, calculated following black body radiation

Harmonic oscillator model

$$E_n = (n + \tfrac{1}{2})\hbar\omega \qquad \text{n=0,1,2...}$$

total energy of N oscillators

$$E_{tot} = \sum_{n=1}^{N} E_n$$

Number n of excited phonons? what is mean quantum number <n> ?

$$< E >= (< n > + \tfrac{1}{2})\hbar\omega$$

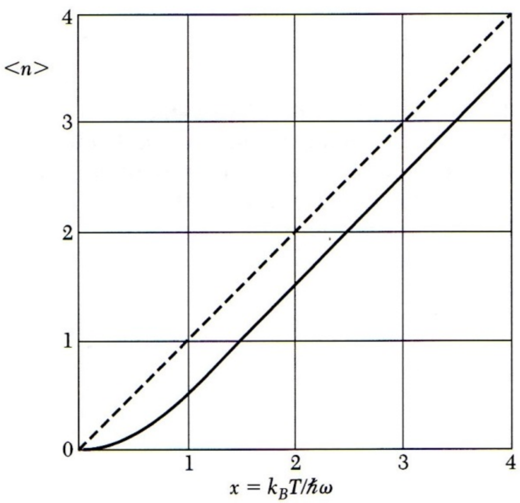
Following Boltzmann

$$\frac{N_{n+1}}{N_n} = \frac{\exp(-\hbar\omega(kT)}{\sum_{s=0}^{\infty} \exp(-s\hbar\omega / kT)}$$

$$< n >= \frac{\sum_{s=0}^{\infty} s \exp(-s\hbar\omega(kT)}{\sum_{s=0}^{\infty} \exp(-s\hbar\omega / kT)}$$

$$\boxed{< n >= \frac{1}{e^{\hbar\omega / kT} - 1}}$$

Bose-Einstein distribution



For T=0 → <n>=0 → $<E>=\frac{1}{2}\hbar\omega$

For low T

→ <n> ≈ exp (- ħω/kT)

For $kT > \hbar\omega$ $<n>=\frac{kT}{\hbar\omega}-\frac{1}{2}$

$$<E>=\hbar\omega(kT/\hbar\omega-\tfrac{1}{2}+\tfrac{1}{2})=kT$$

Classical limit

Total energy of whole phonon spectrum

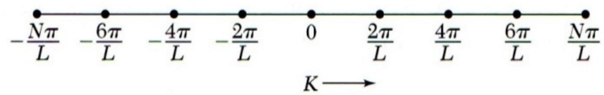
$$<E>=\sum_q(<n>+\tfrac{1}{2})\hbar\omega(q)$$

1D Crystal with length L=Na

Each normal mode has form of standing wave

Propagating waves

$$u_s = u_0 \exp(-i\omega t)\sin(sqa)$$



standing waves at

$$q = \frac{\pi}{L}; \frac{2\pi}{L}; \frac{3\pi}{L};\ldots;\frac{N\pi}{L}$$

Distance :

$$\Delta q = \frac{\pi}{L}$$

Number of modes D(ω) dω

1D Density of states :

$$\boxed{D(\omega)d\omega = \frac{L}{\pi}\frac{dq}{d\omega}d\omega = \frac{L}{\pi}\frac{d\omega}{d\omega/dq} = \frac{L}{\pi}\frac{d\omega}{v_s}}$$

Standing waves in 3D

Number modes in 3D :

$$\boxed{N = (\frac{L}{2\pi})^3 \frac{4\pi}{3} q^3}$$

Spectral density function $S_j(\omega)$ for each branch j

$$\int_0^{\omega_{\max}} S_j(\omega)d\omega = N$$

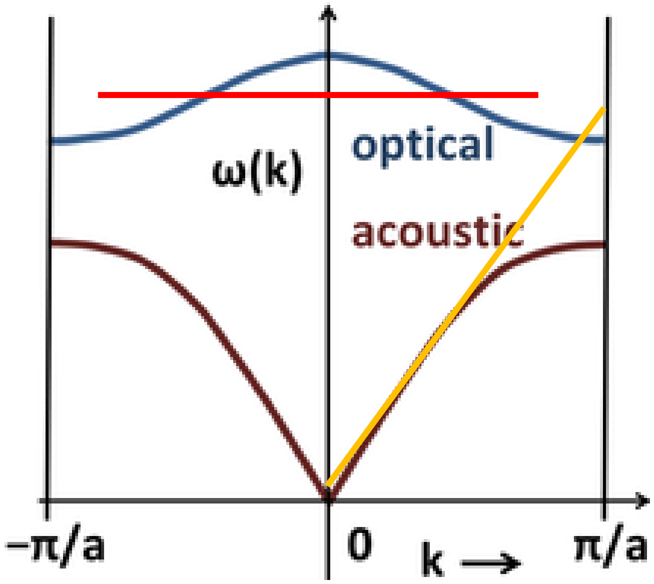
$$\int_0^{\omega_{\max}} S_j(\omega)d\omega = \sum_{j=1}^{3p} S_j(\omega)d\omega = 3pN$$

3N branches , 1L + 2T, for p atoms in unit cell

$$\boxed{S_j(\omega) = (\frac{L}{2\pi})^3 \iint \frac{dF}{|grad_q \omega|}}$$

3D spectral Density of states

Approxomations of the Phonon spectrum



A→ all ω approximated by single ω_E Einstein frequency

B→ ω(q) approximated by $\omega = v_s\, q$ - Debye model

A: Einstein model : $$S_j(\omega) = \begin{cases} 0\_\ for\_\ \omega <> \omega_E \\ 3pN\_\ for\_\ \omega = \omega_E \end{cases}$$

B: Debye model : $$S_j(\omega) = \left(\frac{L}{2\pi}\right)^3 \iint \frac{dF}{v_s} \qquad dF = q^2 4\pi = \frac{\omega^2}{v_s{}^2} 4\pi \qquad S_j(\omega) = \left(\frac{L}{2\pi}\right)^3 \frac{\omega^2}{v_s{}^3} 4\pi$$

$$\boxed{S_j(\omega) = \frac{3N}{\omega_D^3}\omega^2}\_\ for\_\ \omega < \omega_D$$

$$\boxed{\omega_{\max}^3 = \omega_D^3 = \frac{3N}{\left(\frac{L}{2\pi}\right)^3} \frac{v_s^3}{4\pi}}$$

Debye frequency

Specific heat : impact of Phonons

$$c_V = (\frac{\partial E}{\partial T})|_{V=const} \quad c_p = (\frac{\partial E}{\partial T})|_{p=const} \qquad \frac{c_p - c_V}{c_V} \approx 3*10^{-4} \Rightarrow c_p \approx c_V \qquad c_V(\exp) \approx T^3$$

for low T

Energy per degree of freedom 0.5 kT
→ for N atoms with 3N degrees of freedom E= 3NkT=3RT/mol

$$< E >= \sum_q (< n > + \tfrac{1}{2})\hbar\omega(q) = \int_0^\infty d\omega S(\omega)(< n > + \tfrac{1}{2})\hbar\omega$$

$$< E >= \tfrac{1}{2}\int_0^\infty d\omega S(\omega)\hbar\omega + \int_0^\infty d\omega S(\omega)\frac{\hbar\omega}{e^{\hbar\omega/kT} - 1} = E_0 + \int_0^\infty d\omega S(\omega)\frac{\hbar\omega}{e^{\hbar\omega/kT} - 1}$$

Depending on ω

$$\boxed{c_V = (\frac{\partial E}{\partial T})_V = k\int_0^\infty d\omega S(\omega)(\frac{\hbar\omega}{kT})^2 \frac{e^{\hbar\omega/kT}}{(e^{\hbar\omega/kT} - 1)^2}}$$

A: Einstein model :

$$c_V = 3pNk\int_0^\infty d\omega S(\omega)(\frac{\hbar\omega_E}{kT})^2 \frac{e^{\hbar\omega_E/kT}}{(e^{\hbar\omega_E/kT}-1)^2} \approx 3pNk(1+\frac{\hbar\omega}{kT})$$

$\hbar\omega_E < kT$ $\quad \frac{c_V}{Np} = 3k$ Correct : Dolong-Petit law All optical modes excited

$\hbar\omega_E > kT$ $\quad c_V \approx e^{-\hbar\omega_E/kT}$ Wrong !

Debye integral

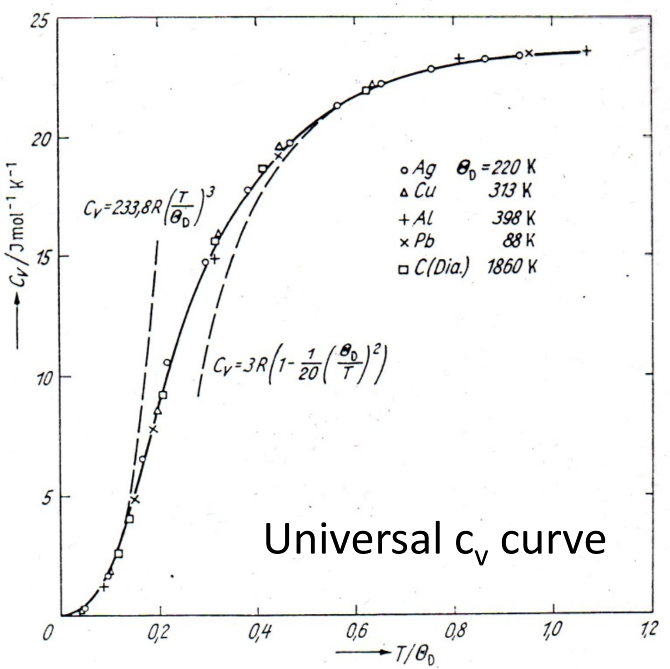
B: Debye model :

$$c_V = 3pNk\int_0^\infty d\omega \frac{3N\omega^2}{\omega_D^3}(\frac{\hbar\omega}{kT})^2 \frac{e^{\hbar\omega/kT}}{(e^{\hbar\omega/kT}-1)^2} = 3pNk(\frac{T}{\theta_D})^3\int_0^{x_D} dx \frac{x^4 e^x}{(e^x-1)^2}$$

$T < \theta$ $\quad c_V \approx (\frac{T}{\theta})^3$ Correct !

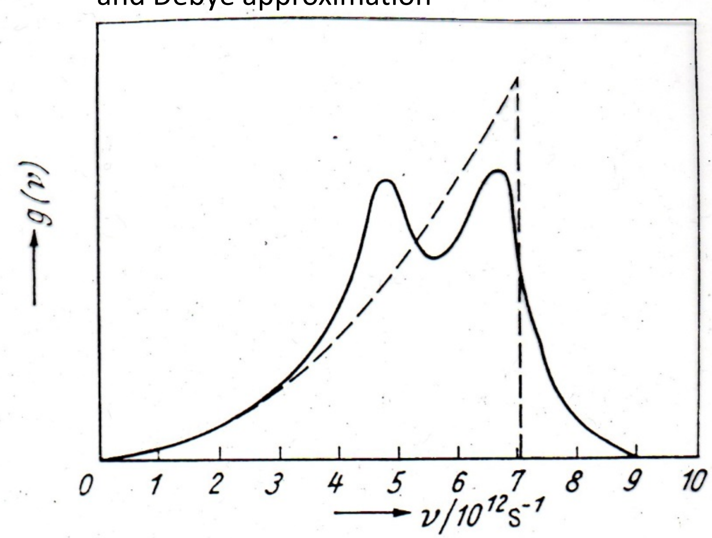
$$x = \frac{\hbar\omega}{kT} \qquad x_D = \frac{\theta}{T}$$

Only acoustic modes excited



Universal c_V curve

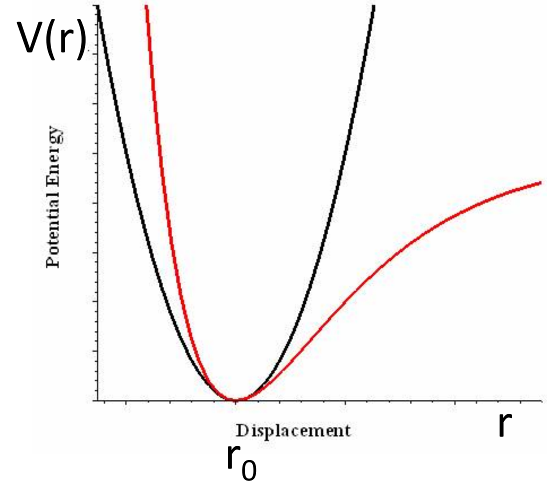
Exp. vibration spectrum of Vanadium, and Debye approximation



Anharmonic effects: thermal expansion

So far phonons are described in terms of Hook´s law: $V(r) = V(r_0) + A(r - r_0)^2$

Based on harmonic oscillator model $\quad M\dfrac{\partial^2 x}{\partial t^2} = Cx \qquad x = r - r_0$



anharmonic oscillator model $\quad M\dfrac{\partial^2 x}{\partial t^2} = Cx - Gx^2 - Fx^3 ....$

$$V(x) = V(x_0) + cx^2 + gx^3 + fx^4 + \ldots$$

$$< x > = \frac{\int_{-\infty}^{\infty} dx\, x \exp(-V(x)/(kT))}{\int_{-\infty}^{\infty} dx \exp(-V(x)/(kT))} \qquad < x > = \frac{\frac{3\sqrt{\pi}}{4}\frac{g}{c^{5/2}} ß^{-3/2}}{\sqrt{\frac{\pi}{ßc}}} = \frac{3g}{4c^2}kT = \alpha \mathrm{T}$$

$$\boxed{\alpha = \frac{3g}{4c^2}k}$$

α(g)=const;
for $\alpha(\mathrm{T})$= α(g, f…)

Anharmonic phonon modes: Grüneisen constants

Frequency of lattice vibrations depends on volume

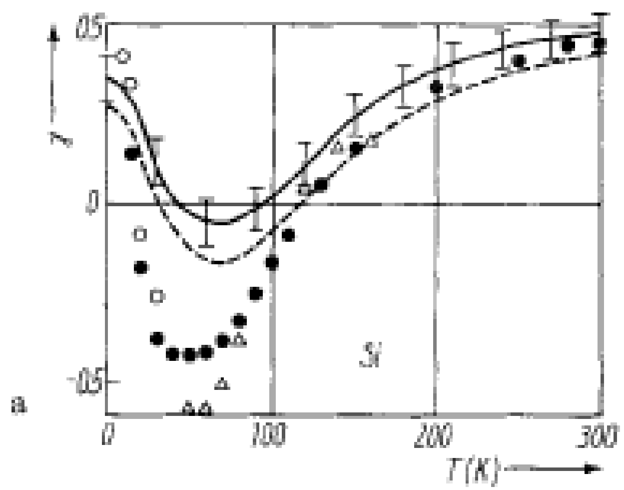
$$\frac{d\omega/\omega}{dV/V} = \frac{gx}{6c} = \frac{aB_T V}{c_V} = -\gamma$$ Grüneisen constant

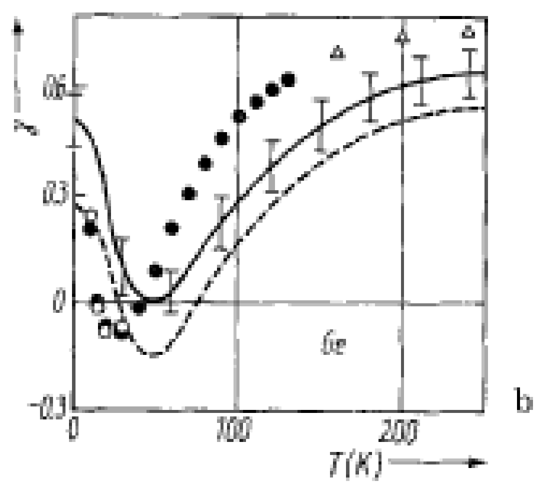
$$\frac{d(\ln\omega(q))}{d(\ln V)} = -\gamma(q)$$ Mode Grüneisen constant $$\gamma = \frac{\sum_i \gamma_i c_{Vi}}{\sum_i c_{Vi}}$$

Phonon dispersion $$\omega^2 = \frac{4C}{M}\sin^2(\tfrac{1}{2}ka) \rightarrow \omega^2(x) = \omega^2\frac{c+gx}{c}$$ Anharmonic correction

T. Soma: Temperature Dependence of the Grüneisen Constant of Si and Ge

phys. stat. sol. (b) 82, 319 (1977)





Thermal conductivity

Heat current density $J_h = -\kappa \nabla T$ κ -Thermal conductivity

In solids calculate J as function of mean number of phonons <n>(x) being different at different positions x. Using $x = v_x \tau$

$$J_{h,x} = \frac{1}{V}\sum_{q,r} \hbar\omega(<n> + \tfrac{1}{2}) v_x(q,r) = \frac{1}{V}\sum_{q,r} \hbar\omega(<n> + \tfrac{1}{2}) \frac{\partial \omega}{\partial q_x}$$

v_x – group velocity

J_h<>0, if <n> ≠ $<n_0>$

$$J_{h,x} = \frac{1}{V}\sum_{q,r} \hbar\omega(<n> - <n_0>) v_x$$

Transport by phonon diffusion, or single phonons can decompose into two phonons

$$\frac{\partial\langle n\rangle}{\partial t} = \frac{\partial\langle n\rangle}{\partial t}\Big|_{diff} + \frac{\partial\langle n\rangle}{\partial t}\Big|_{decay} = -\frac{\langle n\rangle - \langle n_0\rangle}{\tau}$$

τ - mean decay time

$$\frac{\partial\langle n\rangle}{\partial t}\Big|_{diff} = -v_x \frac{\partial\langle n\rangle}{\partial x} = -v_x \frac{\partial\langle n_0\rangle}{\partial T}\frac{\partial T}{\partial x}$$

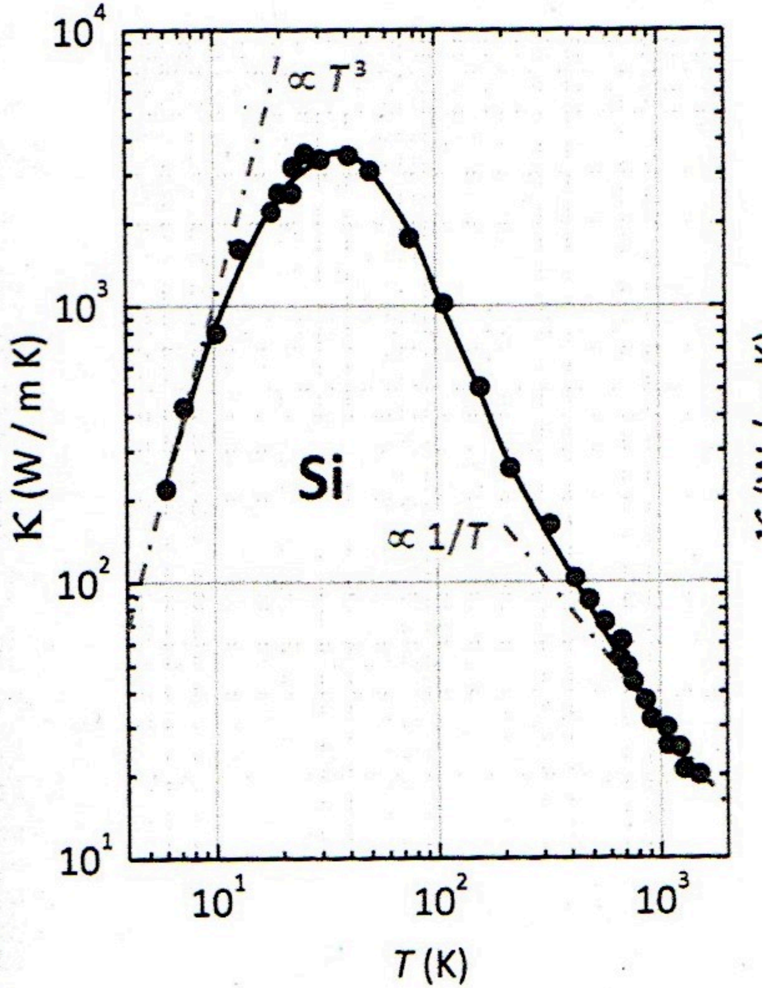
$$J_{h,x} = -\frac{1}{3V}\sum_{q,r} \hbar\omega\tau v^2 \frac{\partial\langle n_0\rangle}{\partial T}\frac{\partial T}{\partial x}$$

using $c_V = \frac{1}{V}\sum_{q,r} \hbar\omega \frac{\partial}{\partial T}\langle n_0\rangle$ and $l = v\tau$ → $\boxed{\kappa = \tfrac{1}{3} c_V v l}$

l - mean free pathway Note: $c_v = c_v(T)$; $l = l(T)$

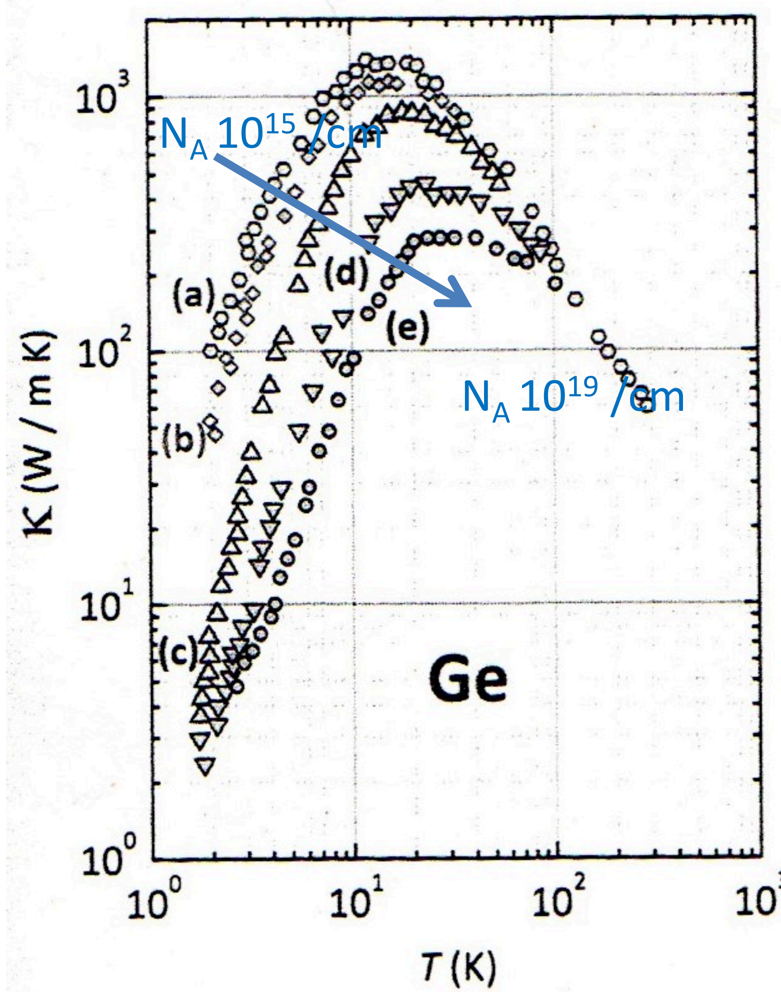
Defect scattering - Experiments

Pure silicon



Phys.Rev.134, 1058(1964)

Doped Germanium



Proc.Royal. Soc. 238, 502 (1957)