

## Lecture 7

### Crystal Vibrations

... and Neutron Scattering

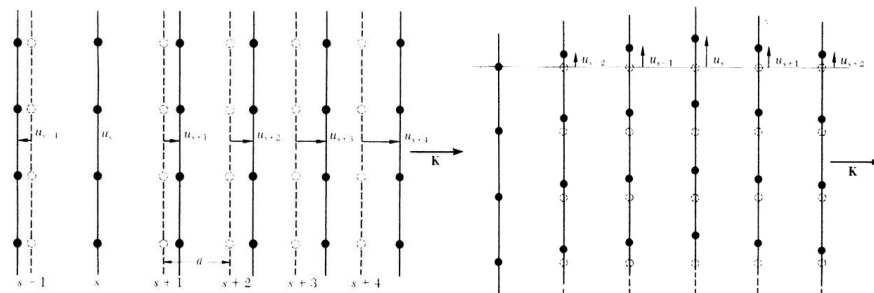
- 7.1 Vibrations of crystals with monatomic basis
- 7.2 Two atoms per primitive basis
- 7.3 Quantization of elastic waves
- 7.4 Phonon momentum
- 7.5 Inelastic neutron scattering for phonons

References:

- 1) Kittel, Chapter 4
- 2) Marder, Chapter 13
- 3) Ashcroft, Chapters 22, 24
- 4) Burns, Chapters 12
- 5) Ziman, Chapter 2
- 6) Ibach, Chapter 6

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## Longitudinal and transverse waves



Planes of atoms as displaced for longitudinal and transverse waves

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## Continuous Elastic Solid

We can describe a propagating vibration of amplitude  $u$  along a rod of material with Young's modulus  $Y$  and density  $\rho$  with the wave equation:

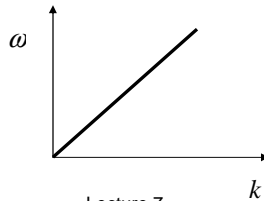
$$\frac{\partial^2 u}{\partial t^2} = \frac{Y}{\rho} \frac{\partial^2 u}{\partial x^2} \quad \text{for wave propagation along the x-direction}$$

By comparison to the general form of the 1-D wave equation:

$$\frac{\partial^2 u}{\partial t^2} = v^2 \frac{\partial^2 u}{\partial x^2} \quad \text{we find that} \quad v = \sqrt{\frac{Y}{\rho}} \quad \text{So the wave speed is independent of wavelength for an elastic medium!}$$

$$\omega = 2\pi f = 2\pi \frac{v}{\lambda} = kv$$

$$\text{group velocity} \quad v_g = \frac{d\omega}{dk}$$



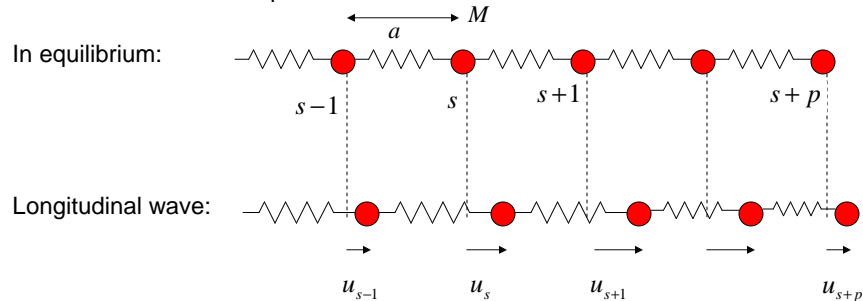
$\omega(k)$  is called the dispersion relation of the solid, and here it is linear (no dispersion!)

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## 7.1 Vibrations of Crystals with Monatomic Basis

By contrast to a continuous solid, a real solid is not uniform on an atomic scale, and thus it will exhibit dispersion. Consider a 1-D chain of atoms:



$$\text{For atom } s \quad F_s = \sum_p c_p (u_{s+p} - u_s) \\ (\text{for plane } s)$$

$p$  = atom label  
 $p = \pm 1$  nearest neighbors  
 $p = \pm 2$  next nearest neighbors  
 $c_p$  = force constant for atom  $p$

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## The equation of motion of the plane s

Elastic response of the crystal is a linear function of the forces (elastic energy is a quadratic function of the relative displacement)

The total force on plane s comes from planes  $s \pm 1$

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

C – the force constant between nearest-neighbor planes (different for transverse and longitudinal waves)

Equation of motion of the plane s:

$$M \frac{d^2 u_s}{dt^2} = C(u_{s+1} + u_{s-1} - 2u_s)$$

Solutions with all displacements having time dependence  $\exp(-i\omega t)$ . Then

$$\frac{d^2 u_s}{dt^2} = -\omega^2 u_s$$

$$-M\omega^2 u_s = C(u_{s+1} + u_{s-1} - 2u_s) \quad \text{This is a **difference equation** in the displacements } u$$

$$u_{s\pm 1} = ue^{isKa} e^{\pm iKa}$$

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## Equation of Motion for 1D Monatomic Lattice

Applying Newton's second law:  $F_s = M \frac{\partial^2 u_s}{\partial t^2} = \sum_p c_p (u_{s+p} - u_s)$

For the expected harmonic traveling waves, we can write  $u_s = ue^{i(kx_s - \omega t)}$   $x_s = sa$  position of atom s

$$\text{Thus: } Mu(-i\omega)^2 e^{i(ksa - \omega t)} = \sum_p c_p (ue^{i(k(s+p)a - \omega t)} - ue^{i(ksa - \omega t)})$$

$$\text{Or: } -M\omega^2 e^{i(ksa - \omega t)} = e^{i(ksa - \omega t)} \sum_p c_p (e^{ikpa} - 1)$$

$$\text{So: } -M\omega^2 = \sum_p c_p (e^{ikpa} - 1) \quad \text{Now since } c_{-p} = c_p \text{ by symmetry,}$$

$$-M\omega^2 = \sum_{p>0} c_p (e^{ikpa} + e^{-ikpa} - 2) = \sum_{p>0} 2c_p (\cos(kpa) - 1)$$

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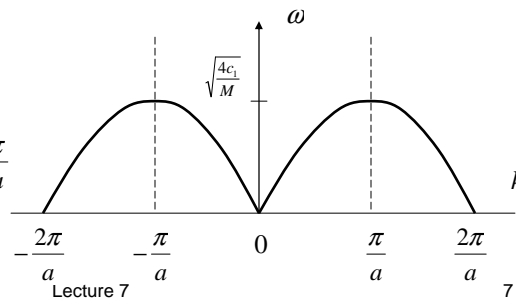
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## Dispersion relation of the monatomic 1D lattice

The result is: 
$$\omega^2 = \frac{2}{M} \sum_{p>0} c_p (1 - \cos(kpa)) = \frac{4}{M} \sum_{p>0} c_p \sin^2\left(\frac{1}{2}kpa\right)$$

Often it is reasonable to make the nearest-neighbor approximation ( $p = 1$ ):  $\omega^2 \cong \frac{4c_1}{M} \sin^2\left(\frac{1}{2}ka\right)$

The result is periodic in  $k$  and the only unique solutions that are physically meaningful correspond to values in the range:  $-\frac{\pi}{a} \leq k \leq \frac{\pi}{a}$



## Theory vs. Experiment

In a 3-D atomic lattice we expect to observe 3 different branches of the dispersion relation, since there are two mutually perpendicular transverse wave patterns in addition to the longitudinal pattern we have considered

Along different directions in the reciprocal lattice the shape of the dispersion relation is different

Note the resemblance to the simple 1-D result we found

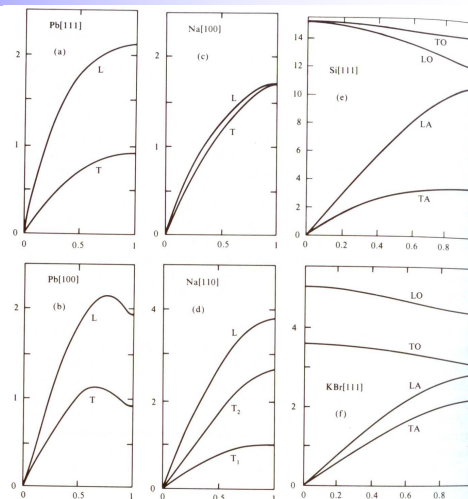


Fig. 12-10  $\omega$  vs.  $k$  for vibrational modes in different directions in reciprocal space and for different crystals as labeled. The  $k$ -values are all given in reduced values, that is,  $k/k_{\max}$  where  $k_{\max}$  is the Brillouin zone edge in that particular direction. Thus all the  $k$ -values go from 0 to 1.  $\omega$  is plotted in units of meV ( $1\text{meV} = 10^{-3}\text{eV} = 8.03\text{cm}^{-1}$ ). T and L stand for transverse and longitudinal branches, respectively.

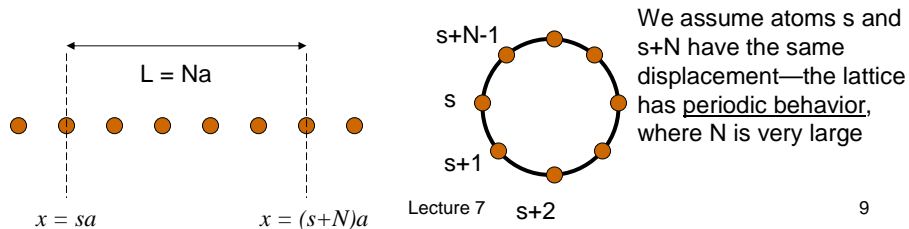
## Counting Modes and Finding $N(\omega)$

A vibrational mode is a vibration of a given wave vector  $\vec{k}$  (and thus  $\lambda$ ), frequency  $\omega$ , and energy  $E = \hbar\omega$ . How many modes are found in the interval between  $(\omega, E, \vec{k})$  and  $(\omega + d\omega, E + dE, \vec{k} + d\vec{k})$ ?

$$\# \text{ modes } dN = N(\omega)d\omega = N(E)dE = N(k)d^3\vec{k}$$

We will first find  $N(k)$  by examining allowed values of  $k$ . Then we will be able to calculate  $N(\omega)$

First step: simplify problem by using periodic boundary conditions for the linear chain of atoms:



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## Step one: finding $N(k)$

Since atoms  $s$  and  $s+N$  have the same displacement, we can write:

$$u_s = u_{s+N} \quad ue^{i(ksa - a\omega t)} = ue^{i(k(s+N)a - a\omega t)} \quad \longrightarrow \quad \boxed{1 = e^{ikNa}}$$

This sets a condition on allowed  $k$  values:  $kNa = 2\pi n \rightarrow k = \frac{2\pi n}{Na} \quad n = 1, 2, 3, \dots$

So the separation between allowed solutions ( $k$  values) is:  $\Delta k = \frac{2\pi}{Na} \quad \Delta n = \frac{2\pi}{Na}$  independent of  $k$ , so the density of modes in  $k$ -space is uniform

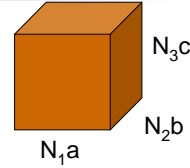
$$\text{Thus, in 1-D: } \frac{\# \text{ of modes}}{\text{interval of } k\text{-space}} = \frac{1}{\Delta k} = \frac{Na}{2\pi} = \frac{L}{2\pi}$$

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## Next step: finding $N(\omega)$

Now for a 3-D lattice we can apply periodic boundary conditions to a sample of  $N_1 \times N_2 \times N_3$  atoms:



$$\frac{\text{\# of modes}}{\text{volume of } k\text{-space}} = \frac{N_1 a}{2\pi} \frac{N_2 b}{2\pi} \frac{N_3 c}{2\pi} = \frac{V}{8\pi^3} = N(k)$$

Now we know from before that we can write the differential # of modes as:

$$dN = N(\omega)d\omega = N(k)d^3\vec{k} = \frac{V}{8\pi^3} d^3\vec{k}$$

We carry out the integration in  $k$ -space by using a “volume” element made up of a constant  $\omega$  surface with thickness  $dk$ :

$$d^3\vec{k} = (\text{surface area}) dk = \left[ \int dS_\omega \right] dk$$

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## Finding $N(\omega)$

Rewriting the differential number of modes in an interval:

$$dN = N(\omega)d\omega = \frac{V}{8\pi^3} \int dS_\omega dk$$

We get the result:

$$N(\omega) = \frac{V}{8\pi^3} \int dS_\omega \frac{dk}{d\omega} = \frac{V}{8\pi^3} \int dS_\omega \frac{1}{\frac{\partial \omega}{\partial k}}$$

A very similar result holds for  $N(E)$  using constant energy surfaces for the density of electron states in a periodic lattice!

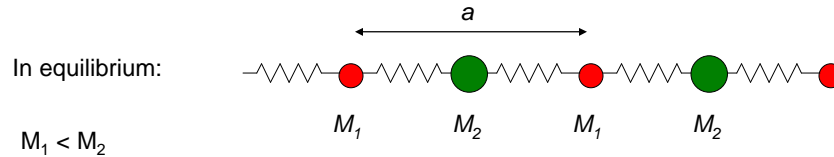
This equation gives the prescription for calculating the density of modes  $N(\omega)$  if we know the dispersion relation  $\omega(k)$ .

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## 7.2 Two Atoms per Primitive Basis

Consider a linear diatomic chain of atoms (1-D model for a crystal like NaCl):



Applying Newton's second law and the nearest-neighbor approximation to this system gives a dispersion relation with two "branches":

$$\omega^2 = c_1 \left( \frac{M_1 + M_2}{M_1 M_2} \right) \pm \left[ c_1^2 \left( \frac{M_1 + M_2}{M_1 M_2} \right)^2 - \frac{4c_1^2}{M_1 M_2} \sin^2 \left( \frac{1}{2} ka \right) \right]^{1/2}$$

$\omega_-(k)$   $\omega \rightarrow 0$  as  $k \rightarrow 0$  acoustic modes ( $M_1$  and  $M_2$  move in phase)

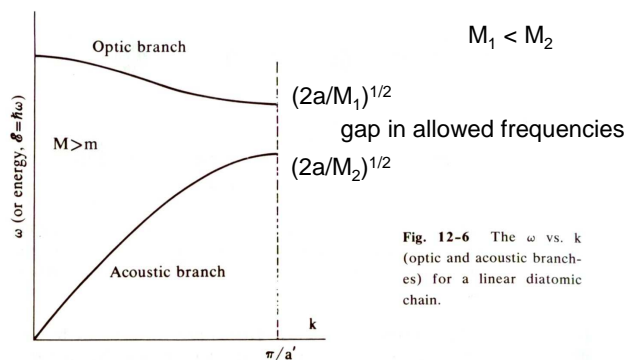
$\omega_+(k)$   $\omega \rightarrow \omega_{\max}$  as  $k \rightarrow 0$  optical modes ( $M_1$  and  $M_2$  move out of phase)

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## Optical and acoustical branches

Two branches may be presented as follows:



**Fig. 12-6** The  $\omega$  vs.  $k$  (optic and acoustic branches) for a linear diatomic chain.

If there are  $p$  atoms in the primitive cell, there are  $3p$  branches to the dispersion relation: 3 acoustical branches and  $3p-3$  optical branches

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## Optical and acoustical branches

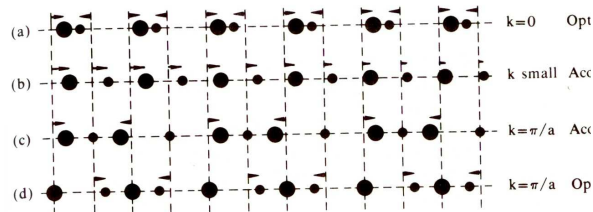
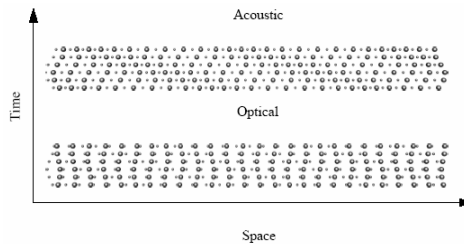


Fig. 12-7 A schematic diagram showing the atomic displacements for (a)  $k = 0$  branch; (b) acoustic branch for small but certainly not zero  $k$ ; (c) and (d) show zone boundary modes for the diatomic chain at  $k = \pi/a$ , that is, the zone boundary; diatomic chain.



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## 7.3 Quantization of Elastic Waves

The energy of a lattice vibrations is **quantized**

**The quantum of energy** is called a **phonon** (analogy with the photon of the electromagnetic wave)

Energy content of a vibrational mode of frequency  $\omega$  is an integral number of energy quanta  $\hbar\omega$ . We call these quanta "phonons".

While a **photon** is a quantized unit of **electromagnetic** energy, a **phonon** is a quantized unit of **vibrational** (elastic) energy.

	Name	Field
	Electron	
	Photon	Electromagnetic wave
	Phonon	Elastic wave
	Plasmon	Collective electron wave

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## 7.4 Phonon Momentum

Associated with each mode of frequency  $\omega$  is a wavevector  $\vec{k}$ , which leads to the definition of a “crystal momentum”:  $\hbar\vec{k}$

Crystal momentum is analogous to but not equivalent to linear momentum. No net mass transport occurs in a propagating lattice vibration, so a phonon **does not carry physical momentum**

But phonons interacting with each other or with electrons or photons obey a conservation law similar to the conservation of linear momentum for interacting particles

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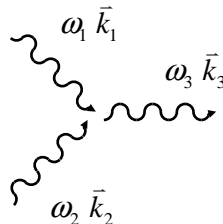
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## Conservation Laws

Lattice vibrations (phonons) of many different frequencies can interact in a solid. In all interactions involving phonons, energy must be conserved and crystal momentum must be conserved to within a reciprocal lattice vector:

$$\begin{aligned}\hbar\omega_1 + \hbar\omega_2 &= \hbar\omega_3 \\ \hbar\vec{k}_1 + \hbar\vec{k}_2 &= \hbar\vec{k}_3 + \hbar\vec{G}\end{aligned}$$

Schematically:



Compare this to the special case of elastic scattering of x-rays with a crystal lattice:

$$\vec{k}' = \vec{k} + \vec{G}$$

Just a special case of the general conservation law!

Photon wave vectors  
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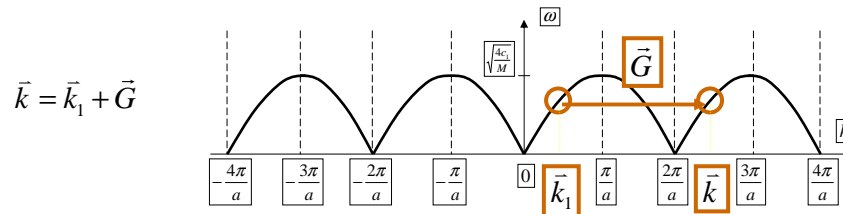
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## Back to Brillouin Zones

The 1st BZ is the region in reciprocal space containing all information about the lattice vibrations of the solid

Only the  $\vec{k}$  values in the 1st BZ correspond to unique vibrational modes.  
Any  $\vec{k}$  outside this zone is mathematically equivalent to a value  $\vec{k}_1$  inside the 1st BZ

This is expressed in terms of a general translation vector of the reciprocal lattice:



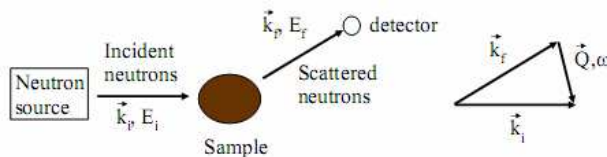
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## 7.5 Neutron scattering measurements

What is a neutron scattering measurement?

- neutron source sends neutron to sample
- some neutrons scatter from sample
- scattered neutrons are detected



Conservation of energy:  $\frac{\hbar^2 k_i^2}{2M} = \frac{\hbar^2 k_f^2}{2M} \pm \Delta E$

When a phonon of wavelength  $|K|$  is created by the inelastic scattering of a photon or neutron, the wavevector selection rule:

$\vec{k}_f + \vec{K} = \vec{k}_i + \vec{G}$  creation of a phonon

$\vec{k}_f = \vec{k}_i + \vec{K} + \vec{G}$  annihilation of a phonon

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## Why neutrons?

Wavelength:  $\lambda = \frac{9.044}{\sqrt{E}}$

- At 10 meV,  $\lambda=2.86\text{\AA} \Rightarrow$  similar length scales as structures of interest

Energy:

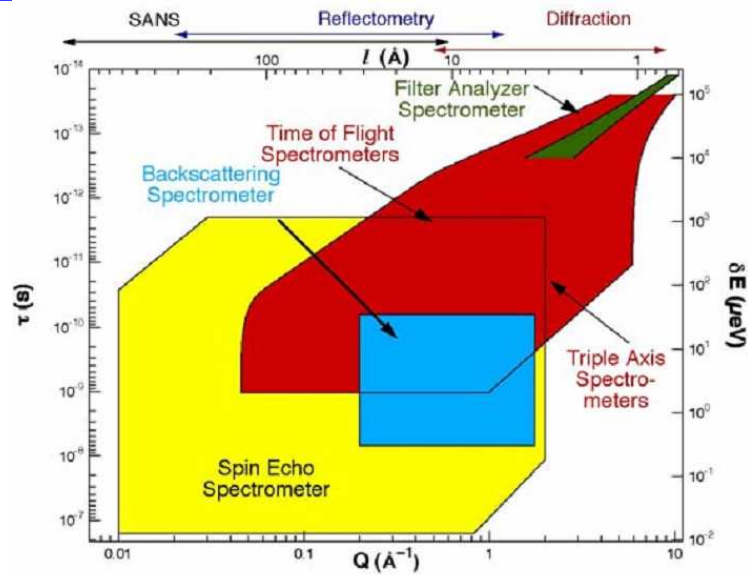
- thermal sources: 5-100meV
- cold sources: 1-10meV
- spallation sources: thermal and epithermal neutrons (>100meV)

can cover range of typical excitation energies in solids and liquids!

<http://www.ncnr.nist.gov/summerschool/ss05/Vajklecture.pdf>

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## Energy and Length Scale



<http://www.ncnr.nist.gov/index.html>

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## Effective Cross Section



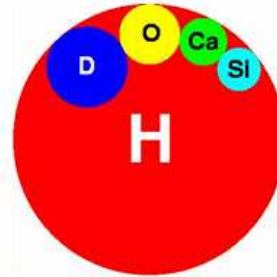
**Cross Section,  $\sigma$ :** an effective area which represents probability that a neutron will interact with a nucleus

$\sigma$  varies from element to element and even isotope to isotope

Typical  $\sigma \sim 10^{-24} \text{ cm}^2$  for a single nucleus

One unit of cross section is a **1 barn** =  $10^{-24} \text{ cm}^2$

... as in "it can't hit the size of the barn"



Total nuclear cross section for several isotopes

<http://www.ncnr.nist.gov/index.html>

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## Neutron Scattering

Number of scattered neutrons is proportional to scattering function,  $S(\mathbf{Q}, \omega)$

Scattering:

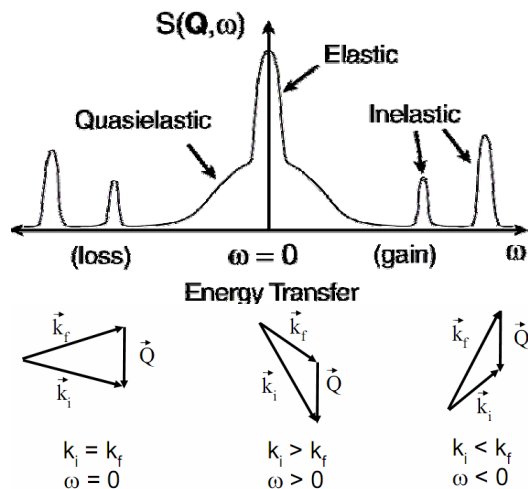
*elastic;*

*quasielastic;*

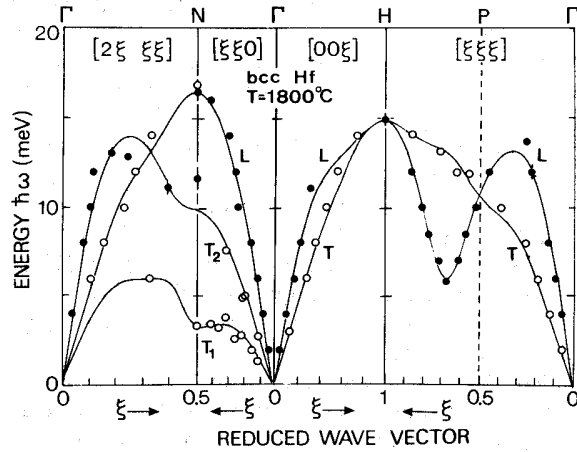
*Inelastic*

Neutrons are sensitive to components of motion parallel to the momentum transfer  $\mathbf{Q}$

Angular width of the scattered neutron beam gives information on the lifetime of phonons

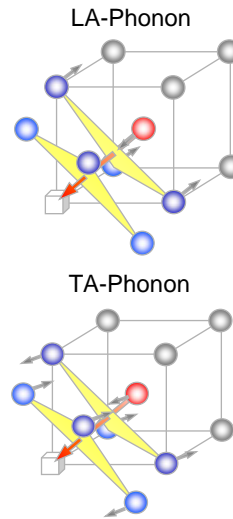


## Phonon dispersion of bcc-Hf



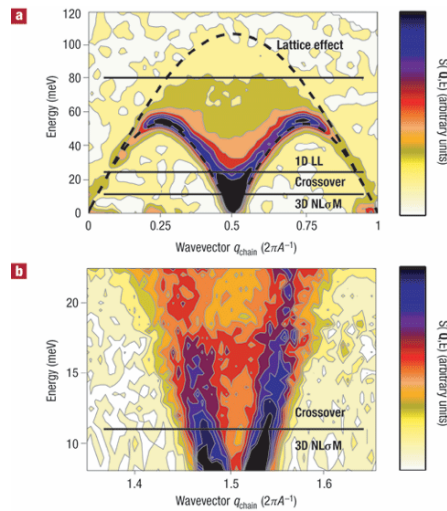
Trampenau *et al.* (1991)

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## Inelastic neutron scattering data for $\text{KCuF}_3$ measured



Bella Lake, D. Alan Tennant, Chris D. Frost and Stephen E. Nagler *Nature Materials* 4, 329 - 334 (2005)

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