Phonon Anharmonic Effects on Physical Properties

$$U(x) = U^{eq} + bx^2 + cx^3 + dx^4$$

harmonic: bx^2

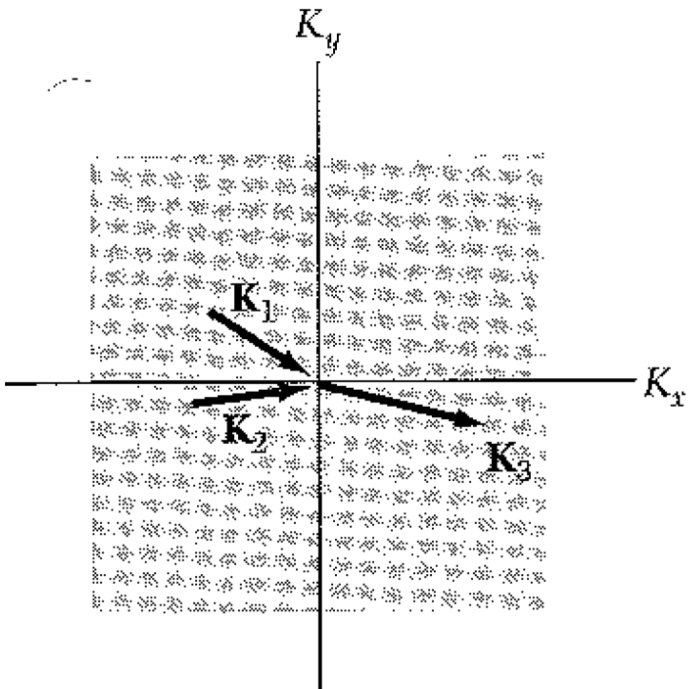
anharmonic: $cx^3 + dx^4$

cx^3: asymmetry of mutual repulsion of atoms

dx^4: softening of vibration

Anharmonic effects – phonon can decay

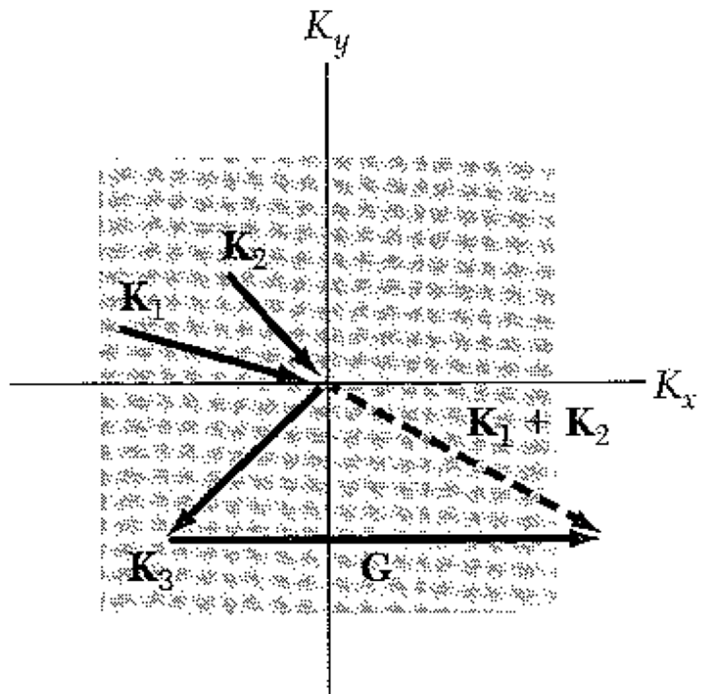
Normal Process



momentum is conserved

$$K_1 + K_2 = K_3$$

Umklapp Process



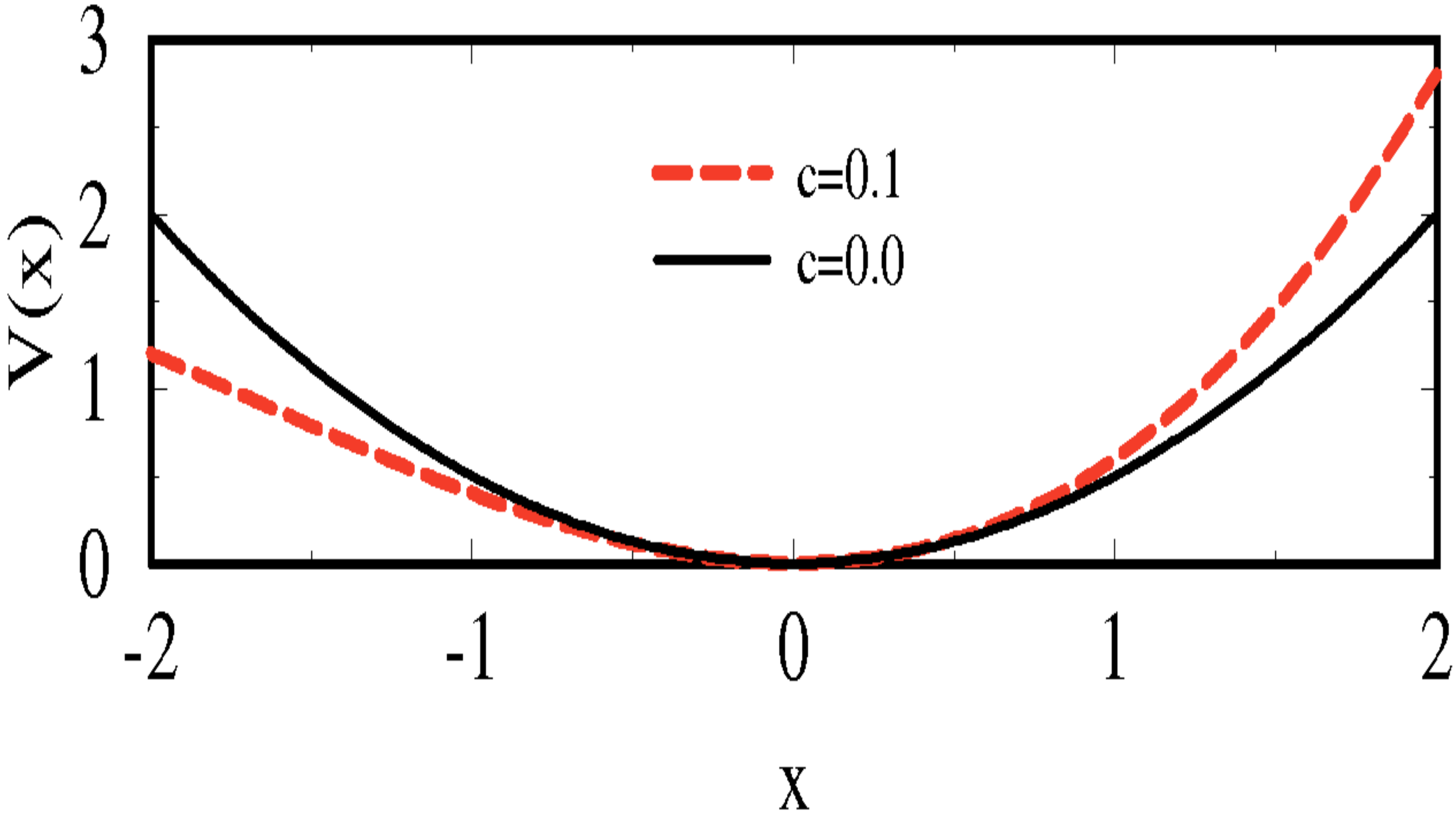
momentum is NOT conserved

$$K_1 + K_2 = K_3 + G$$

→ **Finite phonon thermal conductivity**

Anharmonic Effects

$$U(x) \approx U^{eq} + bx^2 + cx^3$$



Anharmonic Effects

We approximate the cubic term with a mean-field decomposition.

$$cx^3 \approx c\eta x \left\langle x^2 \right\rangle + c(1-\eta)x^2 \left\langle x \right\rangle$$

$$< x > = -\frac{c\eta < x^2 >}{m\omega^2}$$

temperature dependence of the displacement

$$\omega' = \omega \left(1 + \frac{2(1-\eta) < x >}{m\omega^2}\right)^{\frac{1}{2}}$$

frequency change

Anharmonic Effects

$$E_n = \hbar\omega'(< x >)(n + \frac{1}{2}),$$

In equilibrium, where $P = -\left(\frac{\mathrm{d}\mathcal{F}}{\mathrm{d}V}\right)_T = 0$, the free energy of one of the modes is

$$\mathcal{F} = \Phi + \frac{1}{2}\hbar\omega + k_B T \ln\left(1 - e^{-\beta\hbar\omega}\right)$$

Where the lattice potential

$$\Phi = \Phi_0 + \frac{1}{2} f(a - a_0)^2 + \cdots$$

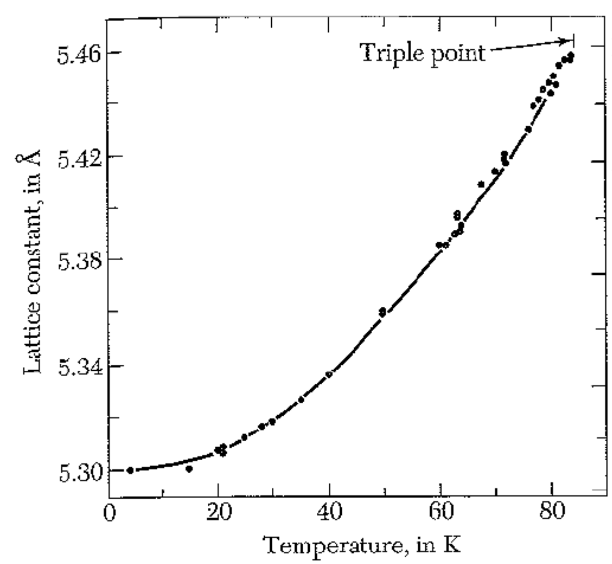
$$0 = P = \left(\frac{\mathrm{d}\mathcal{F}}{\mathrm{d}a}\right)_T = f(a - a_0) + \frac{1}{\omega}\frac{\partial\omega}{\partial a}\left(\frac{1}{2}\hbar\omega - \frac{\hbar\omega}{1 - e^{-\beta\hbar\omega}}\right)$$

Thermal Effect on Crystals

$$0 = P = \left(\frac{\mathrm{d}\mathcal{F}}{\mathrm{d}a}\right)_T = f(a - a_0) + \frac{1}{\omega}\frac{\partial\omega}{\partial a}\left(\frac{1}{2}\hbar\omega - \frac{\hbar\omega}{1 - e^{-\beta\hbar\omega}}\right)$$

$$\| \quad \varepsilon(\omega, T)$$

Lattice parameter $$a = a_0 - \frac{1}{\omega f}\epsilon(\omega, T)\frac{\partial\omega}{\partial a}$$



Thermal Expansion

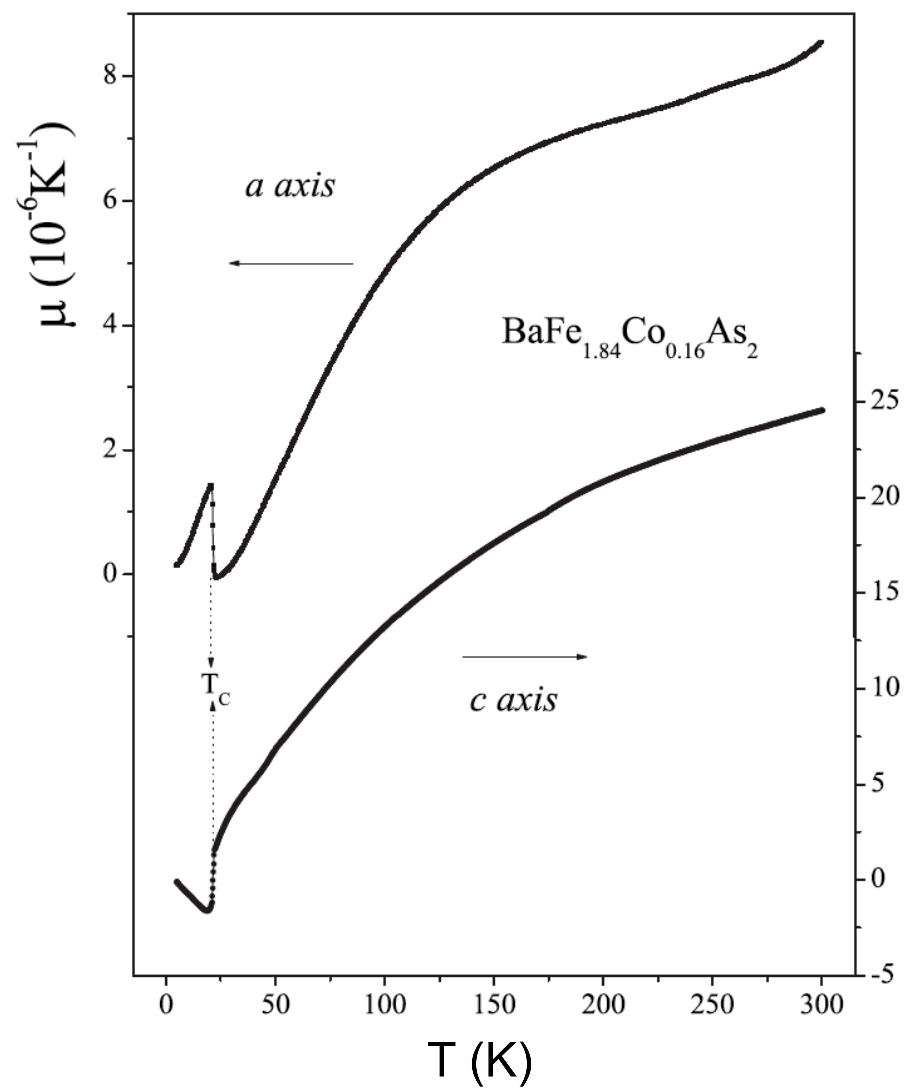
Linear expansion coefficient

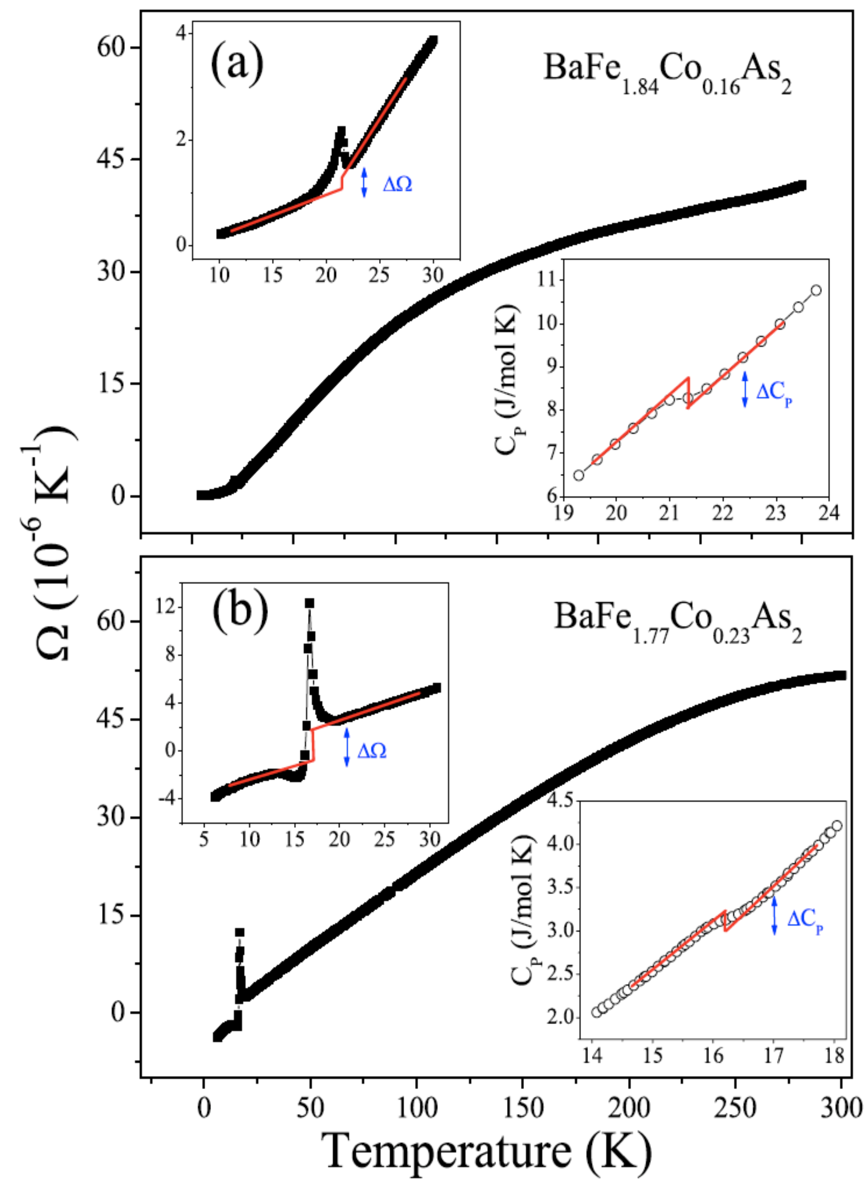
$$\alpha_L = \frac{1}{a_0}\frac{\mathrm{d}a}{\mathrm{d}T} = -\frac{1}{a_0^2 f}\frac{\partial \ln w}{\partial \ln a}\frac{\partial \epsilon(\omega, T)}{\partial T}$$

Volumm expansion coefficient

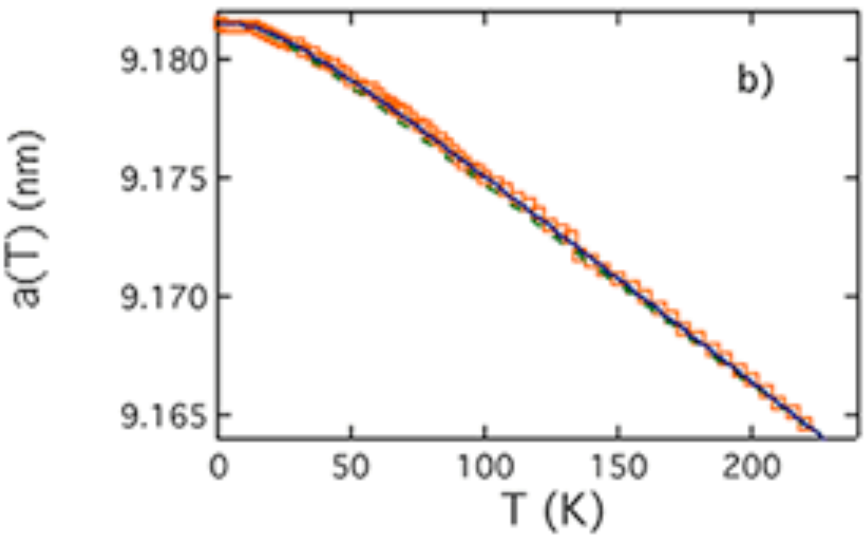
$$\alpha_V = \frac{1}{V}\frac{\mathrm{d}V}{\mathrm{d}T} = \frac{1}{\kappa\ V}\sum_{\mathsf{k},s} -\frac{\partial \ln \omega_s(\mathsf{k})}{\partial \ln V}\frac{\partial \epsilon\left(\omega_s(\mathsf{k}), T\right)}{\partial T}$$

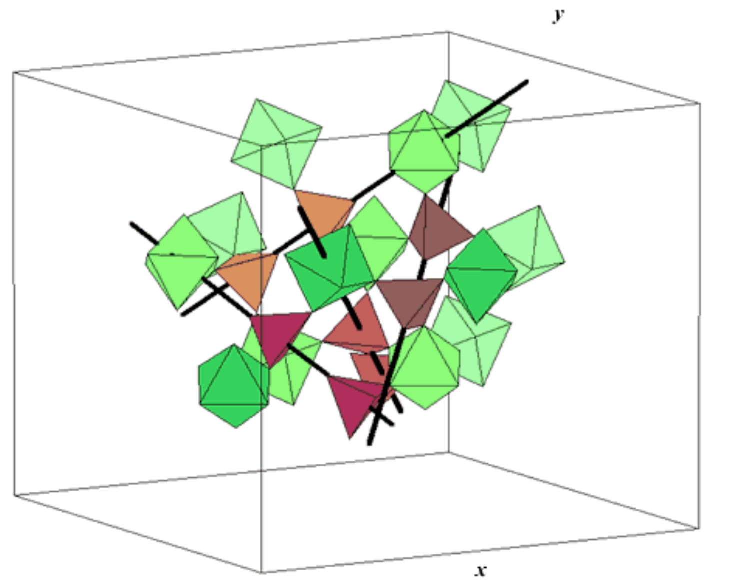
Positive Thermal Expansion



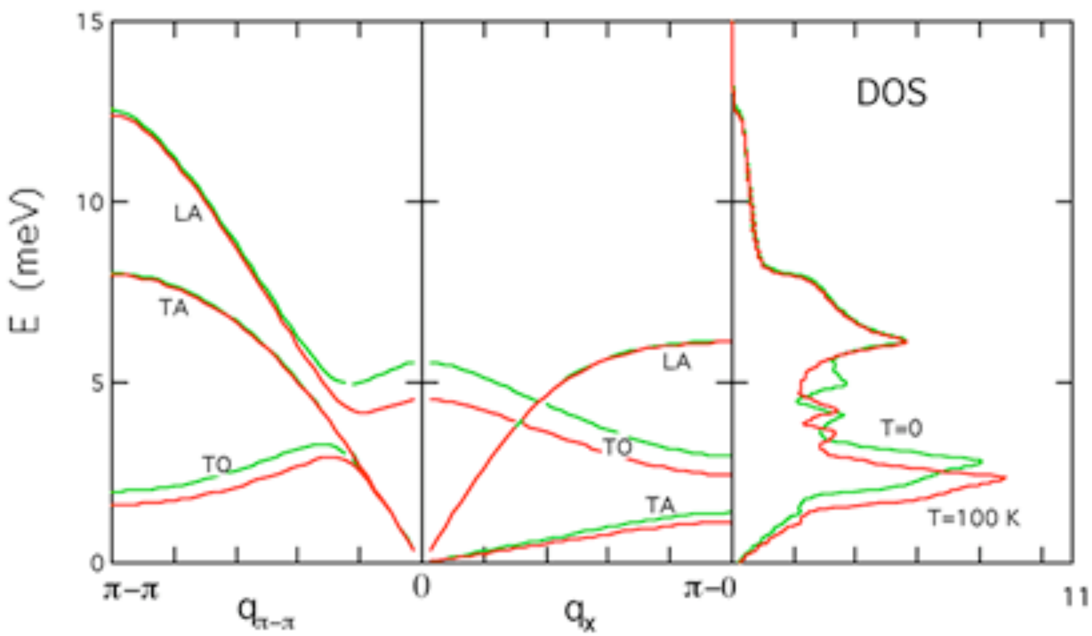


Negative Thermal Expansion





Low frequency lattice vibration mode



Gruneisen Parameter

The **Gruneisen number**

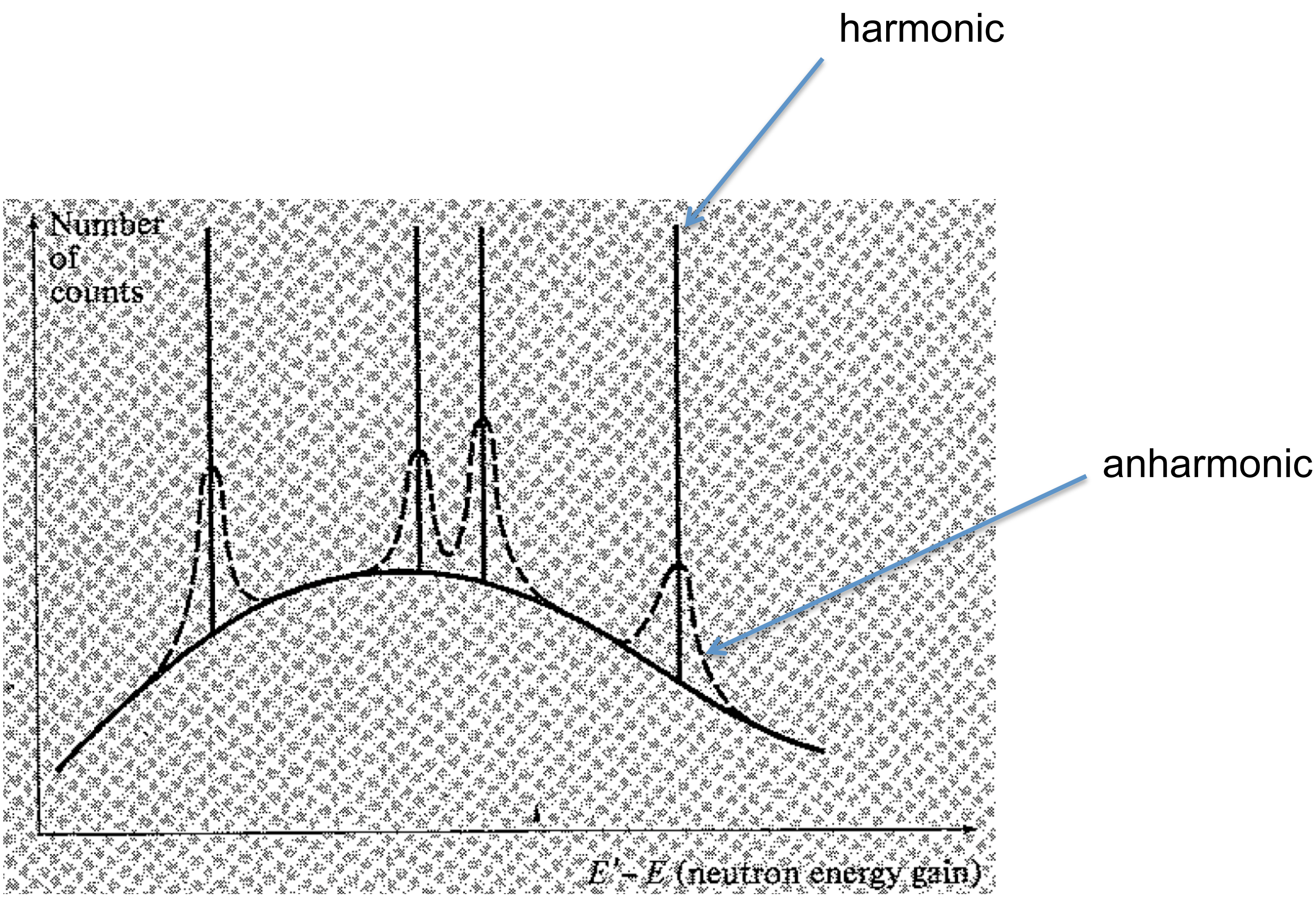
$$\gamma = \frac{\partial \ln \omega_s(\mathbf{k})}{\partial \ln V}$$

In addition, for many lattices, the Gruneisen number shows a weak dependence upon s, k, and may be replaced by its average, called the **Gruneisen parameter**

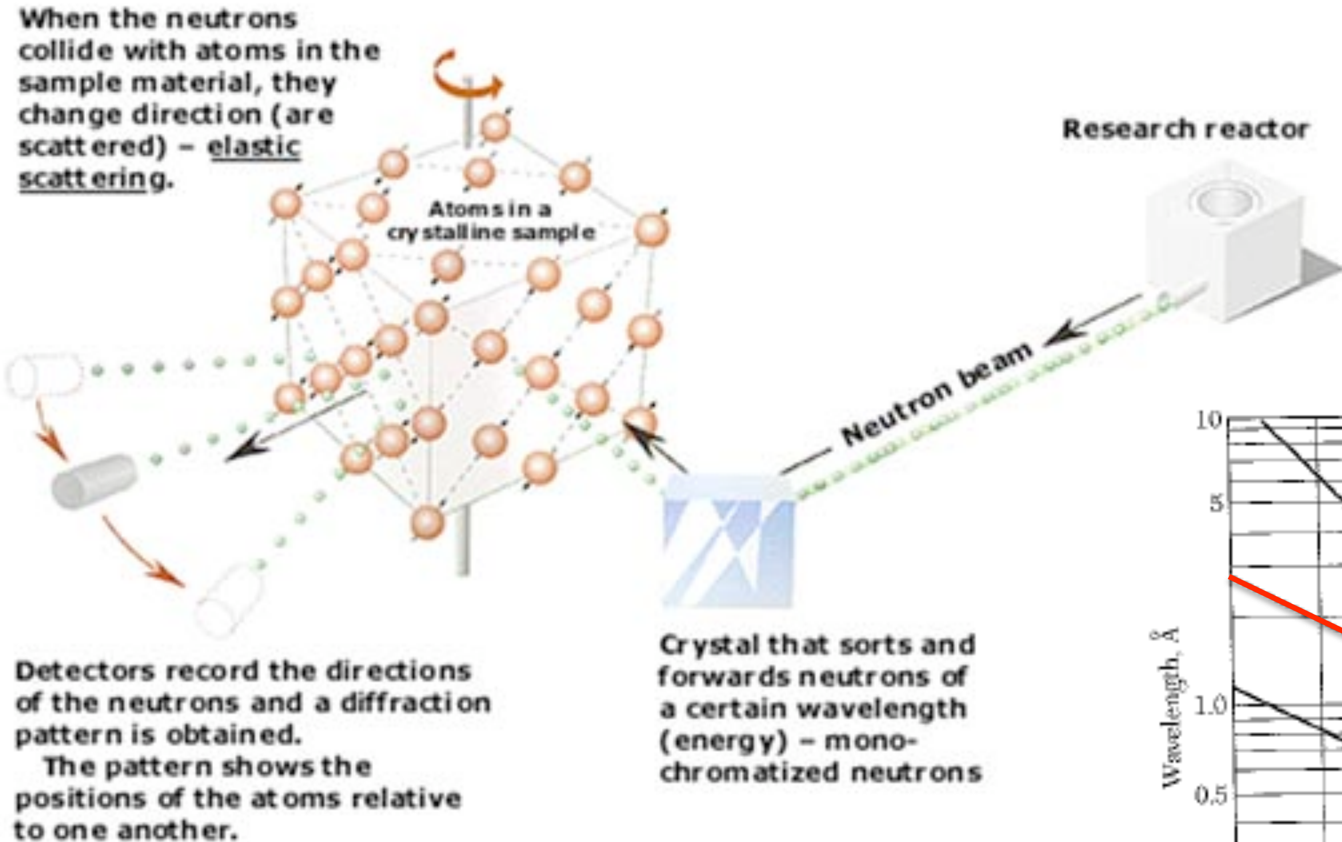
$$\langle \gamma \rangle = \left\langle \frac{\partial \ln \omega_s(\mathbf{k})}{\partial \ln V} \right\rangle$$

$$\gamma = \frac{\alpha K_T}{C_V \rho}$$

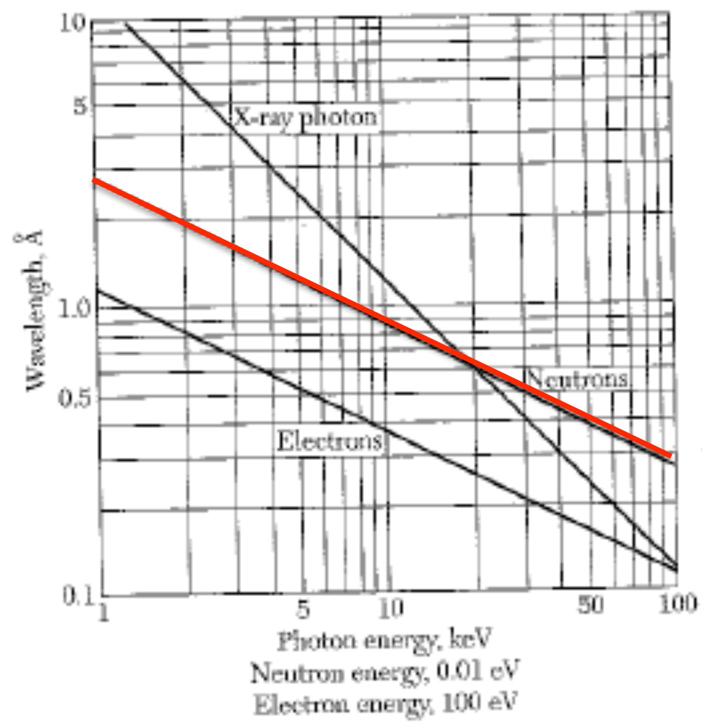
Anharmonic Effects
-- in Neutron Scatting Spectroscopy



Neutron Scattering
-- Probe Phonon Spectra

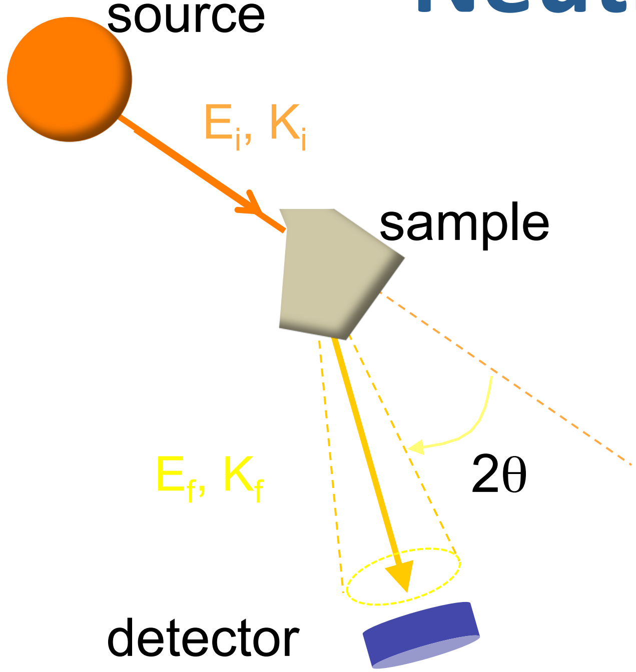


$$E_{neutron} = \frac{p^2}{2M_n}$$



Neutrons interacts with nuclei of the atoms of materials, thus can be used to see the ordering of atoms!

Neutron Scattering -- Principle



Conservation of energy

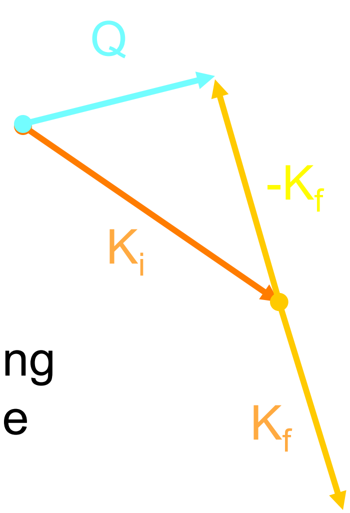
$$\varepsilon = \hbar\omega = E_i - E_f$$

$\varepsilon > 0$ "energy loss"

< 0 "energy gain"

Conservation of momentum

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



scattering triangle

provides kinematic constraints

Why Neutrons?

- No charge
- Energy: meV range -tunable
- Wavelength: Å range
- Great penetration
- Interact with nuclei
- Simple scattering form factor
- Sensitive to lattice degrees of freedom

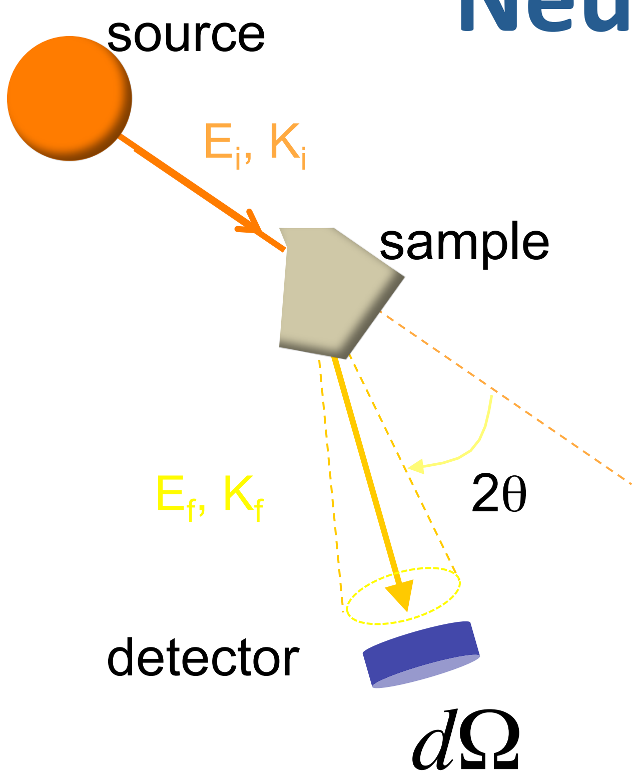
neutron:

$\lambda(\text{Å}) = 6.283/k(\text{Å}^{-1})$

$= 9.045/\sqrt{E}\ (\text{meV})$

$= 30.81/\sqrt{T}\ (\text{K})$

Neutron Scattering Intensity

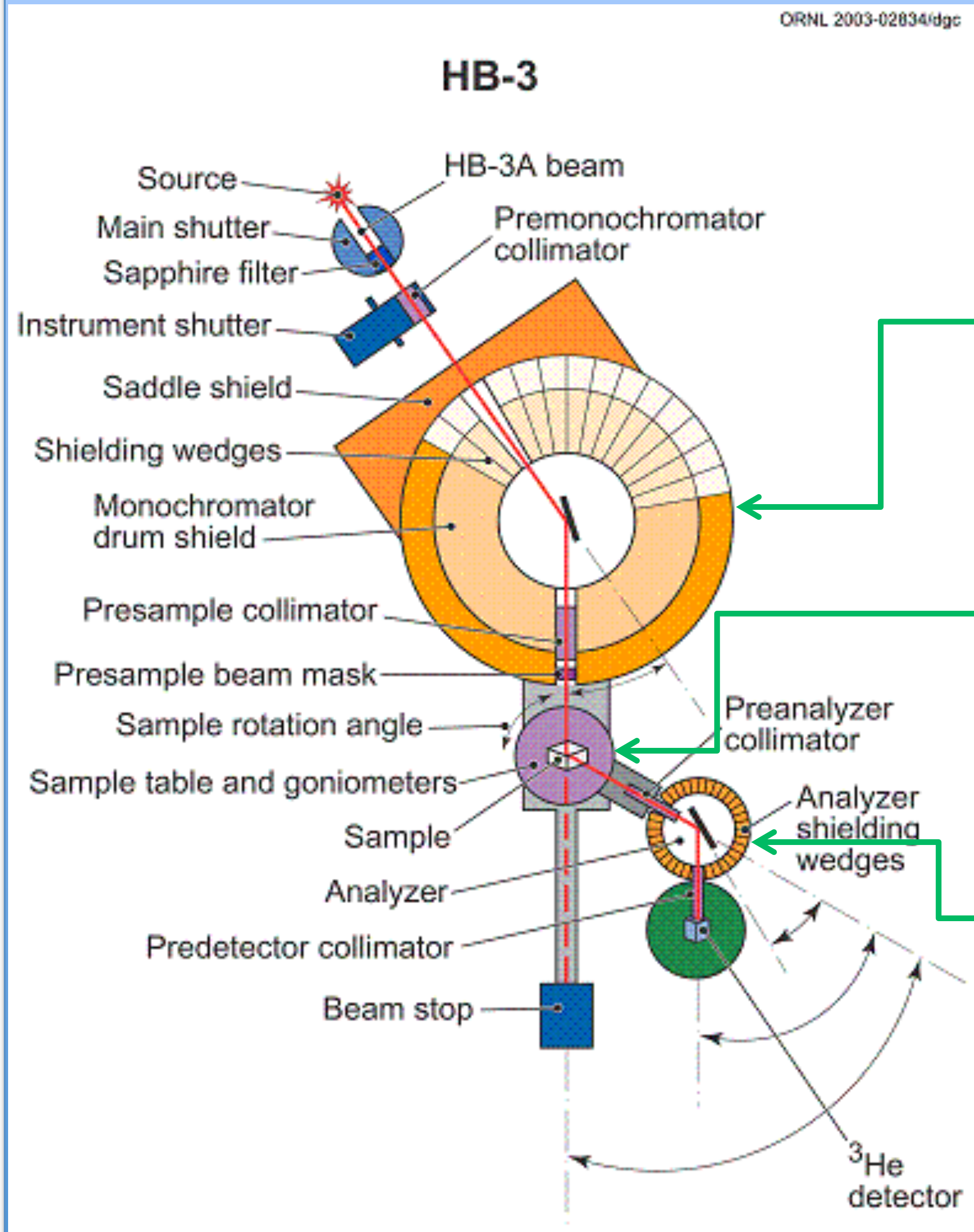


- Measuring cross section

$$\frac{d^2\sigma}{d\Omega dE_f} = \frac{k_f}{k_i} S(Q,\varepsilon)$$

Give the rate of removal of particles from k_i as
The result of being scattered into an angle dΩ
Within an energy range of dE_f

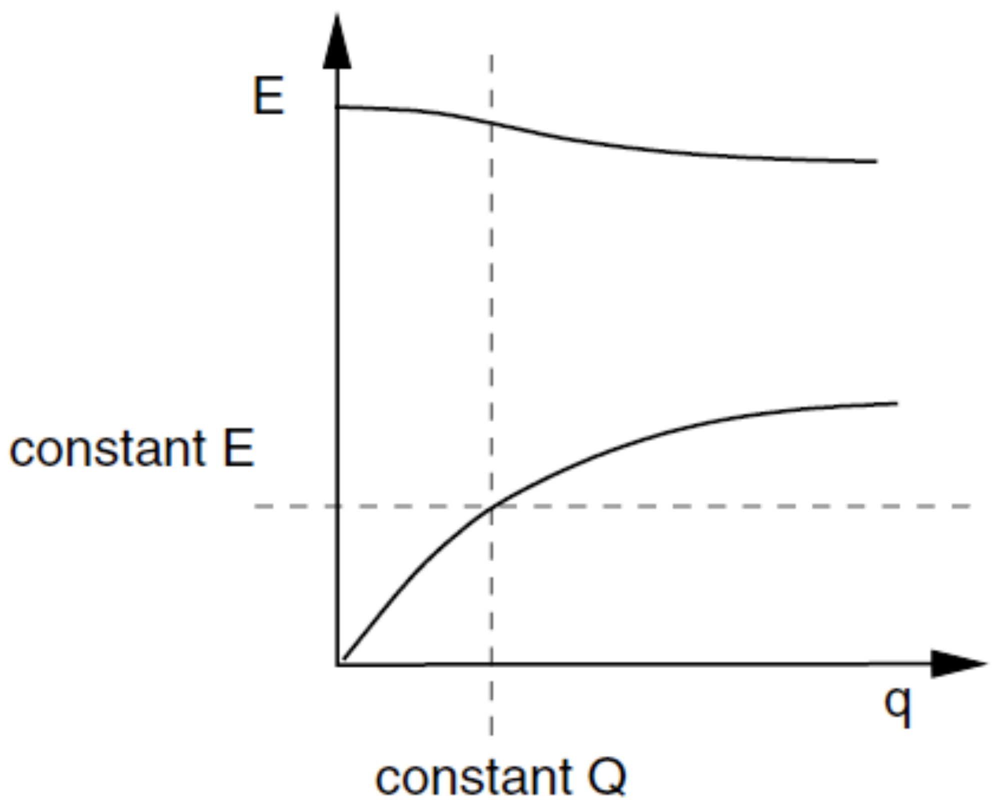
ORNL: Triple-axis spectrometer

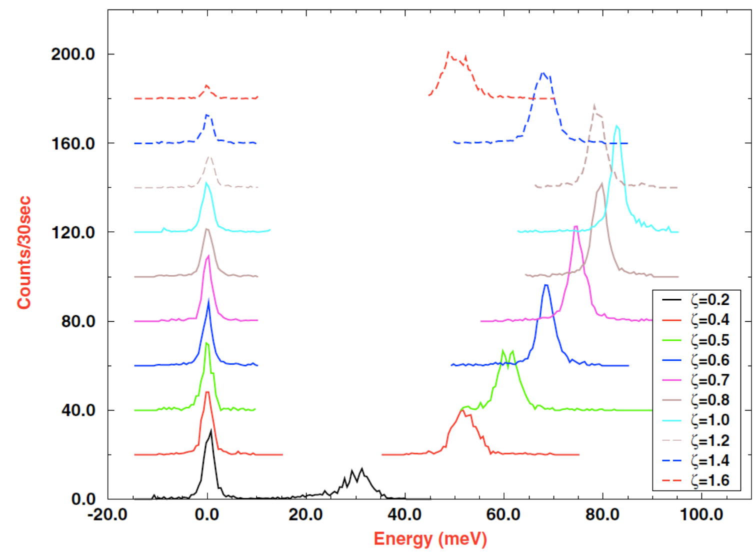


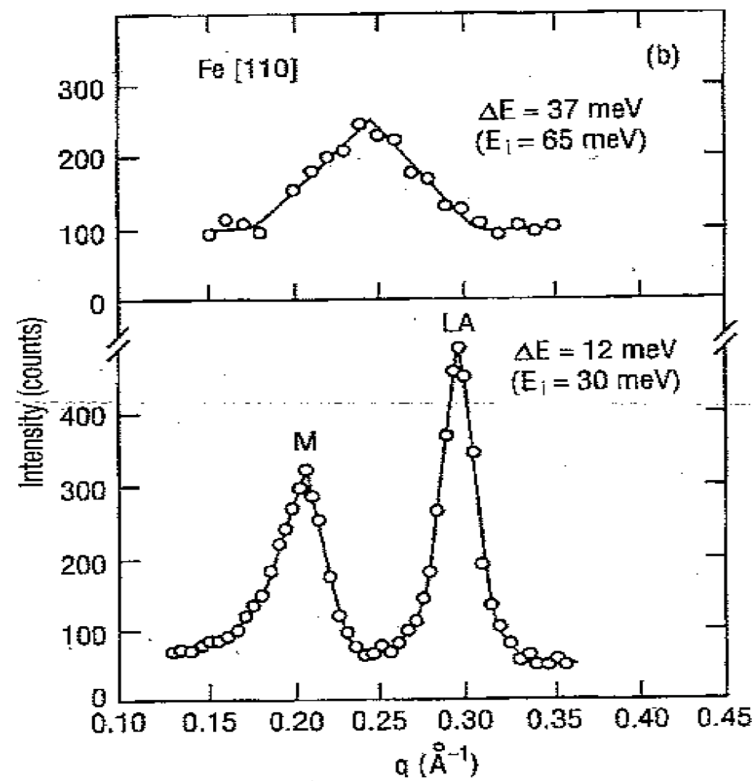
Axis 1: monochromator

Axis 2: sample

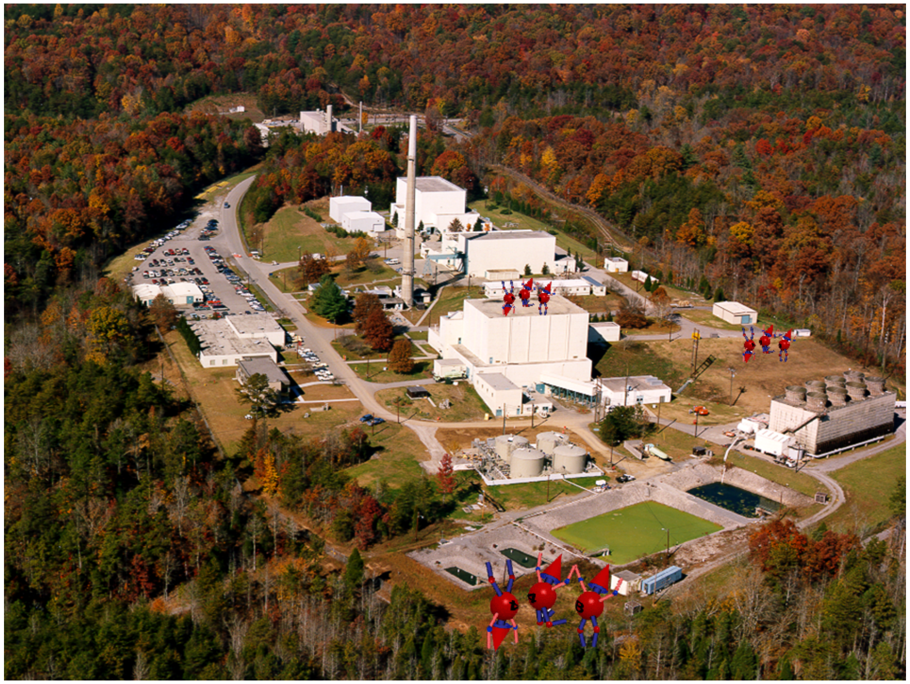
Axis 3: analyzer


E
constant E
q
constant Q


Counts/30sec
Energy (meV)
ζ=0.2
ζ=0.4
ζ=0.5
ζ=0.6
ζ=0.7
ζ=0.8
ζ=1.0
ζ=1.2
ζ=1.4
ζ=1.6


Fe [110]
(b)
ΔE = 37 meV
(E_i = 65 meV)
LA
ΔE = 12 meV
(E_i = 30 meV)
M
Intensity (counts)
q (Å^-1)

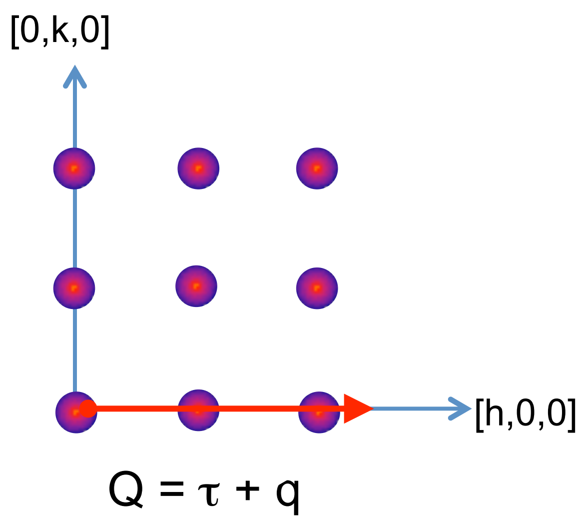
Oak Ridge National Laboratory
-- The Neutron Valley

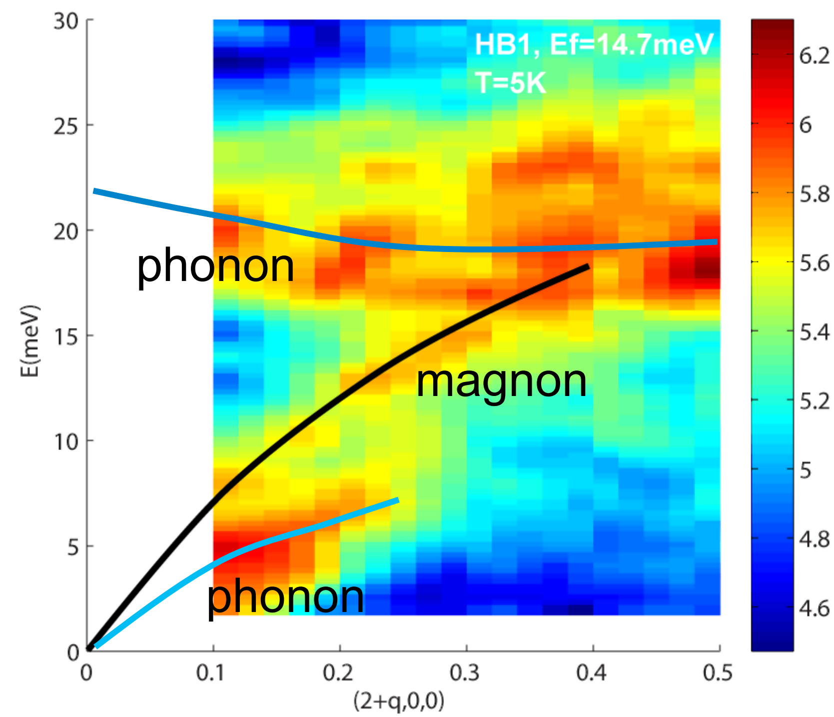


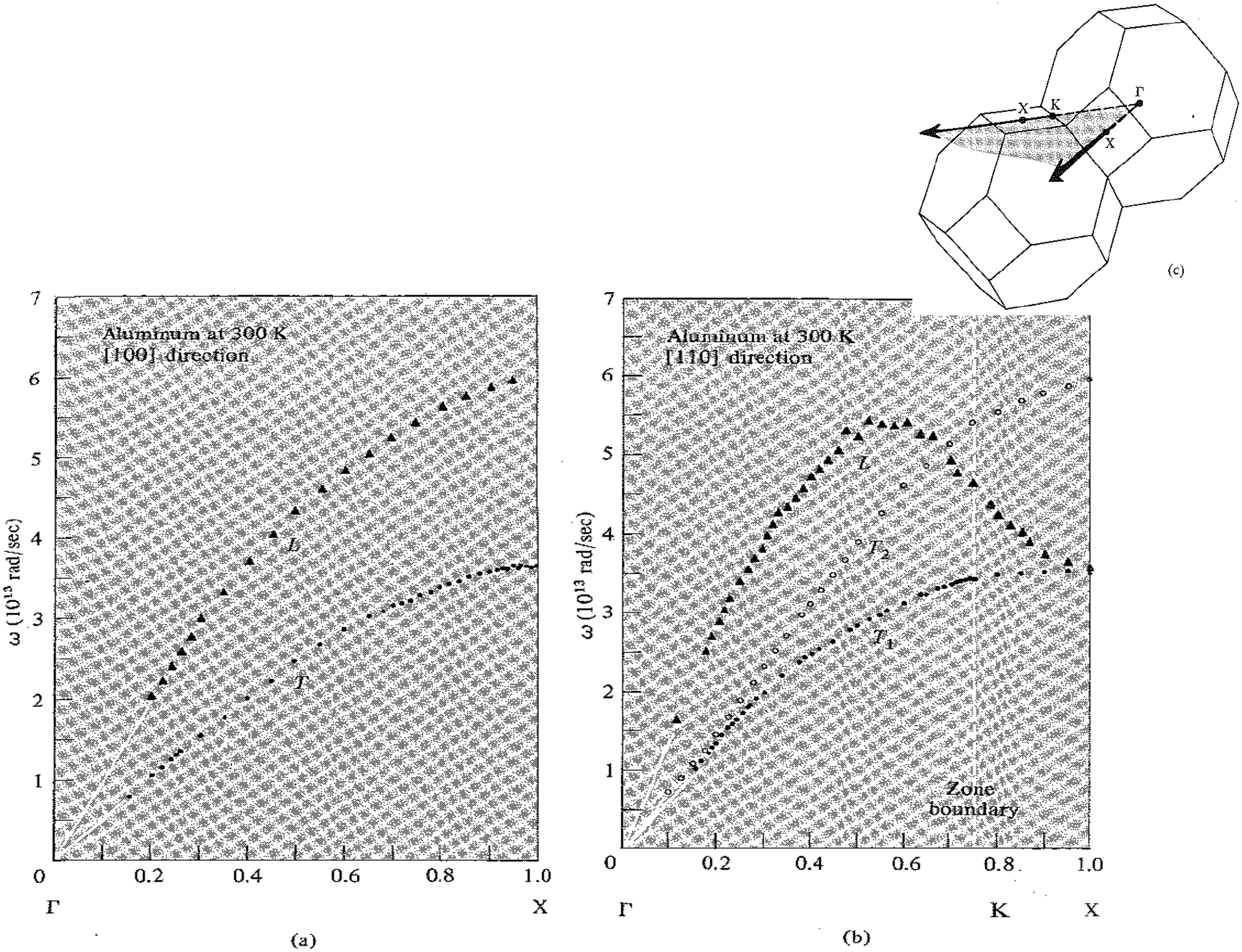
HFIR

SNS

Example: Phonon Dispersion of $La_{0.7}Ca_{0.3}MnO_3$







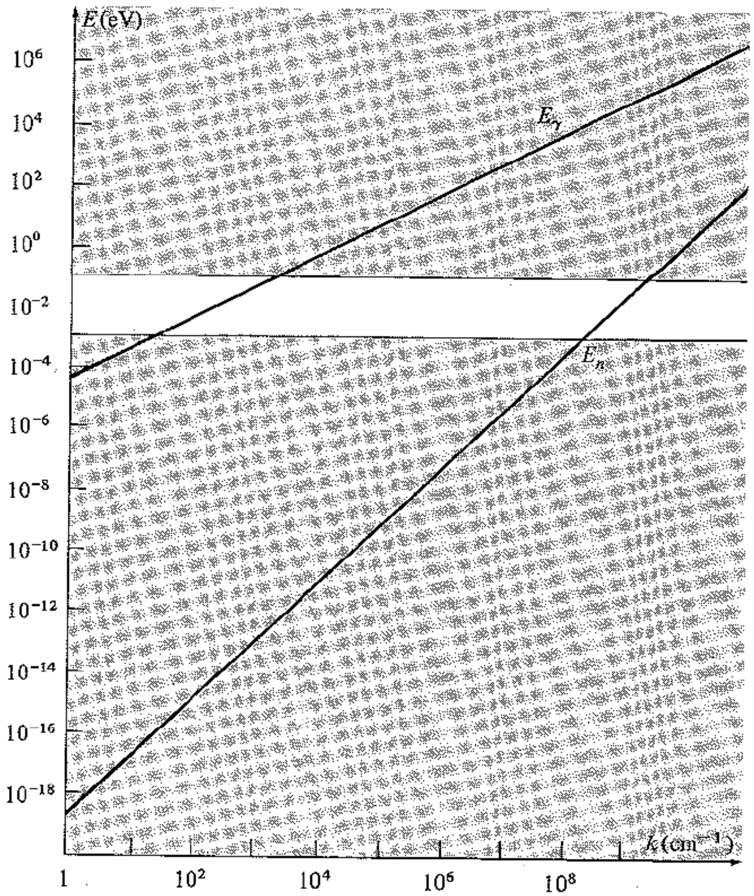
Aluminum at 300 K
[100] direction
L
T
ω (10^{13} rad/sec)
0
0.2
0.4
0.6
0.8
1.0
1
2
3
4
5
6
7
Γ
X
Aluminum at 300 K
[110] direction
L
T_2
T_1
Zone
boundary
K
X
Γ

(a)

(b)

(c)

X-Ray Measurements of Phonon Spectra



⌘ high energy
-- low resolution

⌘ interacting with electrons
-- large background

⌘ high flux
-- sample damage

⌘ requires less sample
-- large background

⌘ also informative to non-crystalline materials

	Neutrons	Photons
Flux at sample position	10^7 cm^{-2} s^{-1}	10^{10} mm^{-2} s^{-1}
Scattering volume	6×10^4 mm^3	5×10^{-2} mm^3
Count rate for a typical LA phonon at maximum	215 min^{-1}	117 min^{-1}
time for a scan range of 10 meV transfer	60 min	65 min

X-Ray versus Neutron

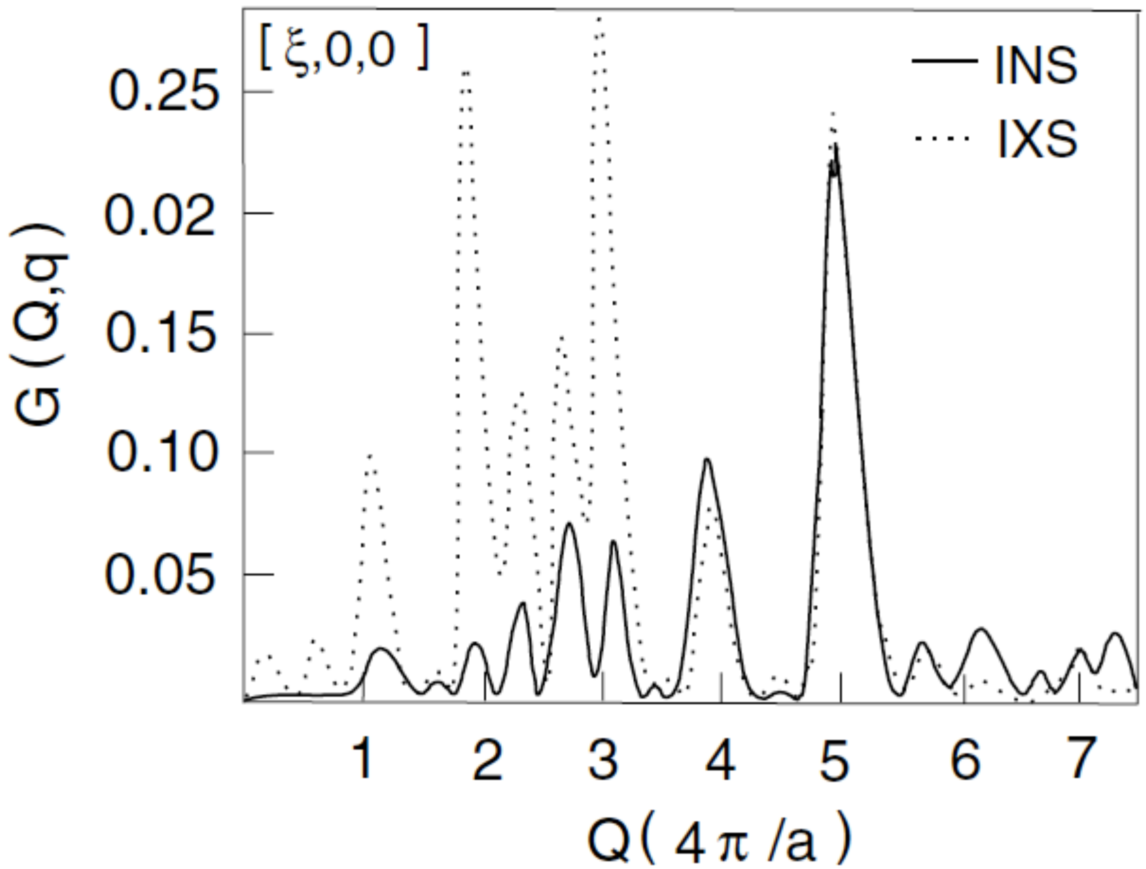


Figure 13. The structure factor ($G(Q, q)$ of α-SiO_2 for the longitudinal acoustic mode along $[\zeta, 0, 0]$ for x-rays (broken line) and neutrons (full line) calculated by Halcoussis (1997).