

NCTS CMRFG
Lectures 2017

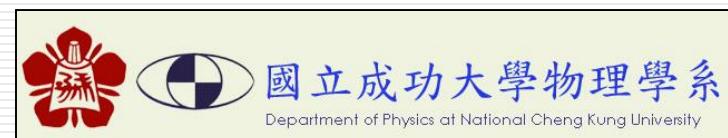


Phonons and Related Thermodynamical Properties: Fundamental Theory and DFT Approaches

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Outline of the Lecture

- ◆ How do we describe lattice dynamics ?
- ◆ How does lattice dynamics determines thermodynamic properties of materials?
- ◆ How are vibration frequencies determined experimentally?
- ◆ What physical properties require descriptions beyond harmonic interaction?
- ◆ How is DFT applied to study lattice dynamics and thermodynamical properties of materials?

Reference : Most of these materials can be found at chap8~chap11 of Martin T. Dove
“Structure and Dynamics: An atomic view of Materials”

Lattice dynamics

How do we describe lattice dynamics ?

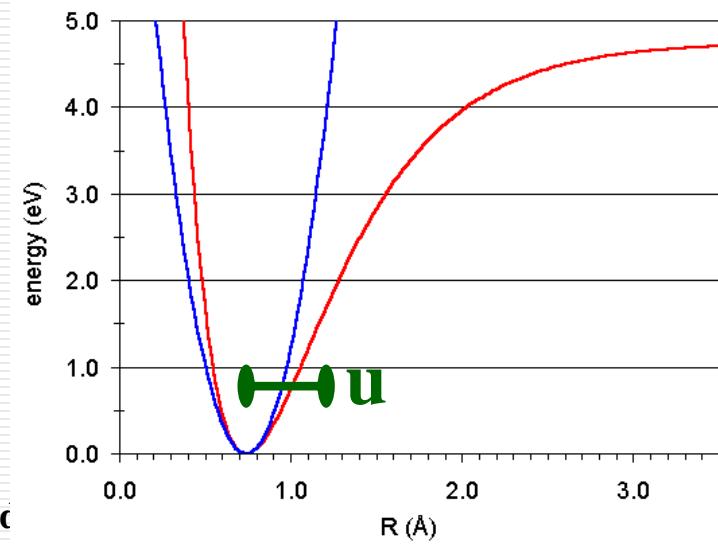
- ◆ The harmonic approximation
- ◆ Lattice vibrations of 1D monatomic crystals
- ◆ Dispersion curves in face-centered cubic materials
- ◆ Lattice vibrations of crystals with several atoms in the unit cell

Harmonic Approximation

$u_{j,x} \ u_{j,y} \ u_{j,z} \rightarrow u_{j,\alpha}$ atomic displacement

$$E = E_0 + \sum_{\substack{j, \\ \alpha}} \frac{\partial E}{\partial u_{j,\alpha}} u_{j,\alpha} + \frac{1}{2} \sum_{\substack{j,j' \\ \alpha,\alpha'}} \frac{\partial^2 E}{\partial u_{j,\alpha} \partial u_{j',\alpha'}} u_{j,\alpha} u_{j',\alpha'} + \dots$$

$$+ \frac{1}{n!} \sum_{\substack{j^{(1)}, \dots, j^{(n)} \\ \alpha^{(1)}, \dots, \alpha^{(n)}}} \frac{\partial^n E}{\partial u_{j^{(1)}, \alpha^{(1)}} \cdots \partial u_{j^{(n)}, \alpha^{(n)}}} u_{j^{(1)}, \alpha^{(1)}} \cdots u_{j^{(n)}, \alpha^{(n)}}$$

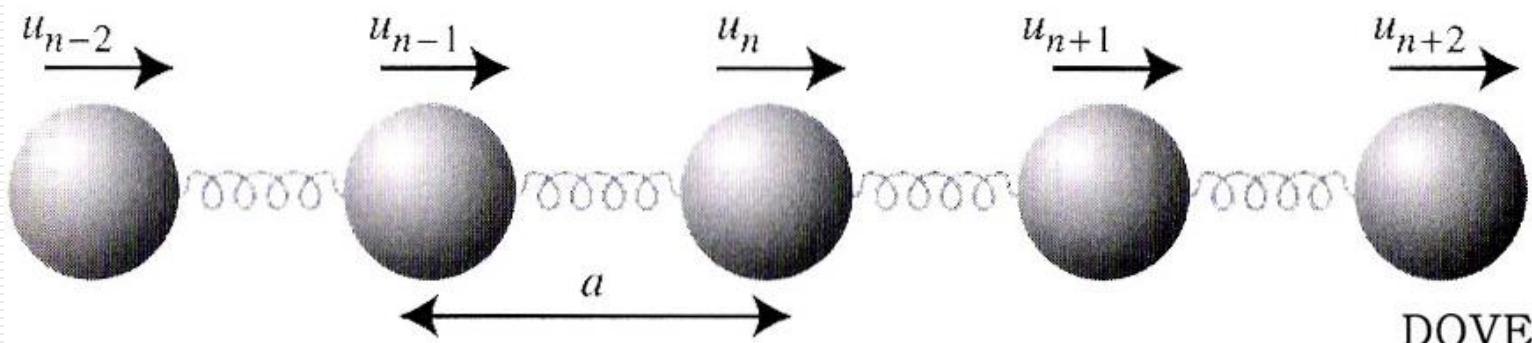


1D monatomic crystals : the linear chain model

- ◆ Consider only nearest-neighbor interaction

$$U^{\text{harm}} = \frac{1}{2}K \sum_n [u(na) - u([n+1]a)]^2$$

$$M\ddot{u}(na) = -\frac{\partial U^{\text{harm}}}{\partial u(na)} = -K [2u(na) - u([n-1]a) - u([n+1]a)]$$



Reciprocal lattice, Brillouin zone, allowed \mathbf{k} 's

- ◆ Periodic boundary conditions

$$u([N+1]a) = u(a); \quad u(0) = u(Na). \quad e^{ikNa} = 1$$

- ◆ Quantized, allowed values of k : $k=2\pi n/Na$
- ◆ Number of allowed wave vectors within one Brillouin zone = number of primitive unit cells in the crystal

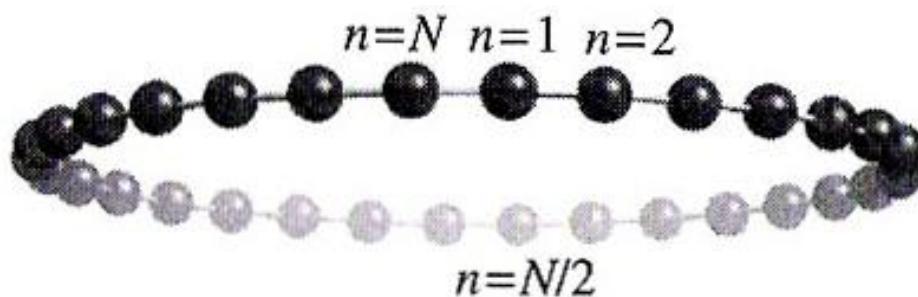


Fig. 8.5 Joined chain to show operation of periodic boundary conditions.

DOVE

Normal Modes of a One-dimensional Monatomic Bravais Lattice

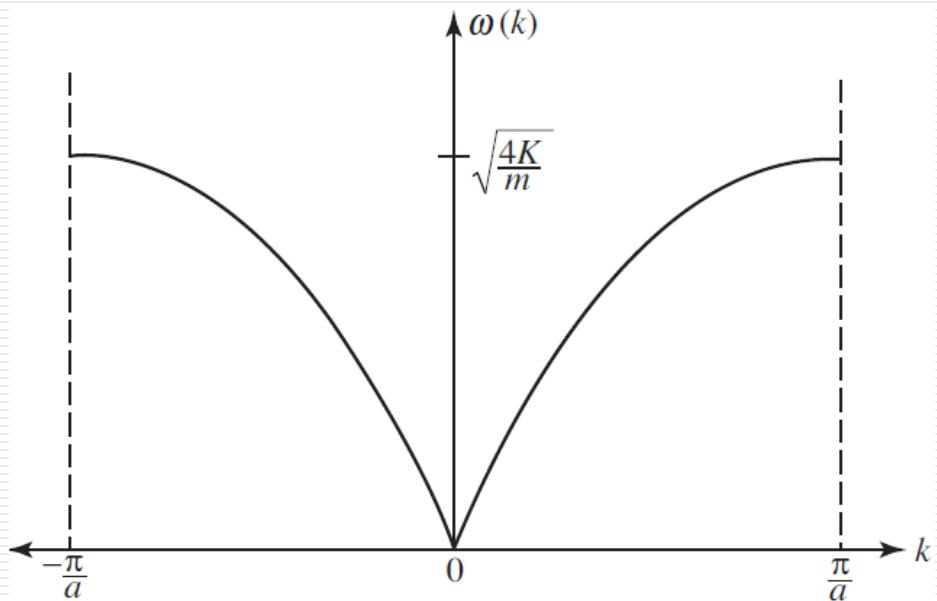
$$\begin{aligned}-M\omega^2 e^{i(kna - \omega t)} &= -K[2 - e^{-ika} - e^{ika}]e^{i(kna - \omega t)} \\&= -2K(1 - \cos ka)e^{i(kna - \omega t)},\end{aligned}$$

$$\omega(k) = \sqrt{\frac{2K(1 - \cos ka)}{M}} = 2\sqrt{\frac{K}{M}} \left| \sin \frac{1}{2}ka \right|$$

Normal Modes of a One-dimensional Monatomic Bravais Lattice

The solutions describe waves propagating along the chain with phase velocity $c=\omega/k$, and group velocity $v=(\partial\omega/\partial k)$.

The frequency ω is plotted against the wave vector k in the figure below. Such a curve is known as a dispersion curve.



If $k \rightarrow 0$

$$\omega = \left(a \sqrt{\frac{K}{M}} \right) |k|$$

Dispersion curve for a monatomic linear chain with only nearest-neighbor interactions. Note that ω is linear for small k , and that $\partial\omega/\partial k$ vanishes at the boundaries of the zone ($k = \pm\pi/a$).

Reciprocal lattice, Brillouin zone, allowed k's

$$u_{n,k} = \tilde{u}_k \exp[i(kna - \omega t)]$$

$$u_{n,k+G} = \tilde{u}_k \exp[i(kna + Gna - \omega t)] = u_{n,k} \exp(iGna) = u_{n,k}$$

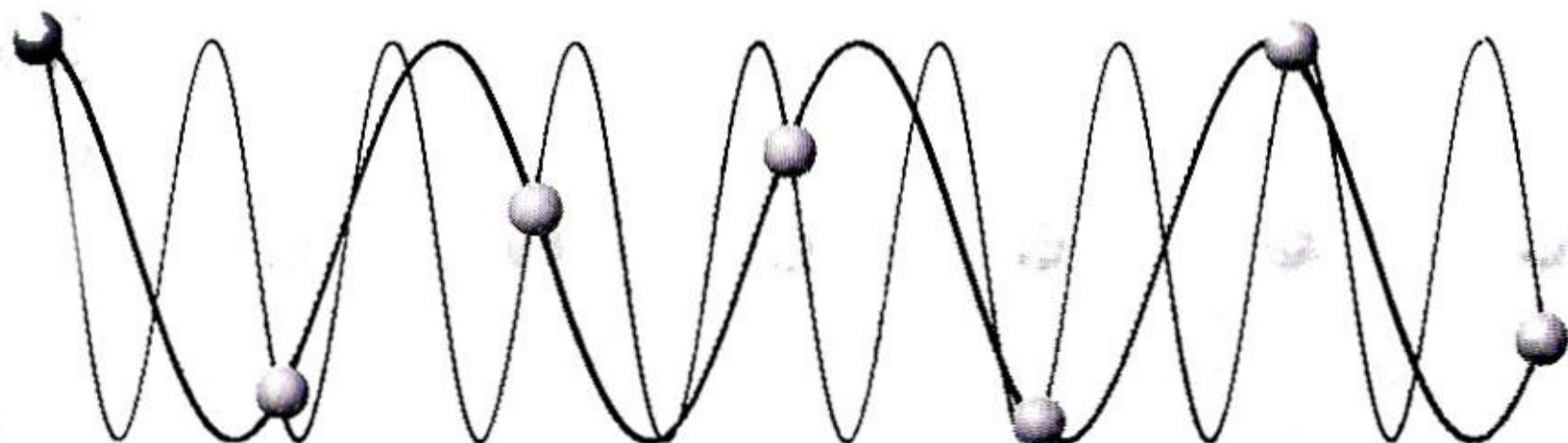


Fig. 8.4 The atomic motions associated with two waves whose wave vectors differ by a reciprocal lattice vector. We see that the two waves have identical effects on the atoms.

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Reciprocal lattice, Brillouin zone, allowed k's

$$u_{n,k+G} = u_{n,k}$$

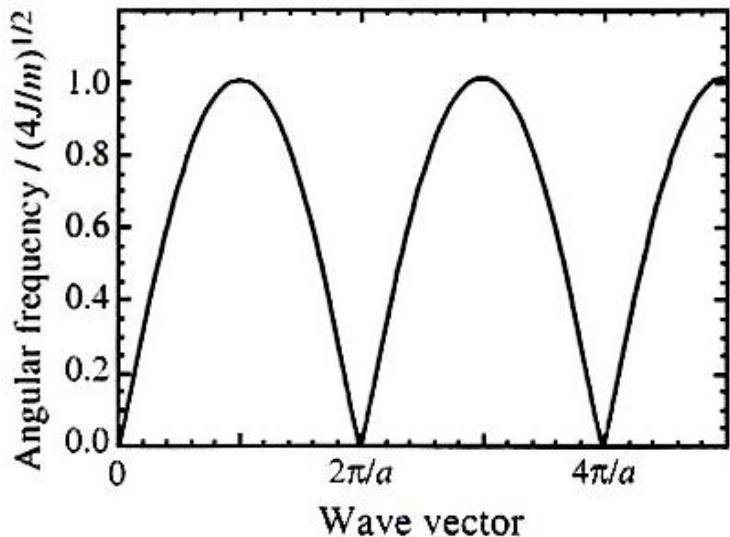
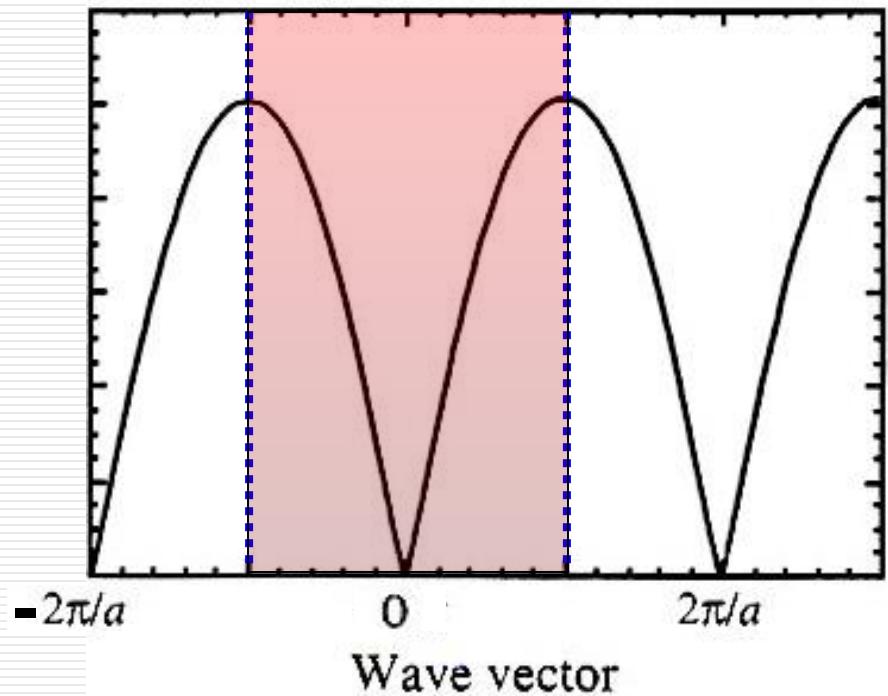


Fig. 8.3 Acoustic mode dispersion curve for the one-dimensional chain.

DOVE



$$v_g = \frac{\partial \omega}{\partial k} \Rightarrow$$

$$v_g(k = \pm\pi/a) = 0$$

Reduced wave vectors

3D monatomic crystals : general principles

- ◆ $u \rightarrow$ displacement of planes of atoms
- ◆ Need to include motions \perp to k
- ◆ 2 transverse acoustic modes (TA)
- ◆ 1 longitudinal acoustic modes (LA)
- ◆ 3-, 4-, and 6-fold rotation axes along $k \rightarrow$ degenerate TA modes

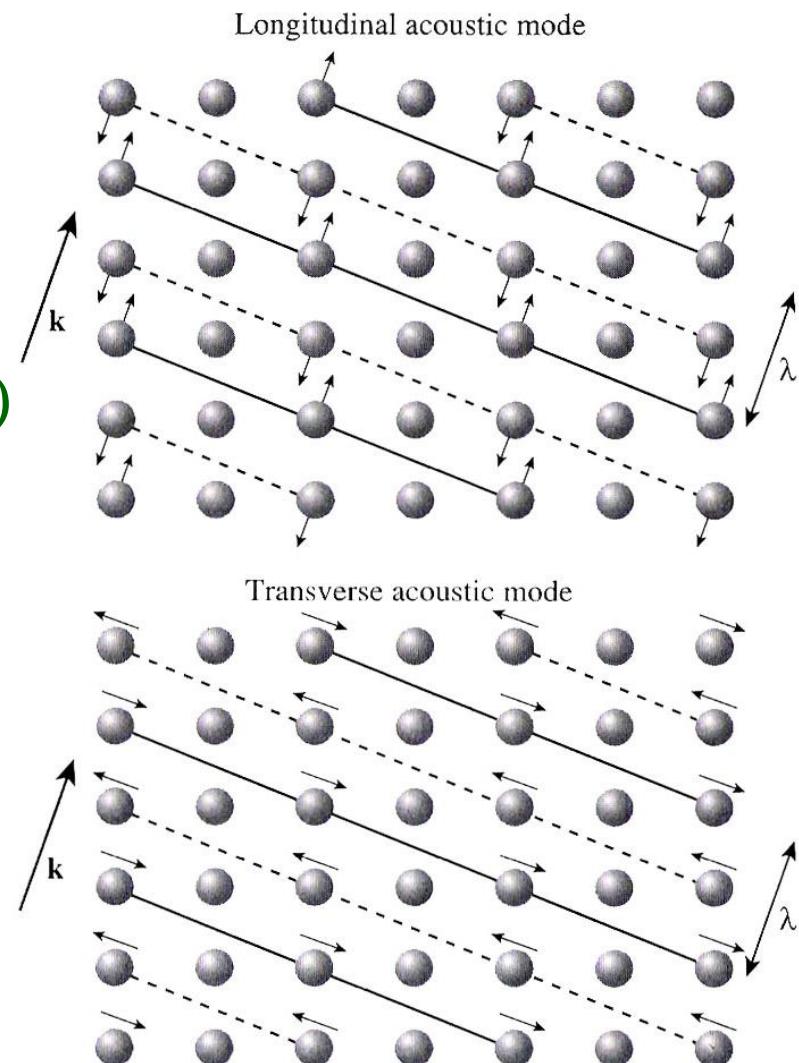


Fig. 8.6 Travelling waves with longitudinal and transverse atomic displacements in a two-dimensional section of a monatomic crystal.

Dispersion curves of neon (FCC)

- ◆ van der Waal's bonding
- ◆ nnn atomic interaction << nn
- ◆ Degenerate TA : [001], [111]
- ◆ nn planar interactions : [001], [111]
- ◆ nnn planar interactions : [110]

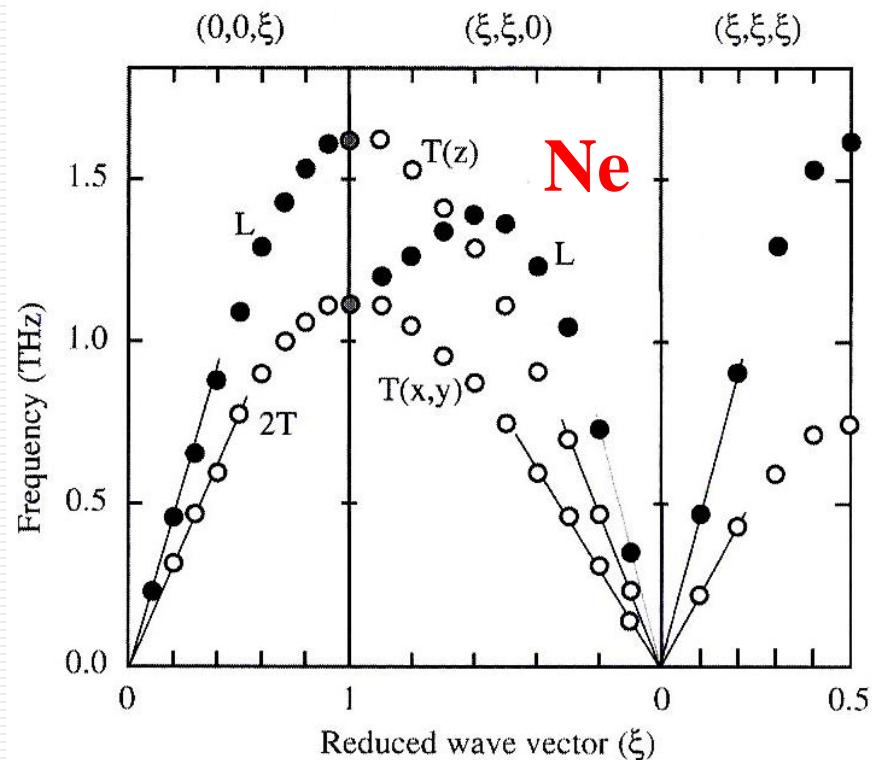


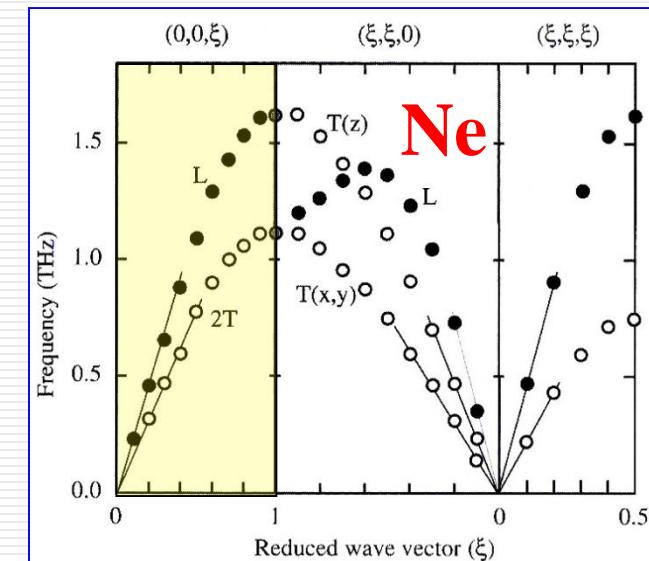
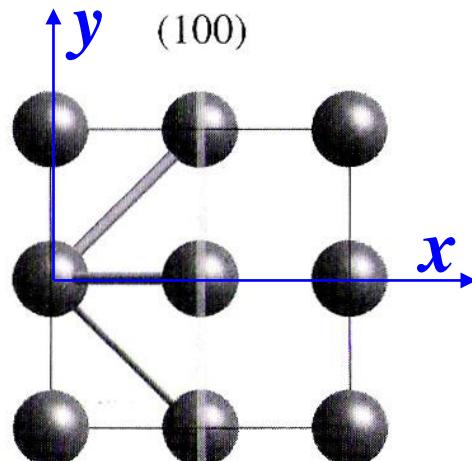
Fig. 8.7 Acoustic mode dispersion curves for neon (ccp structure) measured by inelastic neutron scattering. L and T denote longitudinal and transverse modes respectively. For the [001] and [111] directions the two transverse modes are degenerate (as indicated by the label 2T). Along the [110] direction, the (x,y) and (z) labels indicate the directions of the atomic motions. (Data taken from Endoh *et al.*, *Phys. Rev. B* 11, 1681, 1975.)

$$1\text{THz} = 4.136 \text{ meV}$$
$$1\text{cm}^{-1} = 0.124 \text{ meV}$$

DOVE

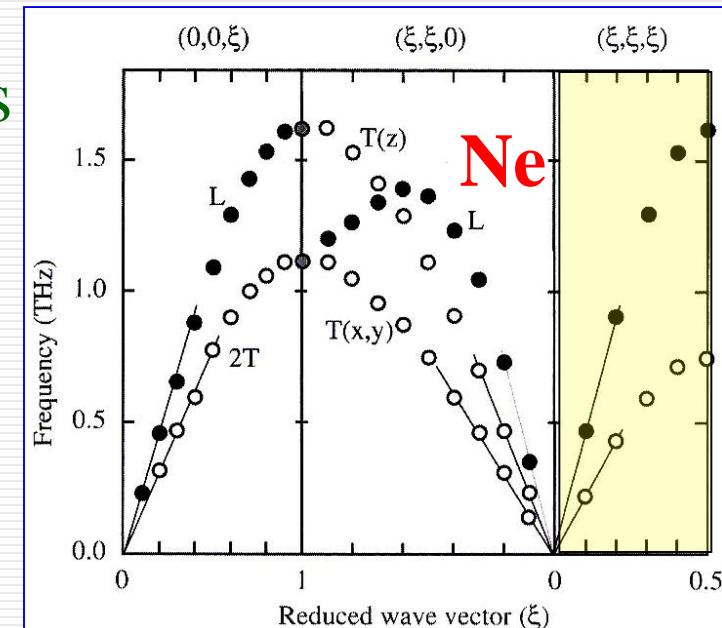
Dispersion curves of neon along [100]

- ◆ Atomic force constants between atoms : $\partial^2\phi/\partial r^2 \equiv K$
- ◆ $r = (x, y, z) \rightarrow \partial^2\phi/\partial x^2 = K(x^2/r^2)$
- ◆ Force constants for the three relative displacements of neighbouring planes : $J_x = \sum_j \frac{\partial^2\phi}{\partial x_j^2} = 2K$ $J_y = K = J_z$
- ◆ 4 nn vectors : $[1, \pm 1, 0]a/2$ $[1, 0, \pm 1]a/2$
- ◆ degenerate TA modes
- ◆ $\omega_{LA} \approx \sqrt{2}\omega_{TA}$



Dispersion curves of neon along [111]

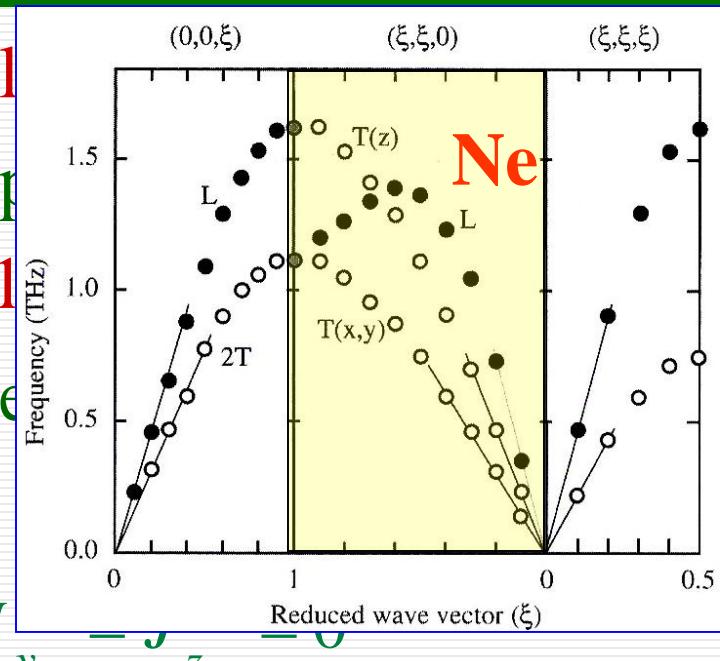
- ◆ Close-packed planes → interacting with 3 atoms in the nn plane
- ◆ New coordinate system with $x \parallel [111]$ and $y \parallel [1-11]$
- ◆ Force constants for the three relative displacements of neighbouring planes : $J_x = \sum_j \frac{\partial^2 \phi}{\partial x_j^2} = 2K$ $J_y = K/2 = J_z$
- ◆ No interactions between nnn planes
- ◆ degenerate TA modes
- ◆ $\omega_{LA} \approx 2\omega_{TA}$



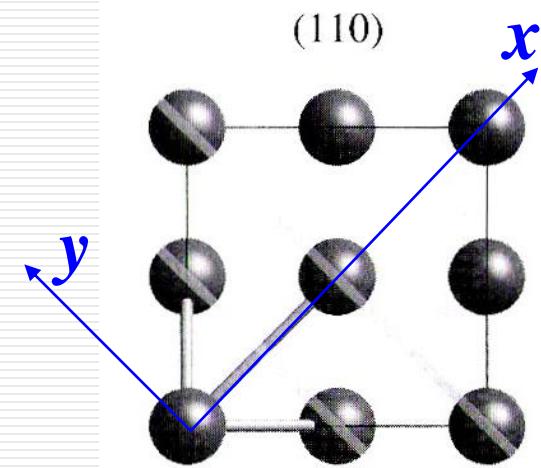
Dispersion curves of neon along [110]

- ◆ interacting with 4 atoms in the nn plane
- ◆ interacting with 1 atom in the nnn plane
- ◆ New coordinate system with $x \parallel [110]$
- ◆ Force constants for the three relative neighbouring planes : $J_x^{(1)} = J_y^{(1)} = K$

$$J_x^{(2)} = K$$



- ◆ $\omega_{TA1} \approx \sqrt{2}\omega_{TA2}$
- ◆ LA $\rightarrow p=1$ and $p=2$ $\omega_k^2 = \frac{4}{m} \sum_p J_p \sin^2(kpa/2)$
- ◆ P=2 \rightarrow maximum at half-way to the BZ boundary, zero contribution at zone boundary
- ◆ $\omega_{LA}(BZB) \approx \omega_{TA2}$



Dispersion curves of lead (FCC)

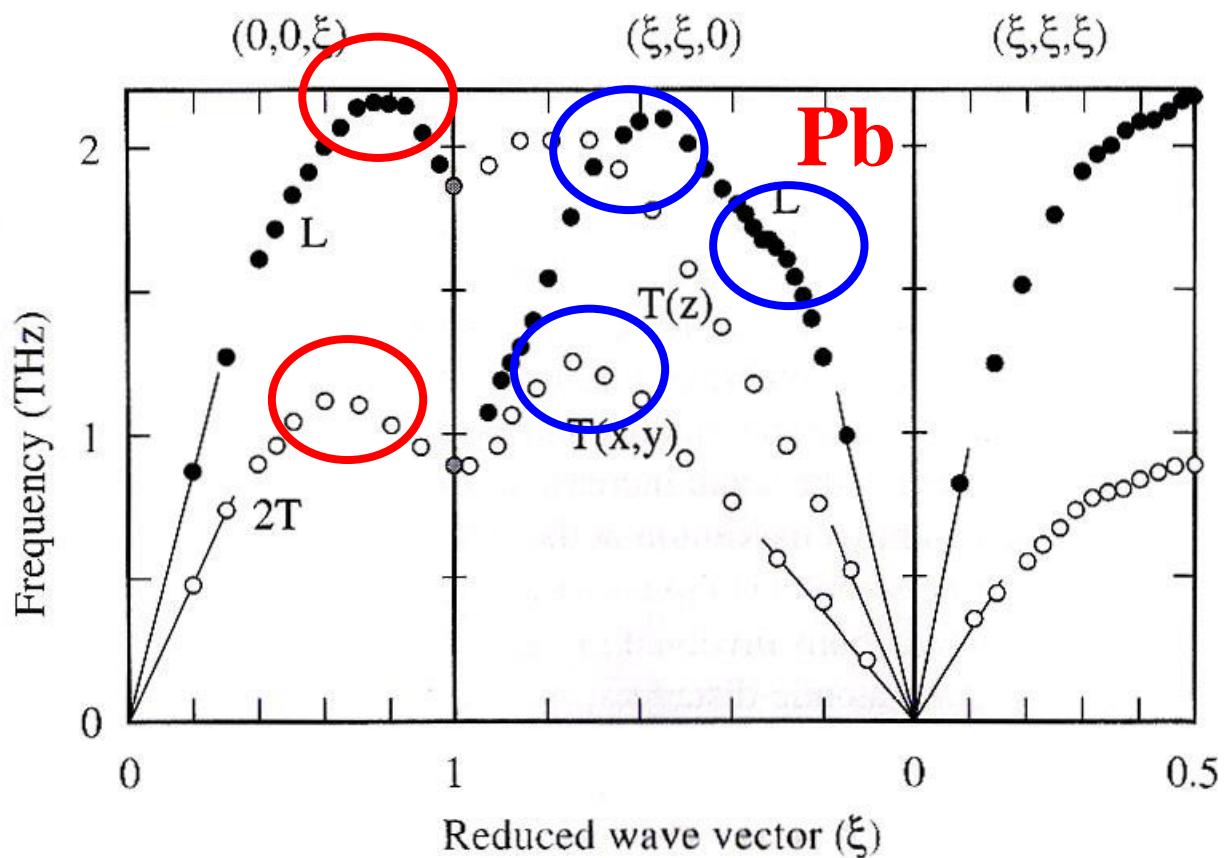
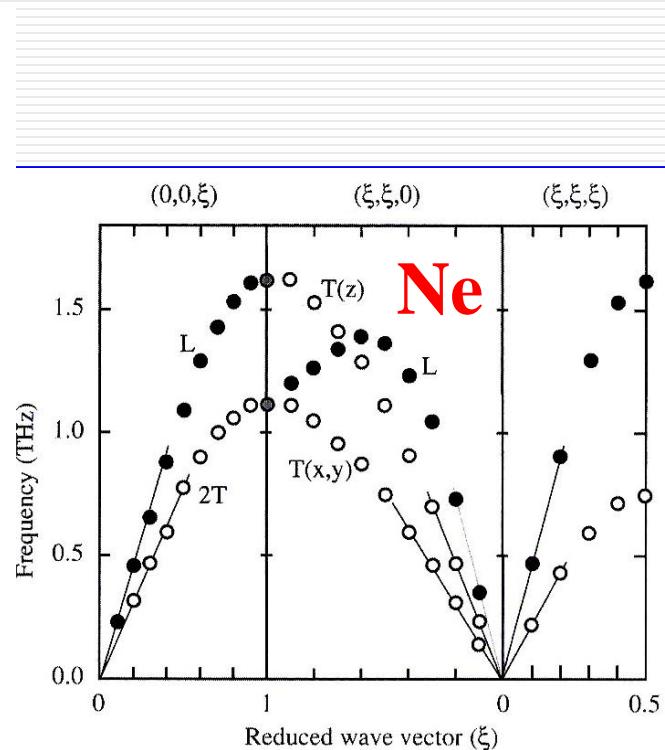


Fig. 8.9 Acoustic mode dispersion curves for lead (fcc) measured by inelastic neutron scattering. (Data taken from Brockhouse *et al.*, *Phys. Rev.* **128**, 1099, 1962.)

DOVE



Phonon dispersion curve : Al

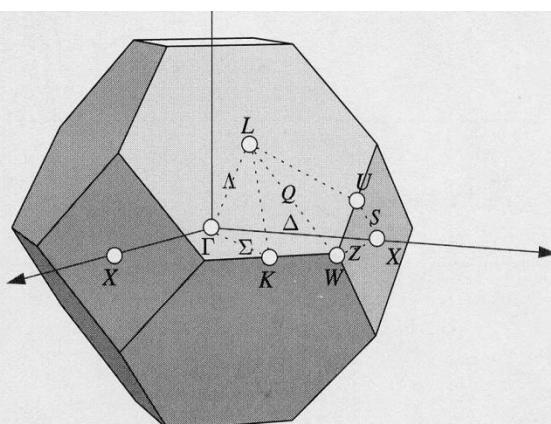
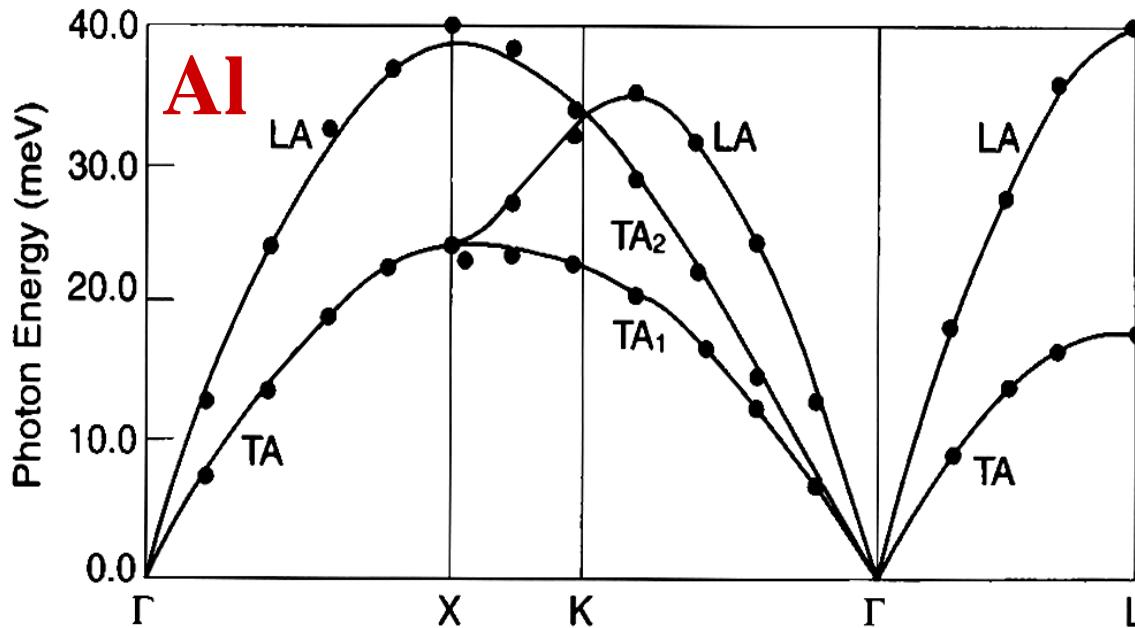


Figure 7.7. First Brillouin zone of the fcc lattice, with conventional notation for points of special symmetry. The reciprocal lattice of fcc is bcc, with lattice spacing of $4\pi/a$, so this figure is the same as Figure 2.6. In units of $2\pi/a$, $\Gamma = (0 \ 0 \ 0)$, $X = (0 \ 1 \ 0)$, $L = (1/2 \ 1/2 \ 1/2)$, $W = (1/2 \ 1 \ 0)$, $K = (3/4 \ 3/4 \ 0)$, and $U = (1/4 \ 1 \ 1/4)$.

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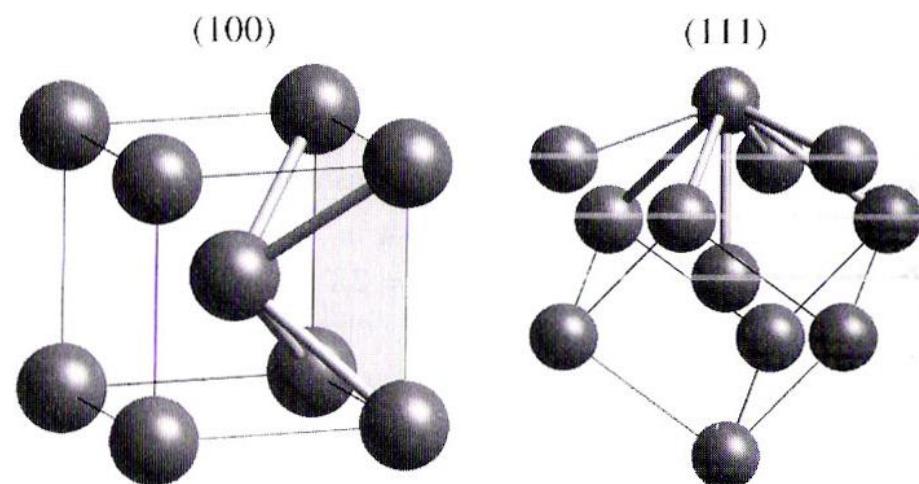
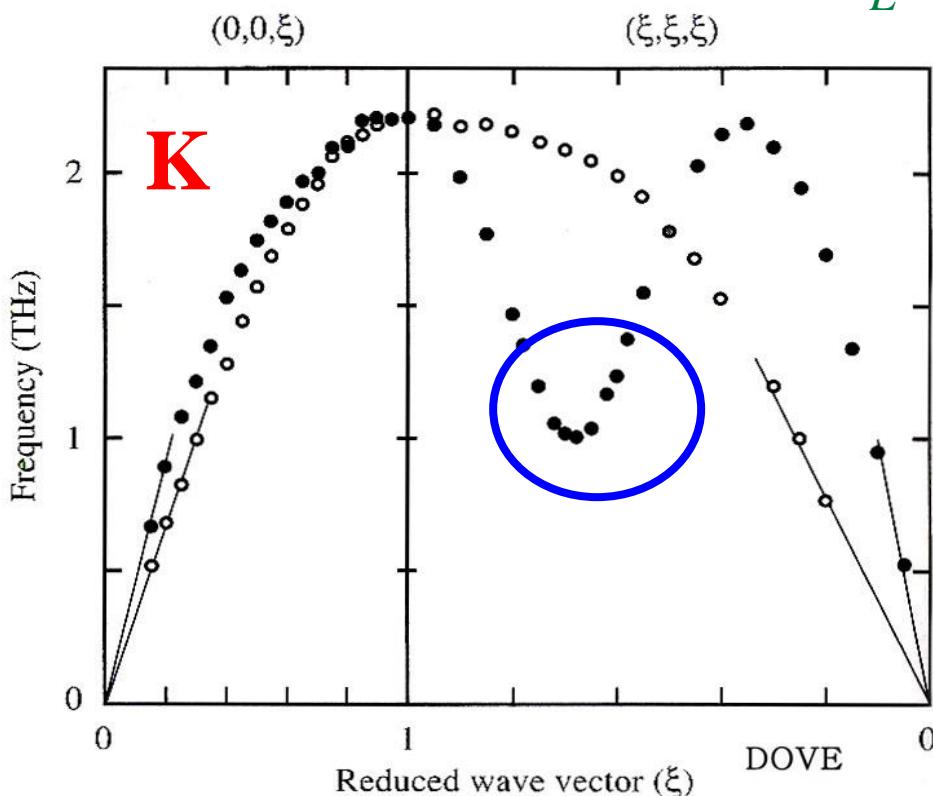
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Grosso-Parravicini

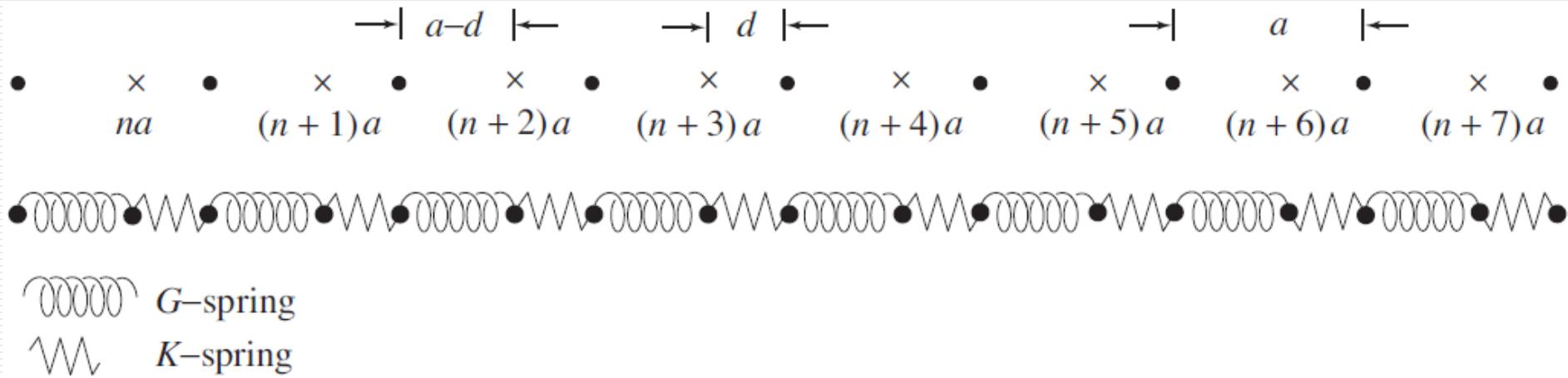
Dispersion curves of K (BCC)

- ◆ 4 nn interactions for (100) $J_x = 2K = J_y = J_z$
- ◆ 3rd neighbour planar interaction for (111)

$$J_L^{(1)} = K/3 \quad J_T^{(1)} = 4K/3 \quad J_T^{(3)} = K$$



Normal Modes of a One-dimensional Lattice with a Basis



The diatomic linear chain of identical atoms, connected by springs of alternating strengths.

$$U^{\text{harm}} = \frac{K}{2} \sum_n [u_1(na) - u_2(na)]^2 + \frac{G}{2} \sum_n [u_2(na) - u_1([n+1]a)]^2$$

Normal Modes of a One-dimensional Lattice with a Basis

$$\begin{aligned}M\ddot{u}_1(na) &= -\frac{\partial U^{\text{harm}}}{\partial u_1(na)} \\&= -K[u_1(na) - u_2(na)] - G[u_1(na) - u_2([n-1]a)], \\M\ddot{u}_2(na) &= -\frac{\partial U^{\text{harm}}}{\partial u_2(na)} \\&= -K[u_2(na) - u_1(na)] - G[u_2(na) - u_1([n+1]a)].\end{aligned}$$

$$u_1(na) = \epsilon_1 e^{i(kna - \omega t)},$$

$$u_2(na) = \epsilon_2 e^{i(kna - \omega t)}.$$

Normal Modes of a One-dimensional Lattice with a Basis

$$[M\omega^2 - (K + G)]\epsilon_1 + (K + Ge^{-ika})\epsilon_2 = 0,$$

$$(K + Ge^{ika})\epsilon_1 + [M\omega^2 - (K + G)]\epsilon_2 = 0.$$

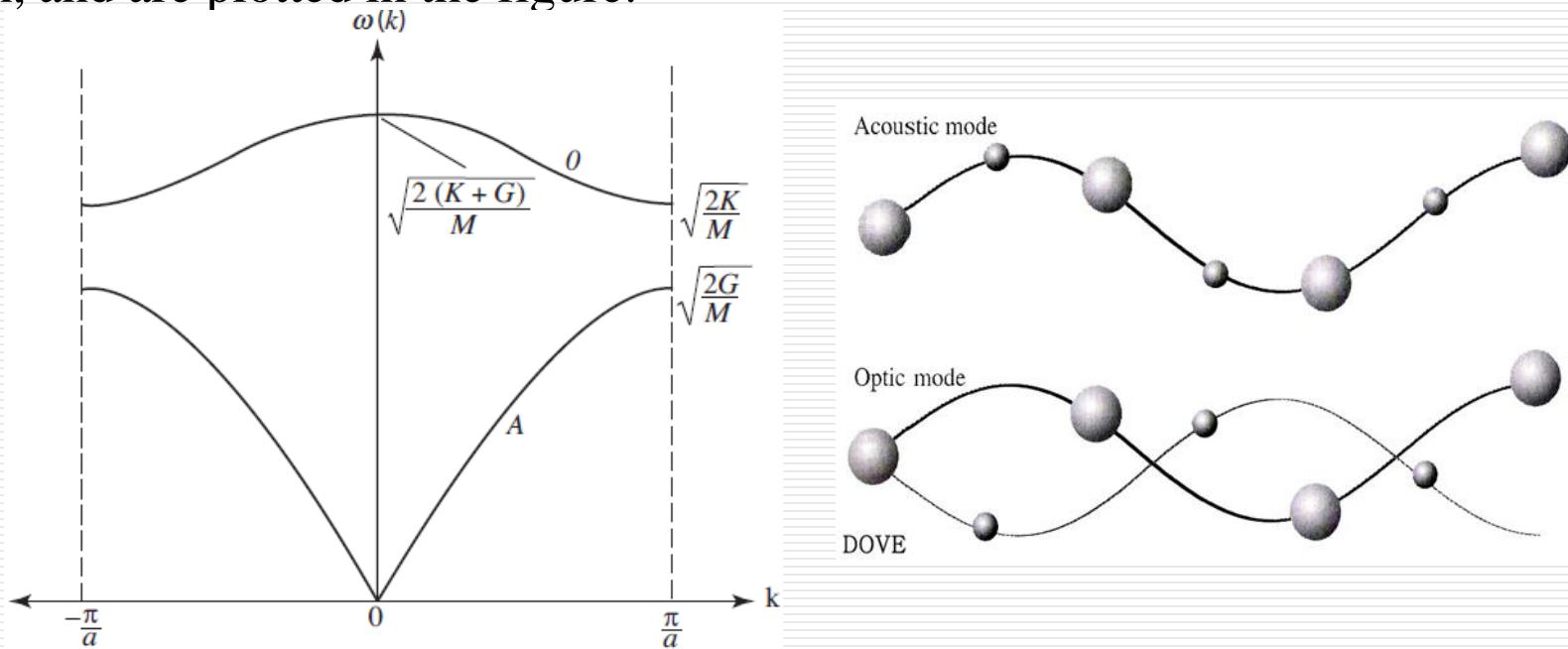
$$[M\omega^2 - (K + G)]^2 = |K + Ge^{-ika}|^2 = K^2 + G^2 + 2KG \cos ka.$$

$$\omega^2 = \frac{K + G}{M} \pm \frac{1}{M} \sqrt{K^2 + G^2 + 2KG \cos ka},$$

$$\frac{\epsilon_2}{\epsilon_1} = \mp \frac{K + Ge^{ika}}{|K + Ge^{ika}|}.$$

Normal Modes of a One-dimensional Lattice with a Basis

- For each of the N values of k , there are thus two solutions, leading to a total of $2N$ normal modes, as is appropriate to the $2N$ degrees of freedom.
- The two ω versus k curves are referred to as the two branches of the dispersion relation, and are plotted in the figure.



Dispersion relation for the diatomic linear chain. The lower branch is the acoustic branch and has the same structure as the single branch present in the monatomic case. In addition, there is now an optical branch (upper branch).

NORMAL MODES OF A ONE-DIMENSIONAL MONATOMIC BRAVAIS LATTICE

- The lower branch has the same structure as the single branch we found in the monatomic Bravais lattice: ω vanishes linearly in k for small k , and the curve becomes flat at the edges of the Brillouin zone. This branch is known as the acoustic branch because its dispersion relation is of the form $\omega = v k$ characteristic of sound waves, at small k .
- The second branch starts at $\omega = \sqrt{2(K + G)/M}$ at $k = 0$ and decreases with increasing k down to $\sqrt{2K/M}$ at the zone edge. This branch is known as the optical branch because the long wavelength optical modes in ionic crystals can interact with electromagnetic radiation, and are responsible for much of the characteristic optical behaviour of such crystals.
- We can gain some insight into the nature of the two branches by considering some special cases in more detail:

NORMAL MODES OF A ONE-DIMENSIONAL MONATOMIC BRAVAIS LATTICE

Case 1: $k \ll \pi/a$. Here $\cos ka \approx 1 - (ka)^2/2$, and to leading order in k the roots become

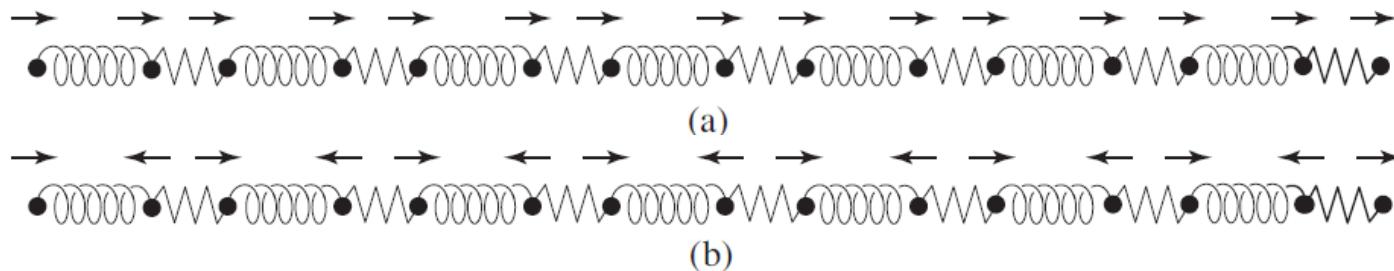
$$\omega = \sqrt{\frac{2(K + G)}{M}} - O(ka)^2,$$
$$\omega = \sqrt{\frac{KG}{2M(K + G)}}(ka).$$

- When k is very small, reduces to $\varepsilon_2 = \mp \varepsilon_1$.

$$\frac{\epsilon_2}{\epsilon_1} = \mp \frac{K + Ge^{ika}}{|K + Ge^{ika}|}.$$

- The lower sign belongs to the acoustic mode, and describes a motion in which the two ions in the cell move in phase with one another.
- The upper sign belongs to the high-frequency optical mode, and describes a motion in which the two atoms in the cell are 180° out of phase.

NORMAL MODES OF A ONE-DIMENSIONAL MONATOMIC BRAVAIS LATTICE



The long wavelength acoustic (a) and optical (b) modes in the diatomic linear chain. The primitive cell contains the two ions joined by the K -spring, represented by a jagged line. In both cases, the motion of every primitive cell is identical, but in the acoustic mode, the ions within a cell move together, while they move 180° out of phase in the optical mode.

Case 2: $k = \pi/a$. Now the roots are

$$\omega = \sqrt{\frac{2K}{M}}, \quad \epsilon_1 = -\epsilon_2,$$

$$\omega = \sqrt{\frac{2G}{M}}, \quad \epsilon_1 = \epsilon_2.$$

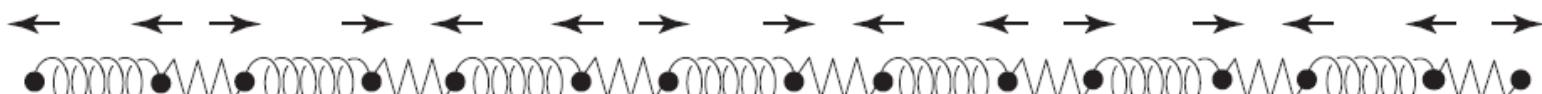
- When $k = \pi/a$, the motions in neighbouring cells are 180° out of phase, and therefore the two solutions must be as pictured in the figure on the next slide. In each case, only one type of spring is stretched.

NORMAL MODES OF A ONE-DIMENSIONAL MONATOMIC BRAVAIS LATTICE

- Note that if the two spring constants were the same, there would be no gap between the two frequencies at $k = \pi/a$.



(a)



(b)

The acoustic (a) and optical (b) modes of the diatomic linear chain, when $k = \pm\pi/a$, at the edges of the Brillouin zone. Now the motion changes by 180° from cell to cell.

However, the ions within each cell move in phase in the acoustic mode, and 180° out of phase in the optical mode. Note that if the K - and G -springs were identical, the motion would be the same in both cases. This is why the two branches become degenerate at the edges of the zone when $K = G$.

NORMAL MODES OF A ONE-DIMENSIONAL MONATOMIC BRAVAIS LATTICE

Case 3: $K \gg G$. To leading order in G/K we have

$$\omega = \sqrt{\frac{2K}{M}} \left[1 + O\left(\frac{G}{K}\right) \right], \quad \epsilon_1 \approx -\epsilon_2,$$

$$\omega = \sqrt{\frac{2G}{M}} |\sin \frac{1}{2}ka| \left[1 + O\left(\frac{G}{K}\right) \right], \quad \epsilon_1 \approx \epsilon_2.$$

- The optical branch now has a frequency that is independent of k , to leading order in G/K , and equal to the vibrational frequency of a single diatomic molecule composed of two mass M ions connected by a spring K .
- Consistent with this picture of independent molecular vibrations in each primitive cell, the atomic motions within each cell are 180° out of phase whatever the wavelength of the normal mode.
- Because G/K is not zero, these molecular vibrations are very weakly coupled, and the result is a small spread of order G/K in the optical band frequencies, as k varies through the Brillouin zone.

NORMAL MODES OF A ONE-DIMENSIONAL MONATOMIC BRAVAIS LATTICE

- The acoustic branch is just that for a linear chain of atoms of mass $2M$ coupled by the weak spring G . This is consistent with the fact that $\varepsilon_1 = \varepsilon_2$; that is, within each cell, the atoms move in phase, and the strong K-spring is hardly stretched at all.
- An acoustic mode is one in which all ions within a primitive cell move essentially in phase, as a unit, and the dynamics are dominated by the interaction between cells.
- An optical mode is one in which the ions within each primitive cell are executing what is essentially a molecular vibratory mode, which is broadened out into a band of frequencies by virtue of the intercellular interactions.
- Both branches belong to phonon dispersions.

NORMAL MODES OF A ONE-DIMENSIONAL MONATOMIC BRAVAIS LATTICE

Case 4: $K = G$.

- In this case, we are really dealing with a monatomic Bravais lattice of lattice constant $a/2$, and the analysis of the preceding section is applicable.
- It is nevertheless instructive to see how that analysis emerges in the limit $K \rightarrow G$.

NORMAL MODES OF A THREE-DIMENSIONAL LATTICE WITH A BASIS

- Just as in one dimension, the chief effect of introducing a polyatomic basis is to produce optical branches.
- The description of these is made notationally more complicated by the introduction of an index to specify which of the ions in the basis is being referred to.
- The lattice harmonic Hamiltonian is very similar to $\textcolor{blue}{U^{\text{harm}}} = \frac{1}{2} \sum_{RR'} u_\mu(\vec{R}) D_{\mu\nu}(\vec{R} - \vec{R}') u_\nu(\vec{R}')$ except that now we have to use two subindices for the position vector \vec{R}_{lj} , l for a primitive unit cell, and j for the atoms or ions in the basis:

$$\mathcal{H} = \frac{1}{2} \sum_{lj} M_j \ddot{\vec{u}}_{lj}^2 + \frac{1}{2} \sum_{lj} \sum_{l'j'} \vec{u}_{lj} \cdot \tilde{D}(\vec{R}_{lj}, \vec{R}_{l'j'}) \cdot \vec{u}_{l'j'}$$

- The mass M_j might be different among inequivalent sites j inside the PUC. The \vec{u}_{lj} is the atomic vibration displacement around the site \vec{R}_{lj} . The matrix

$$D_{\mu\nu}(\vec{R}_{lj}, \vec{R}_{l'j'}) = \delta_{\vec{R}_{lj}, \vec{R}_{l'j'}} \left(\sum_{l''j''} \phi_{\mu\nu}(\vec{R}_{lj} - \vec{R}_{l''j''}) \right) - \phi_{\mu\nu}(\vec{R}_{lj} - \vec{R}_{l'j'})$$

if interatomic potential can be written in this simple form $\phi(\vec{r})$.

NORMAL MODES OF A THREE-DIMENSIONAL LATTICE WITH A BASIS

- The displacement of ion j in the cell about $\vec{R}_{lj} = \vec{R}_l + \vec{\delta}_j$, the equation of motion in the k -space, the dynamic matrix and its eigenequation are given by

$$\vec{u}_s^j(\vec{R}_l, t) = \vec{\epsilon}_s^j(\vec{k}) e^{i(\vec{k} \cdot \vec{R}_l - \omega_s(\vec{k})t)},$$
$$\omega_s^2 \left(\sqrt{M_j} \vec{\epsilon}_s^j(\vec{k}) \right) = \sum_{j'} \left(\frac{1}{\sqrt{M_j M_{j'}}} \tilde{D}_{j,j'}(\vec{k}) \right) \cdot \left(\sqrt{M_{j'}} \vec{\epsilon}_s^{j'}(\vec{k}) \right),$$
$$\tilde{D}_{j,j'}(\vec{k}) = \sum_{l'} \tilde{D}(\vec{R}_{lj}, \vec{R}_{l'j'}) e^{-i\vec{k} \cdot (\vec{R}_l - \vec{R}_{l'})}.$$

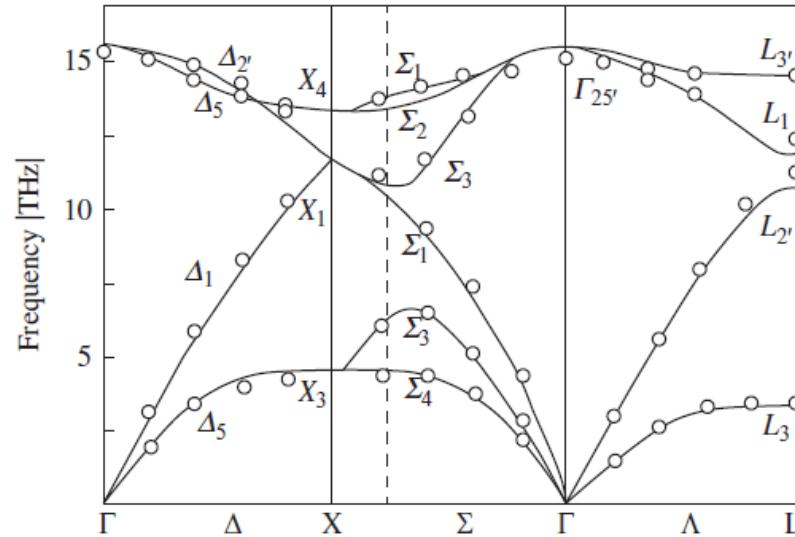
- The dynamic matrix $\tilde{D}_{j,j'}$ is actually a $3n_a \times 3n_a$ matrix, where n_a is the number of ions in the basis.
- The polarization vectors can be chosen to satisfy the $3n_a$ generalized orthogonality relations. In general, the polarization vectors need not be real:

$$\sum_{j=1}^{n_a} \left(\sqrt{M_j} \vec{\epsilon}_s^{j*}(\vec{k}) \right) \cdot \left(\sqrt{M_j} \vec{\epsilon}_{s'}^j(\vec{k}) \right) = \sum_{j=1}^{n_a} M_j \vec{\epsilon}_s^{j*}(\vec{k}) \cdot \vec{\epsilon}_{s'}^j(\vec{k}) = \delta_{ss'},$$

where M_j is the mass of the j th type of basis.

NORMAL MODES OF A THREE-DIMENSIONAL LATTICE WITH A BASIS

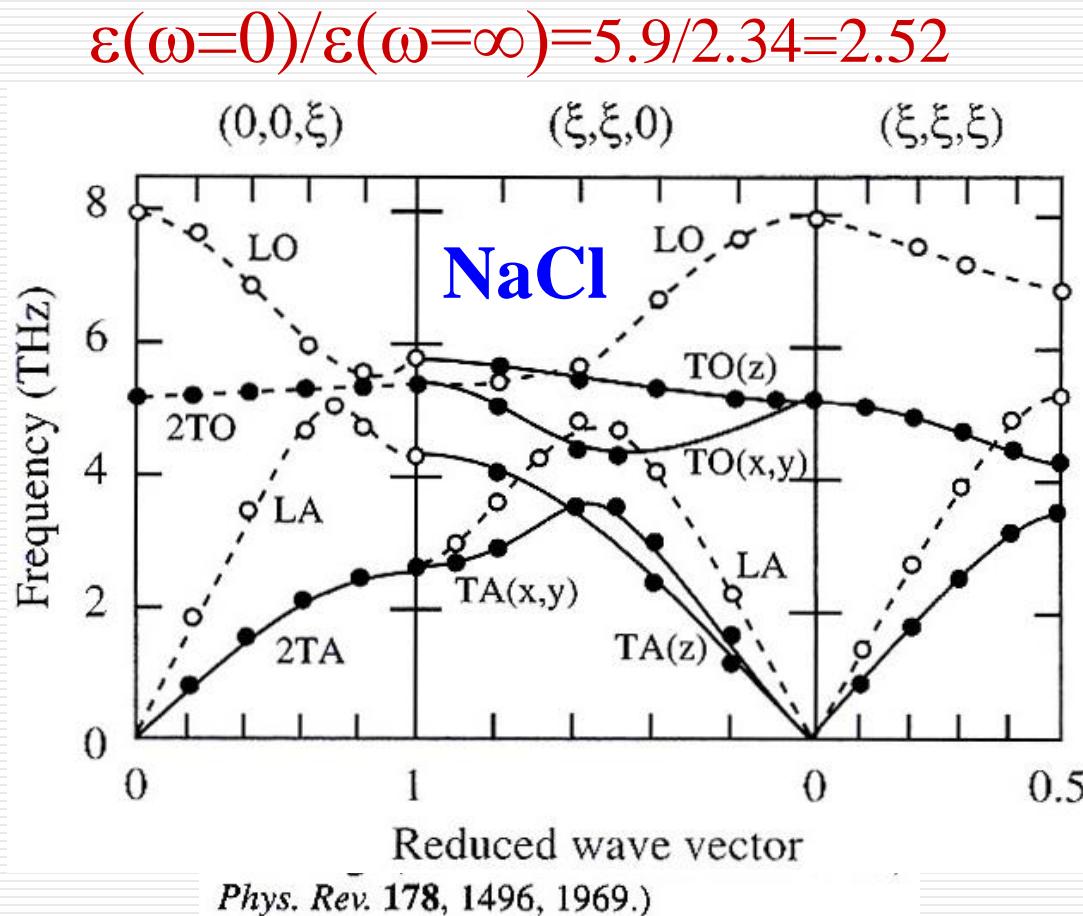
- Three of the $3n_a$ branches are acoustic; that is, with $\omega \approx v k$ type of dispersion in the long-wavelength limit.
- The other $3(n_a - 1)$ branches are optical; that is, their frequencies do not vanish in the long-wavelength limit.
- Typical phonon dispersion curves, for the case of silicon with $n_a = 2$, are shown in the following figure.



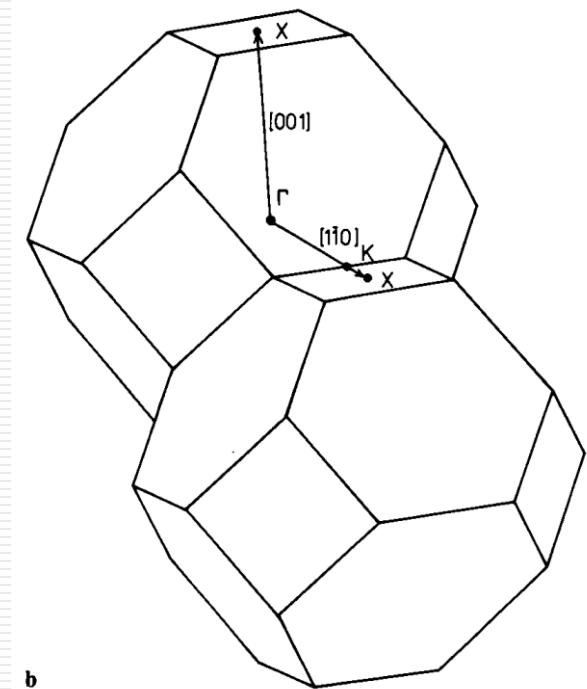
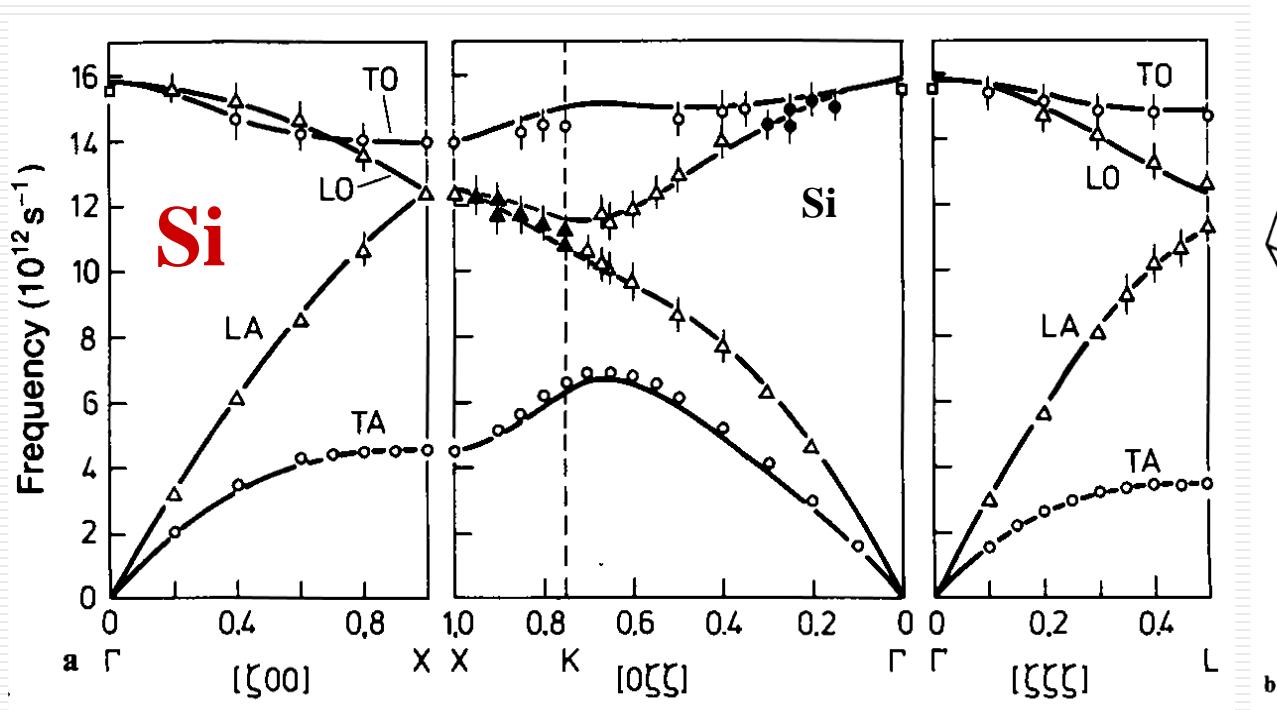
Phonon dispersion of silicon crystals. There are $3n_a = 6$ branches.

The lattice dynamics of the alkali halides

- ◆ 2 atoms in the primitive cell → 3 acoustic + 3 optic
- ◆ [001] [111] 2 degenerate TO and TA modes
- ◆ $(\omega_{LO}/\omega_{TO})^2 = (8/5)^2 = 2.56$
- ◆ separation of optic and acoustic (111): alternating planes of cations and anions
- ◆ Not for (001) (110)
- ◆ anticrossing

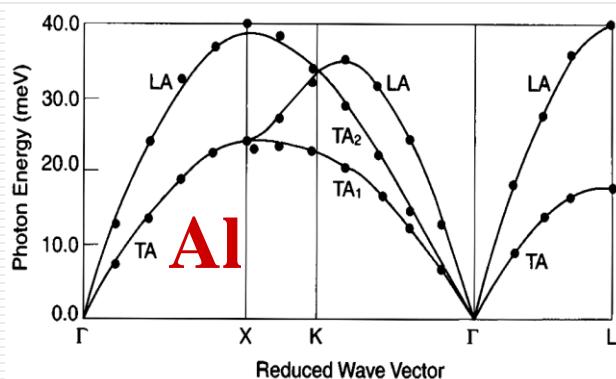


Phonon dispersion curve : Si

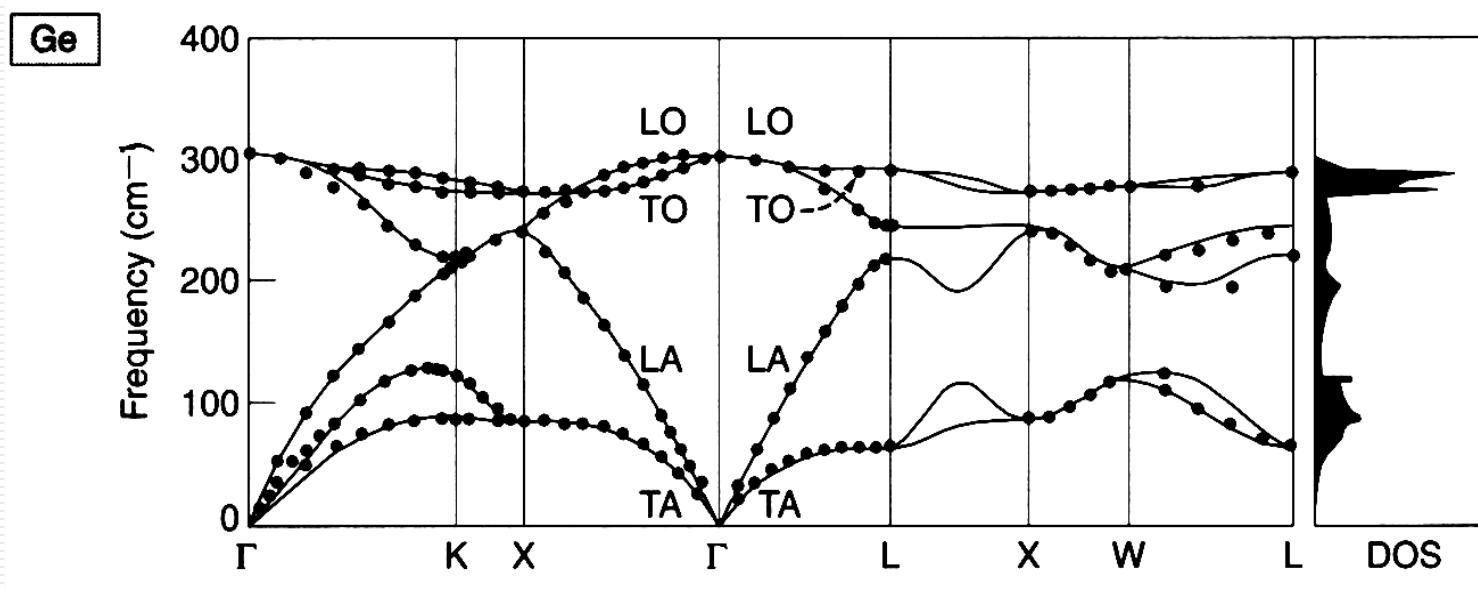
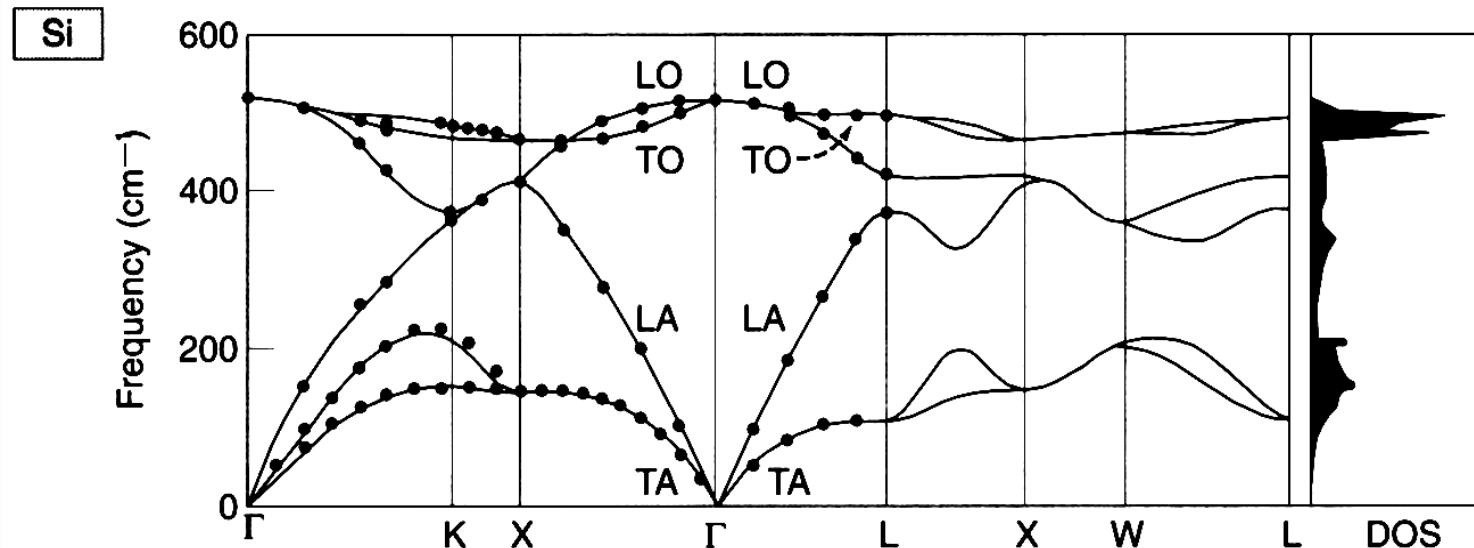


Along the $[1\bar{1}0]$ direction the transverse branches are degenerate. Concerning the degeneracy of LO and TO at Γ , see also Sect. 11.4. **b** A sketch of two neighboring Brillouin zones showing that by moving along $[1\bar{1}0]$ from Γ to K one can arrive at X by continuing along the adjoining Brillouin zone boundary. Thus the point X can be described either by the wave vector $q = 2\pi/a [001]$ or by $q = 2\pi/a [1\bar{1}0]$. By studying the fcc lattice (Figs. 2.8, 12), one can convince oneself that these two points have the same atomic me

Ibach_Luth



Phonon dispersion curve : Si Ge



Grosso_Parravicini

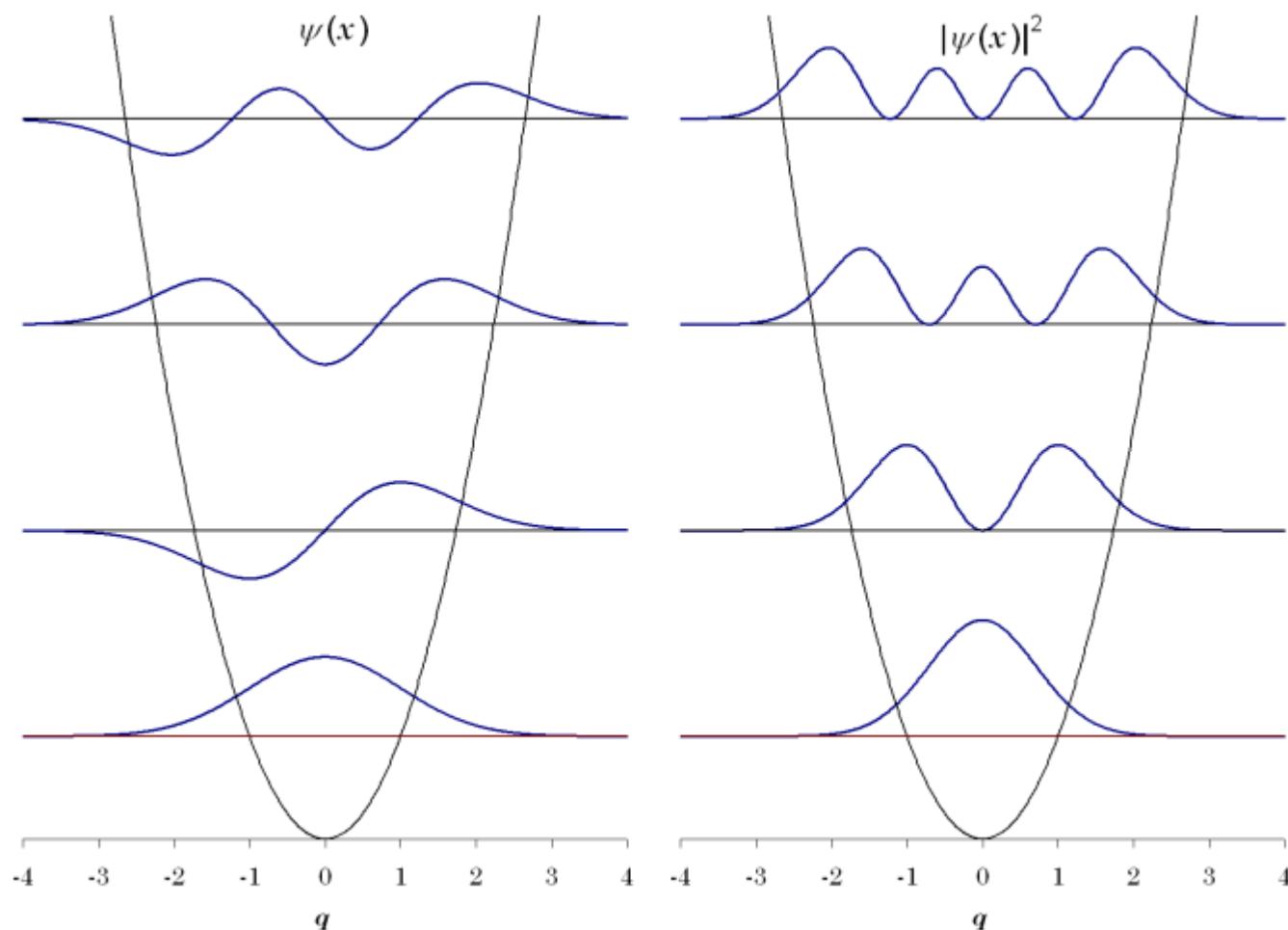
by P. Gianni
copyright 1991
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Thermodynamics of Lattice Dynamics

How does lattice dynamics determines thermodynamic properties of materials?

- ◆ The quantization of lattice vibration
The Bose-Einstein relation, $n(\omega, T)$
High-temperature behaviour
Heat capacity
Phonon free energy and entropy
- ◆ Thermodynamic functions: Debye and Einstein model
Density of States
Debye model of heat capacity

Energy quantization of a harmonic oscillator

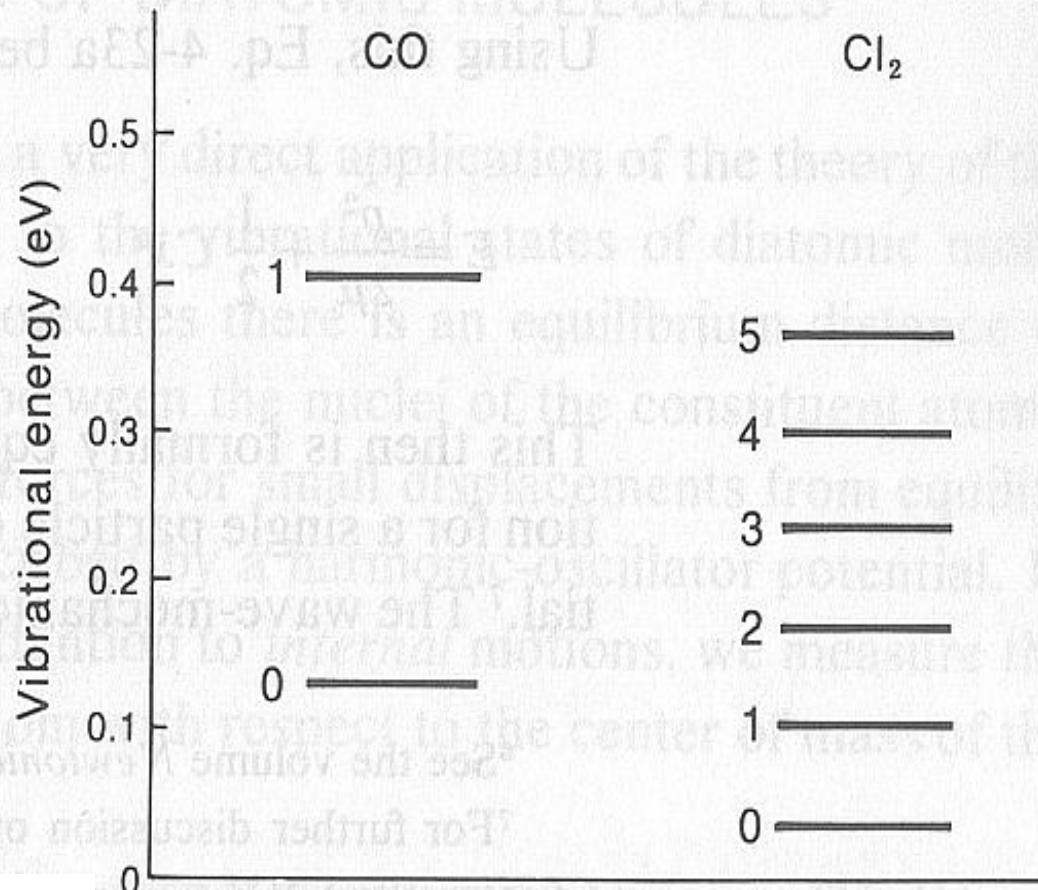


http://physchem.ox.ac.uk/~hill/tutorials/qm1_tutorial/sho/index.html

Energy quantization of a harmonic oscillator

Fig. 4-5 System of pure vibrational levels of the diatomic molecules CO and Cl₂, as inferred from spectroscopic data.

French_Taylor



Phonons : quanta of harmonic lattice vibration

- ◆ Quantized harmonic vibrations
- ◆ Zero-point energy and zero-point motion
- ◆ The mean energy of each vibrational mode is given by

$$E = \hbar\omega \left[\frac{1}{2} + n(\omega, T) \right]$$

where $n(\omega, T)$ is the number of phonons with frequency ω at temperature T : the phonon number

The Bose-Einstein relation, $n(\omega, T)$

- ◆ A system has a variable q and the energy $E(q)$ can be written as a function of q , the equilibrium value of q is

$$\langle q \rangle = \frac{\sum_q q \exp(-\beta E(q))}{\sum_q \exp(-\beta E(q))} = \frac{\sum_q q \exp(-\beta E(q))}{Z \equiv \text{partition function}}$$

- ◆ Consider a system with a vibration of frequency ω and $\varepsilon = \hbar\omega$. The partition function is $Z = \sum_n \exp(-\beta n \varepsilon)$

$$\langle n \rangle = \frac{1}{Z} \sum_n n \exp(-\beta n \varepsilon) = -\frac{1}{\beta Z} \frac{\partial Z}{\partial \varepsilon}$$

The Bose-Einstein relation, $n(\omega, T)$

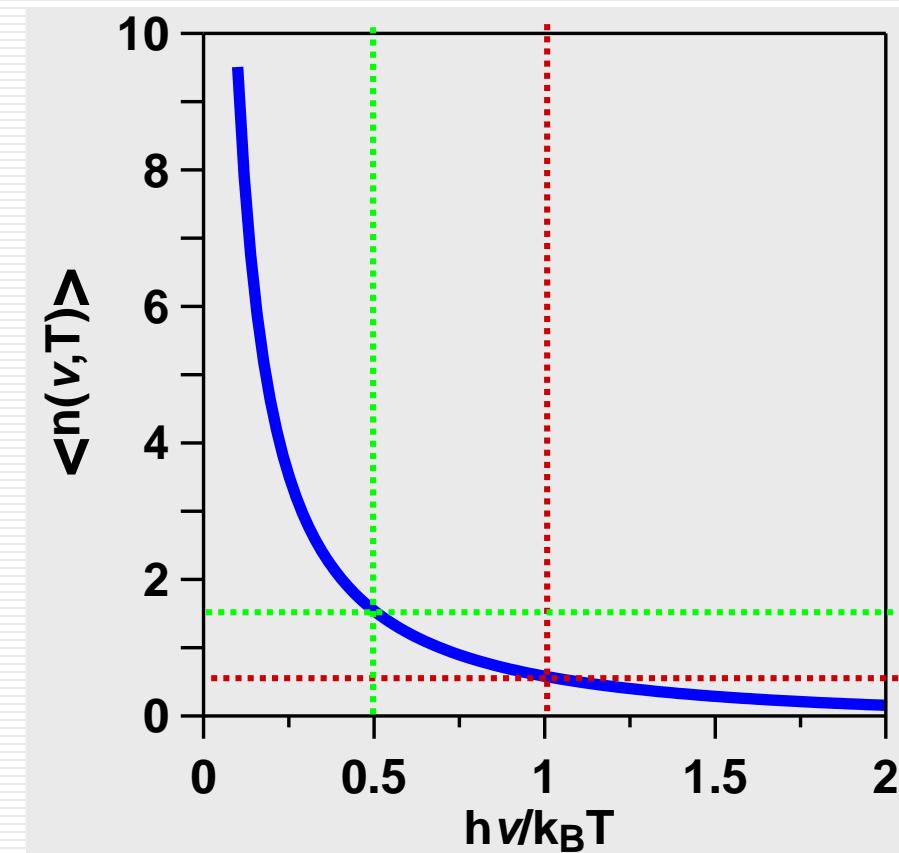
$$\langle n \rangle = \frac{1}{Z} \sum_n n \exp(-\beta n \varepsilon) = -\frac{1}{\beta Z} \frac{\partial Z}{\partial \varepsilon}$$

$$\sum_n x^n = \frac{1}{1-x} \quad x = \exp(-\beta \varepsilon)$$

$$\Rightarrow Z = \frac{1}{1 - \exp(-\beta \varepsilon)}$$

$$\langle n \rangle = \frac{1}{\exp(\beta \varepsilon) - 1} \Rightarrow$$

$$n(\omega, T) = \frac{1}{\exp(\hbar \omega / k_B T) - 1}$$



NORMAL MODES VERSUS PHONONS

The contribution to the total energy of a particular normal mode with angular frequency $\omega_s(\vec{k})$ can have only the discrete energy of a quantum oscillator:

$$\varepsilon_{\vec{k}s} = \left(n_{\vec{k}s} + \frac{1}{2} \right) \hbar \omega_s(\vec{k}),$$

The total energy is the sum of the energies of the individual normal modes:

$$E = \sum_{\vec{k}s} \varepsilon_{\vec{k}s} = \sum_{\vec{k}s} \left(n_{\vec{k}s} + \frac{1}{2} \right) \hbar \omega_s(\vec{k}).$$

The term ‘phonon’ stresses this analogy with ‘phonon’. The latter is the quanta of the radiation field that (in the appropriate frequency range) describes classical light; the former is the quanta of the ionic displacement field that (in the appropriate frequency range) describes classical sound.

GENERAL FORM OF THE LATTICE SPECIFIC HEAT

The phonon is a quasiparticle living in the environment of a crystal, and it is a boson. Thus, the thermal average of the quantum number $n_{\vec{k}s}$ at temperature T simply follows

$$n_s(\vec{k}) = \langle n_{\vec{k}s} \rangle = \frac{1}{e^{\beta \hbar \omega_s(\vec{k})} - 1}.$$

Thus, the simple classical expression for the energy density of a harmonic crystal at temperature T ,

$$u = u^{\text{eq}} + \frac{1}{V} \sum_{\vec{k}s} \frac{1}{2} \hbar \omega_s(\vec{k}) + \frac{1}{V} \sum_{\vec{k}s} \frac{\hbar \omega_s(\vec{k})}{e^{\beta \hbar \omega_s(\vec{k})} - 1}$$

$$c_v = \frac{1}{V} \sum_{\vec{k}s} \frac{\partial}{\partial T} \frac{\hbar \omega_s(\vec{k})}{e^{\beta \hbar \omega_s(\vec{k})} - 1} = k_B \int d\omega g(\omega) \frac{(\beta \hbar \omega)^2 e^{\beta \hbar \omega}}{(e^{\beta \hbar \omega} - 1)^2}$$

DENSITY OF NORMAL MODES (PHONON DENSITY OF STATES)

- The density of the states can be written as

$$\begin{aligned}\frac{1}{V} \sum_{\vec{k}s} Q(\omega_s(\vec{k})) &= \sum_s \int \frac{d\vec{k}}{(2\pi)^3} Q(\omega_s(\vec{k})) \\ &= \int d\omega g(\omega) Q(\omega).\end{aligned}$$

- The density of normal modes can be represented in the form

$$g(\omega) = \sum_s \int \frac{d\vec{k}}{(2\pi)^3} \delta(\omega - \omega_s(\vec{k}))$$

- alternatively,

$$g(\omega) = \sum_s \int \frac{dS}{(2\pi)^3} \frac{1}{|\nabla \omega_s(\vec{k})|}$$

Phonon density of states

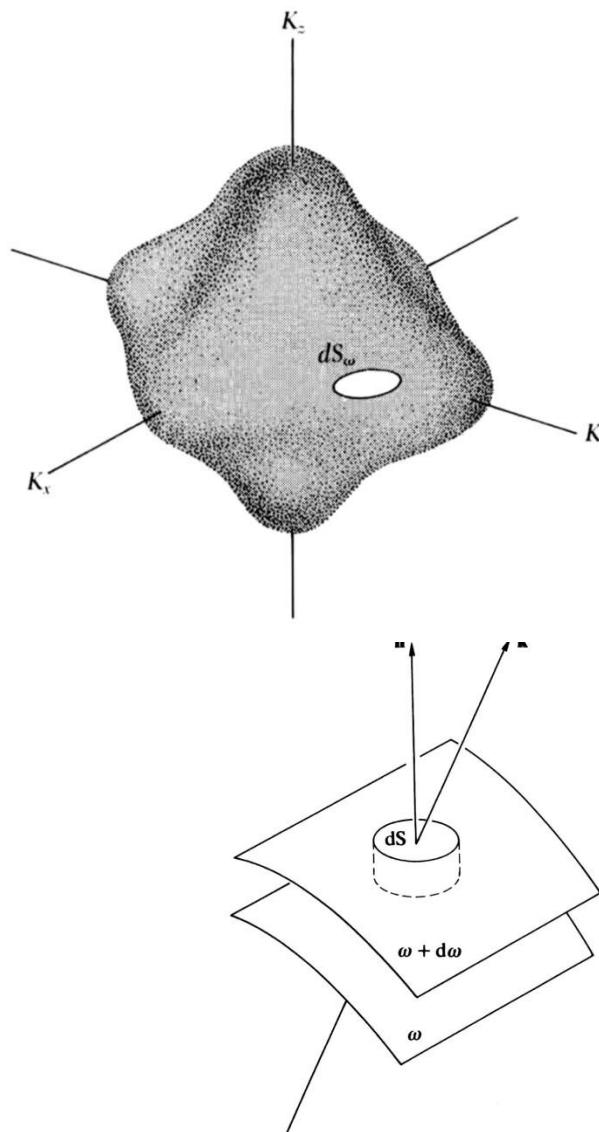


Fig. 5.12 A small element of \mathbf{k} space bounded by surfaces of constant frequency ω and $\omega + d\omega$.
Myers

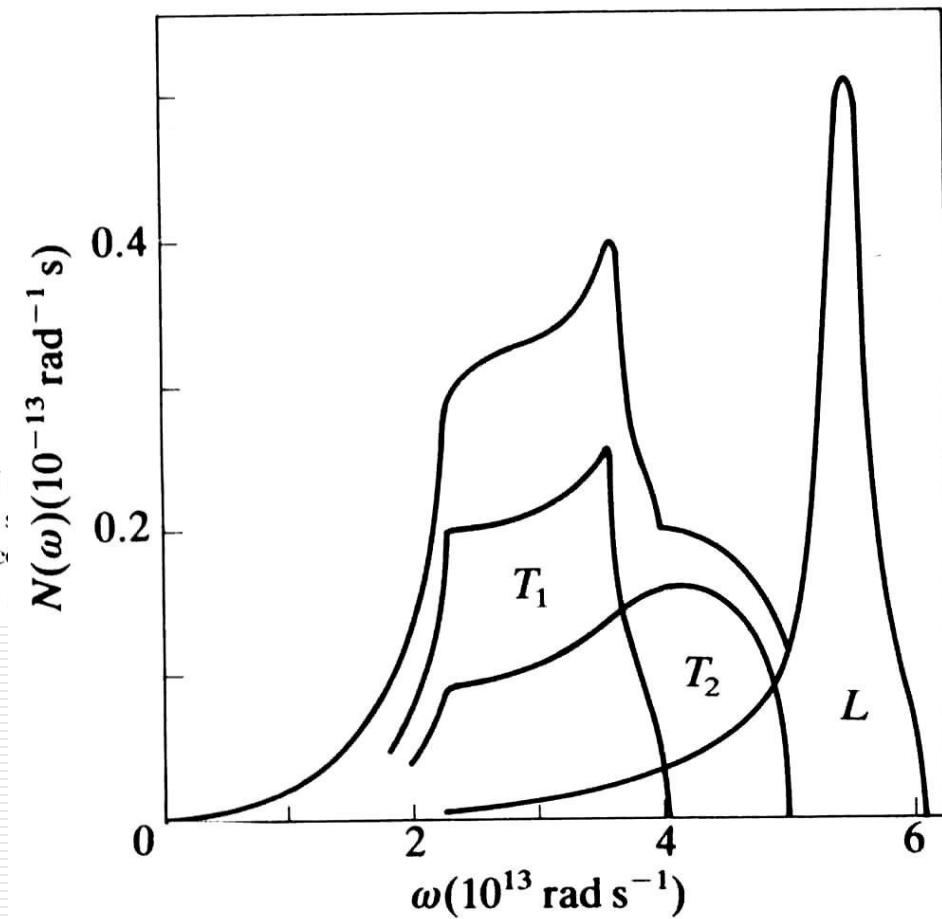
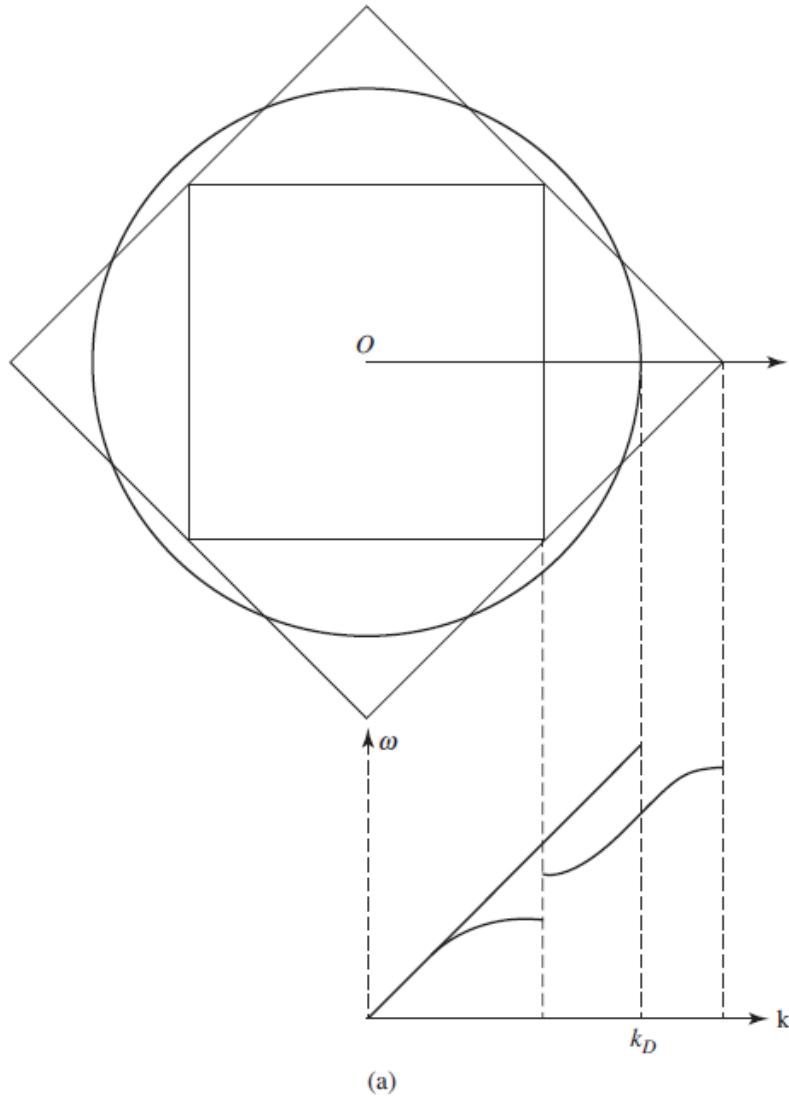
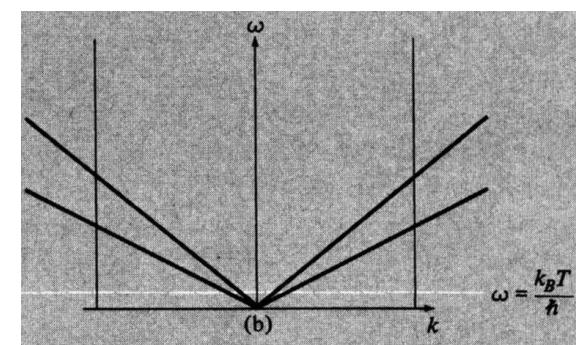
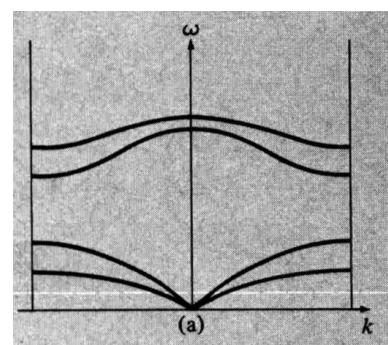


Fig. 5.13 The measured vibrational spectrum for Al. (After Stedman *et al.* (1967).)
Myers

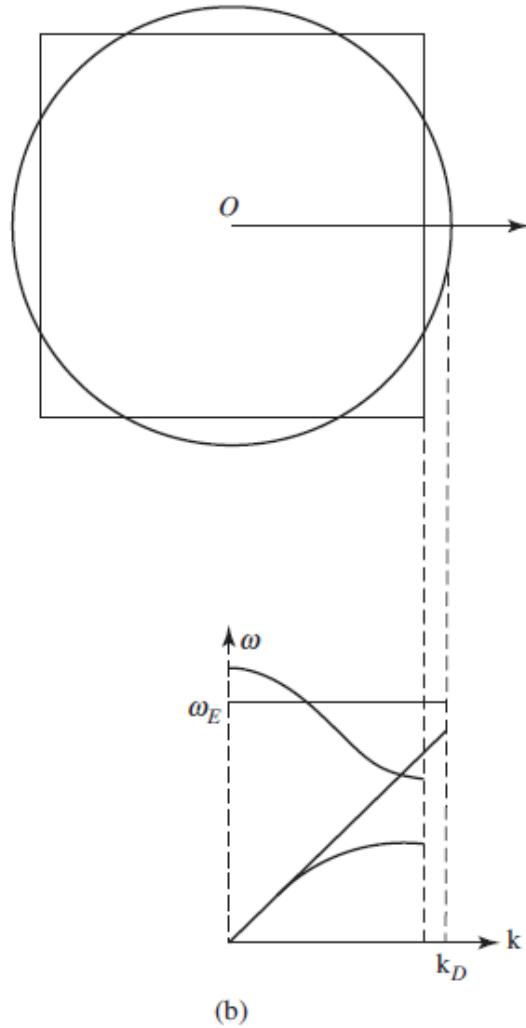
THE DEBYE PHONON MODEL



Two different ways of approximating the acoustic and optical branches of a diatomic crystal (illustrated in two dimensions along a line of symmetry). (a) *The Debye approximation*. The first two zones of the square lattice are replaced by a circle with the same total area, and the entire spectrum is replaced by a linear one within the circle.



THE DEBYE PHONON MODEL



(b) *Debye approximation for the acoustic branch and Einstein approximation for the optical branch.* The first zone is replaced by a circle with the same area; the acoustic branch is replaced by a linear branch within the circle; and the optical branch is replaced by a constant branch within the circle.

THE DEBYE PHONON MODEL

The total energy of atomic vibrations can be calculated as following:

$$\begin{aligned}\bar{\mathcal{E}} &= \sum_{s=1}^3 \sum_{\vec{k}} \frac{\hbar\omega_s(k)}{e^{\beta\hbar\omega_s(k)} - 1} \\ &= \sum_{s=1}^3 \int dk \rho(k) \frac{\hbar\omega_s(k)}{e^{\beta\hbar\omega_s(k)} - 1} \\ &= \int d\omega G(\omega) \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1} ,\end{aligned}$$

where $\rho(k)$ is the density of levels in the reciprocal space,

$$\rho(k) = \frac{4\pi k^2}{\Omega^*/N_L} = \frac{V}{2\pi^2} k^2$$

THE DEBYE PHONON MODEL

and $G(\omega)$ is the density of states of phonons, or called the frequency distribution

$$G(\omega) = \sum_{s=1}^3 \rho(k) \frac{dk}{d\omega_s} = \frac{V}{2\pi^2} \left(\sum_{m=1}^3 \frac{1}{v_s^3(\hat{k})} \right) \omega^2$$

Debye introduced a cut-off frequency, namely, the Debye frequency ω_D

$$3N = \int_0^{\omega_D} d\omega G(\omega) = \frac{V}{2\pi^2} \frac{1}{v^3} \omega_D^3 \quad \rightarrow \quad G(\omega) = \frac{9N}{\omega_D^3} \omega^2$$

The physical meaning of ω_D is the maximum frequency of atomic vibrations.

Debye wave vector k_D

$$\omega_D = k_D v, \quad k_D = (6\pi^2 n)^{1/3},$$

Where $n = N/V$ is the ion density.

THE DEBYE PHONON MODEL

The average sound velocity v is defined based on the dispersion relations

$\omega_s = v_s(\hat{k})k$ of three acoustic branches:

$$\frac{1}{v^3} = \frac{1}{3} \sum_s \int \frac{d\Omega}{4\pi} \frac{1}{v_s(\hat{k})^3}.$$

with the frequency distribution known, the specific heat $C_v = d\bar{\mathcal{E}}/dT$ of photons

$$\begin{aligned} C_v &= \int_0^{\omega_D} d\omega G(\omega) \frac{\hbar^2 \omega^2}{k_B T^2} \frac{e^{\beta \hbar \omega}}{(e^{\beta \hbar \omega} - 1)^2} \\ &= 9N k_B \left(\frac{T}{\Theta_D} \right)^3 \int_0^{\Theta_D/T} dx \frac{x^4 e^x}{(e^x - 1)^2} \end{aligned}$$

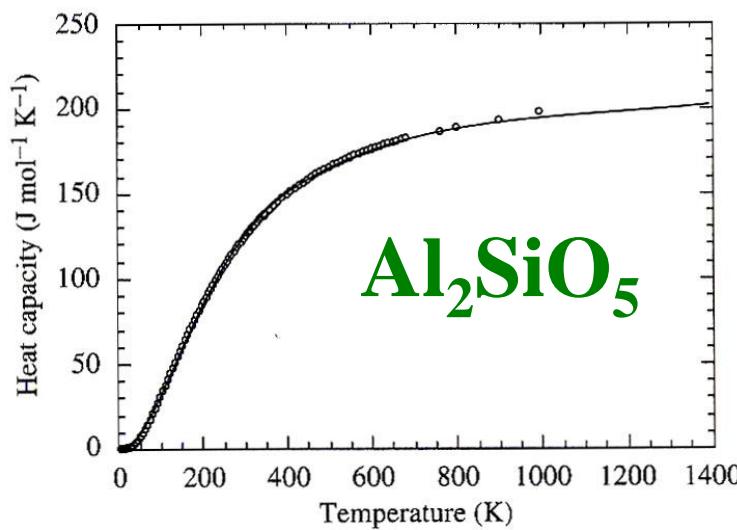
where $\Theta_D = \hbar \omega_D / k_B$ is defined as the Debye temperature.

THE DEBYE PHONON MODEL

The high-temperature and low-temperature expansions of the specific heat are

$$C_v(T) \sim 3Nk_B \left[1 - \frac{1}{20} \left(\frac{\Theta_D}{T} \right)^2 \right], \quad T \gg \Theta_D,$$

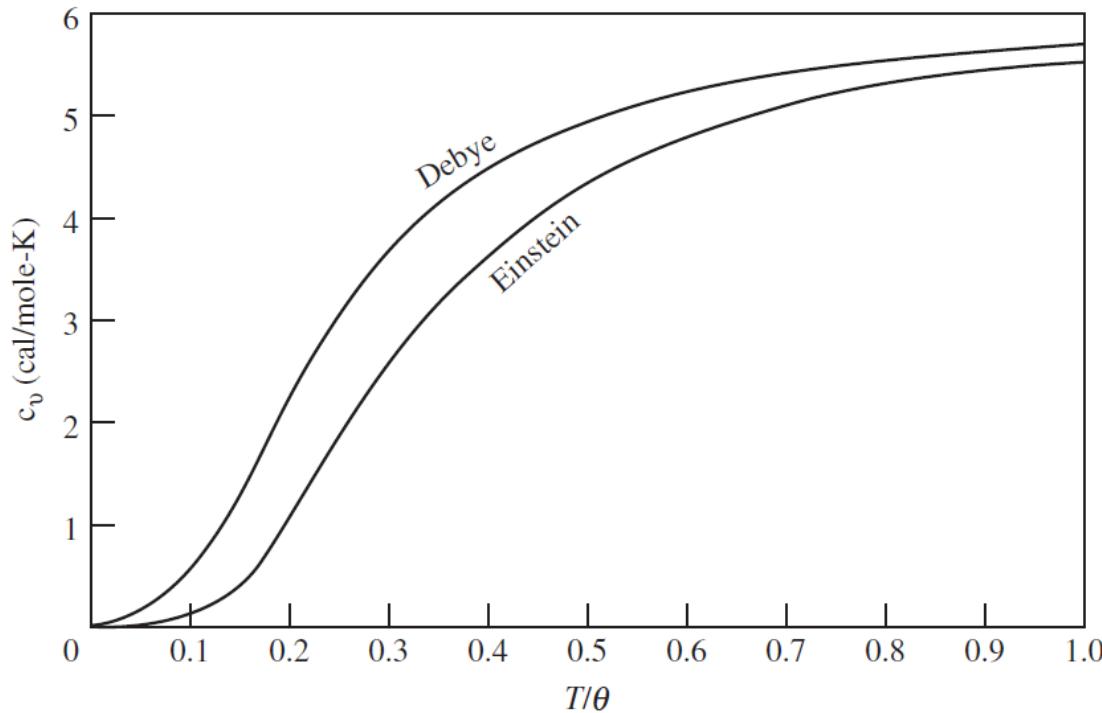
$$C_v(T) \sim \frac{12\pi^4}{5} Nk_B \left(\frac{T}{\Theta_D} \right)^3 = 234 Nk_B \left(\frac{T}{\Theta_D} \right)^3, \quad T \ll \Theta_D.$$



$$\begin{aligned} 100 \text{ J/mol} &\approx 12k_B \\ 1R &= 8.35 \text{ J/mol/K} \end{aligned}$$

THE DEBYE PHONON MODEL

- The high-temperature expansion in Debye model decreases more slowly than that in the Einstein model as shown in the following figure.



A comparison of the Debye and Einstein approximations to the specific heat of an insulating crystal. Θ is either the Debye or the Einstein temperature, depending on which curve is being examined. Both curves are normalized to approach the Dulong and Petit value of 5.96 cal/mole-K at high temperatures.

Free energy and entropy

$$F = -\frac{1}{\beta} \ln Z \quad Z = \frac{1}{1 - \exp(-\beta\varepsilon)}$$

$$F = \frac{1}{2}\varepsilon + \frac{1}{\beta} \ln[1 - \exp(-\beta\varepsilon)] = \frac{1}{\beta} \ln[2 \sinh(\beta\varepsilon/2)]$$

at high T $\Rightarrow \beta\varepsilon < 1 \Rightarrow F = \frac{1}{\beta} \ln(\beta\varepsilon)$

$$S = -\partial F / \partial T$$

$$S(\text{at high } T) = k_B [1 - \ln(\beta\varepsilon)]$$

Thermodynamic functions for crystals

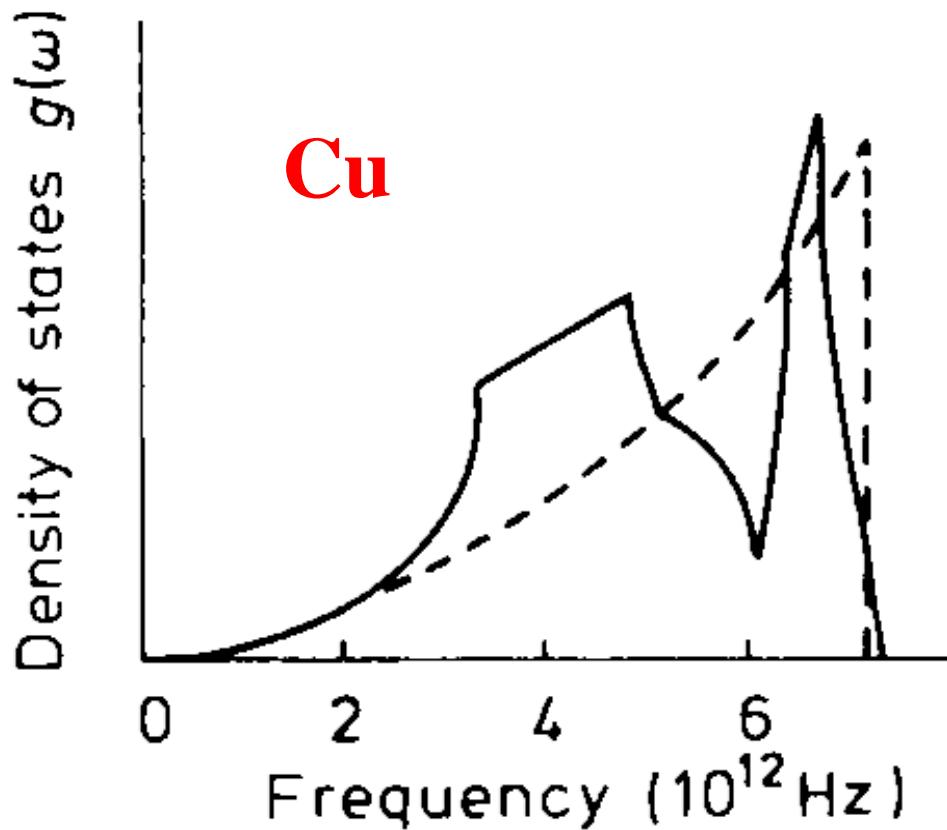
sum over all vibrations using, e.g. model interatomic pot

$$F = \frac{1}{\beta} \sum_{k,\nu} \ln \{ 2 \sinh[\beta \hbar \omega(k, \nu) / 2] \}$$

$$F = \frac{3N_A}{\beta} \ln \{ 2 \sinh[\beta \hbar \langle \omega \rangle / 2] \} \quad \text{Einstein model}$$

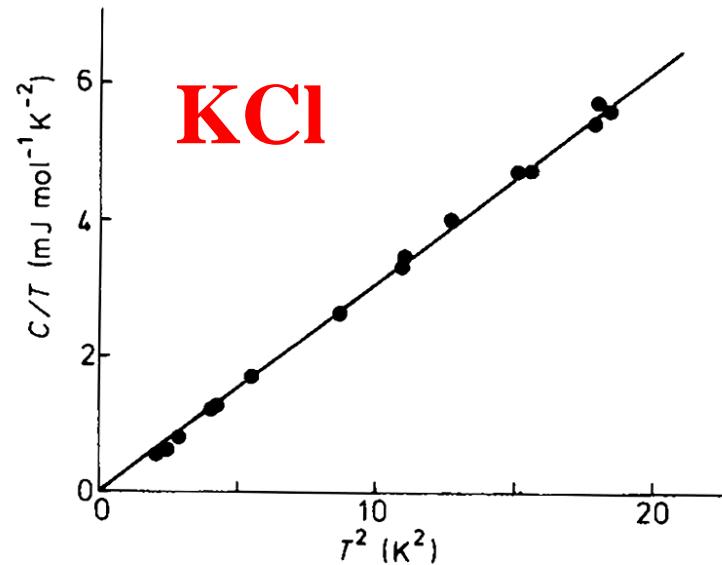
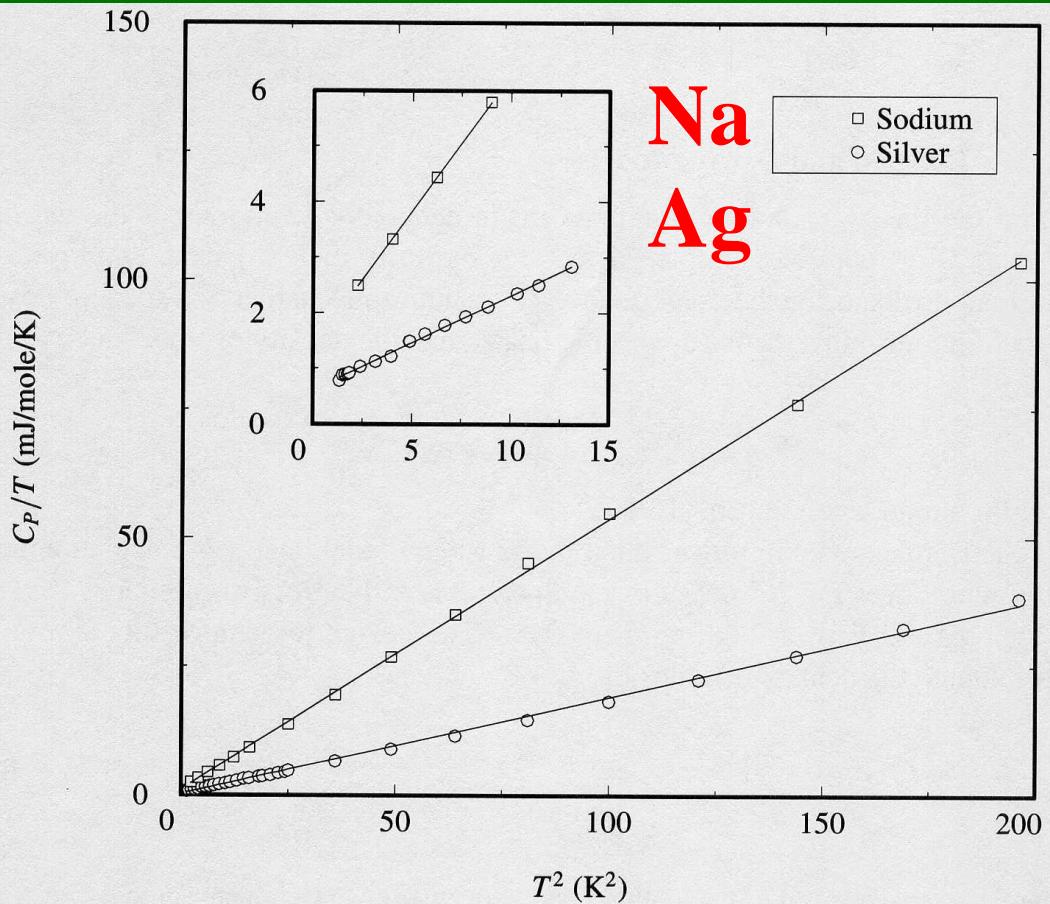
$$c_V = 3R \left(\beta \hbar \langle \omega \rangle \right)^2 \frac{\exp(\beta \hbar \langle \omega \rangle)}{\left[\exp(\beta \hbar \langle \omega \rangle) - 1 \right]^2}$$

Debye model : DOS



(a) Density of states for copper deduced from **neutron scattering** experiments (full curve) compared to the Debye density of states (broken curve) calculated using sound velocities obtained from the measured elastic moduli Hook_Hall

Debye model & C_V



P. H. Keesom and N. Pearlman, *Phys. Rev.* **91**, 1354 (1953))

Figure 13.10. The specific heats of sodium and silver are displayed, illustrating the validity of the form (13.71). The intercepts of regression lines accurately reproduce the experimental values given in Table 6.2. [Source: Tououloukian et al. (1975).] **Marder**

Debye temperature : Θ_D

Table 23.3
DEBYE TEMPERATURES FOR SELECTED ELEMENTS^a *Ashcroft*

ELEMENT	Θ_D (K)	ELEMENT	Θ_D (K)
Li	400	A	85
Na	150	Ne	63
K	100	Cu	315
Be	1000	Ag	215
Mg	318	Au	170
Ca	230	Zn	234
B	1250	Cd	120
Al	394	Hg	100
Ga	240	Cr	460
In	129	Mo	380
Tl	96	W	310
C (diamond)	1860	Mn	400
Si	625	Fe	420
Ge	360	Co	385
Sn (grey)	260	Ni	375
Sn (white)	170	Pd	275
Pb	88	Pt	230
As	285	La	132
Sb	200	Gd	152
Bi	120	Pr	74

$$\Theta_D = \hbar\omega_D / k_B$$

$$= \hbar c / k_B \left(6\pi^2 N/V \right)^{1/3}$$

Specific heat capacity - C_V

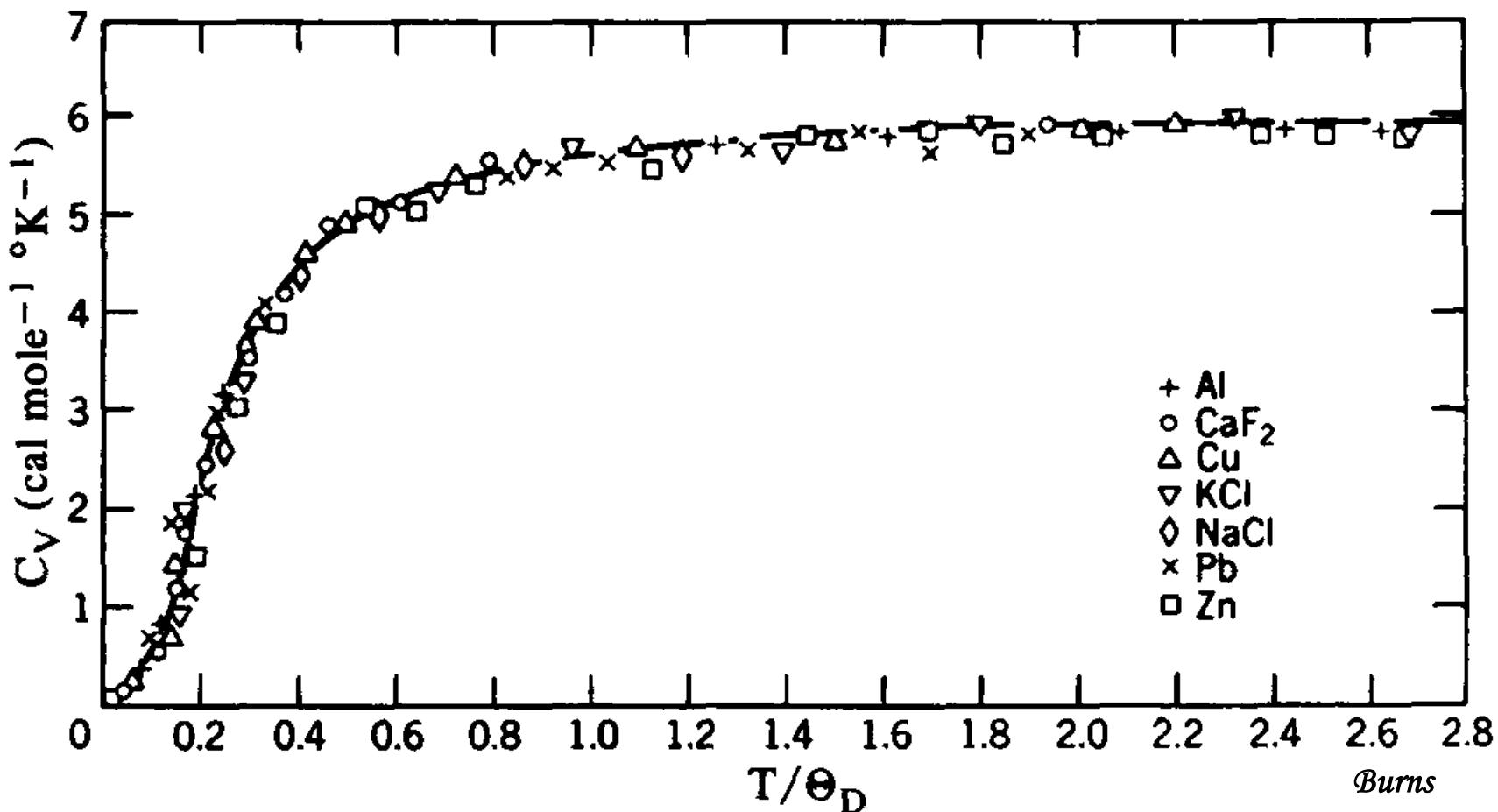


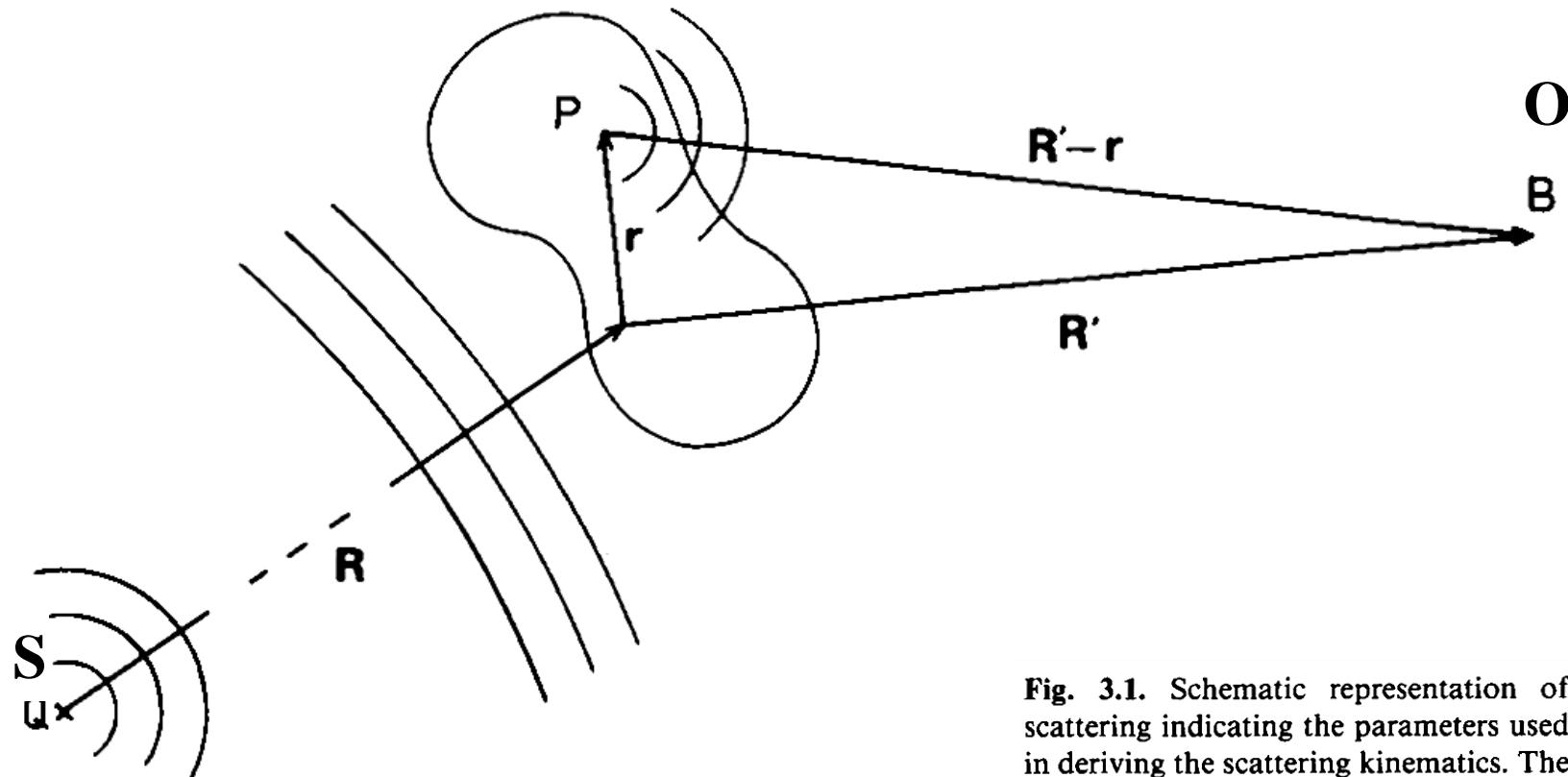
Fig. 11-5 Heat capacity vs. reduced temperature for a number of materials.

Experimental methods for ν

How are vibration frequencies determined experimentally?

- ◆ Basic ideas of spectroscopy
- ◆ Neutron scattering techniques
- ◆ Light scattering
- ◆ Inelastic X-ray scattering
- ◆ Infrared absorption spectroscopy

General Theory of Diffraction



S : Source
O : Observer
P : Scattering center

Fig. 3.1. Schematic representation of scattering indicating the parameters used in deriving the scattering kinematics. The source Q is assumed to be sufficiently far away from the target that the spherical waves reaching the target can be well approximated by plane waves. The same condition is assumed for the point of observation relative to the scattering centers

Ibach_Luth

General Theory of Diffraction

Figure 24.1

Neutron (n) and photon (γ) energy-momentum relations. When $k = 10^n \text{ cm}^{-1}$, $E_n = 2.07 \times 10^{2n-19} \text{ eV}$ and $E_\gamma = 1.97 \times 10^{n-5} \text{ eV}$. Typical thermal energies lie in or near the white band. Ashcroft

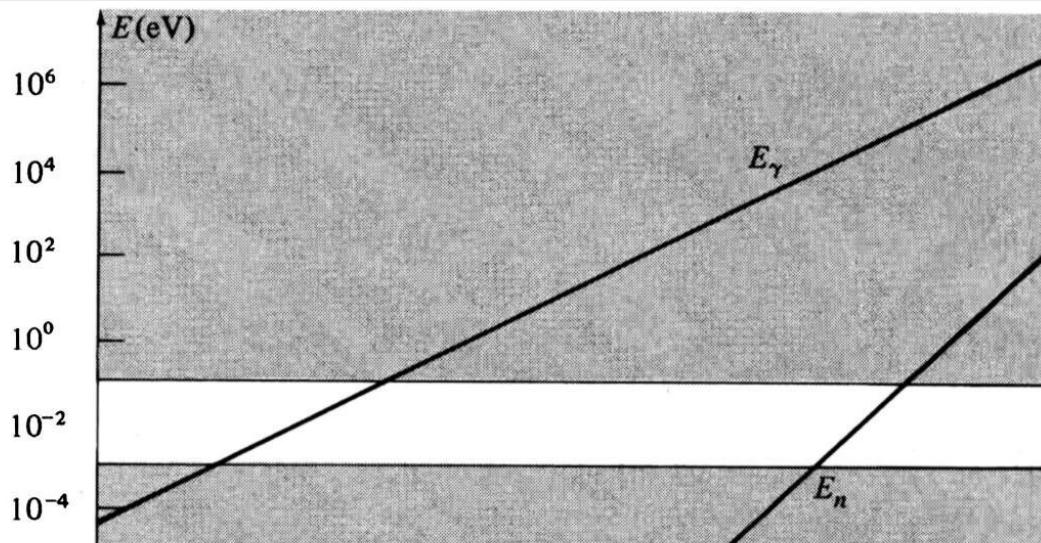


TABLE 5.1

Myers

	Energy (eV)	Frequency (rad s^{-1})	Approximate wavelength (Å)	Approximate wave vector (\AA^{-1})
Phonon	0.013	2×10^{14}	3	2
X-ray photon	4100		3	2
Electron	16		3	2
Neutron	0.009		3	2

Neutron Scattering

Phonon creation:

$$\text{Intensity} \propto n(\omega, T) + 1$$

Phonon absorption:

$$\text{Intensity} \propto n(\omega, T)$$

Stokes

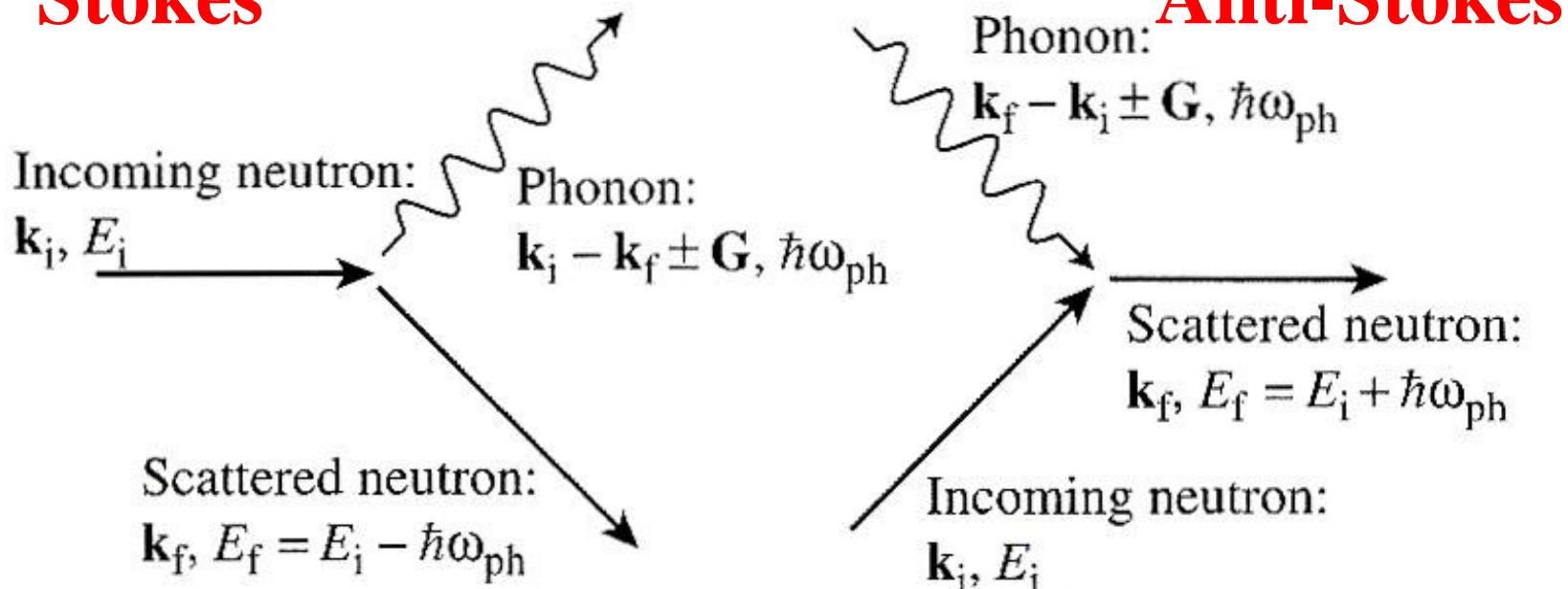


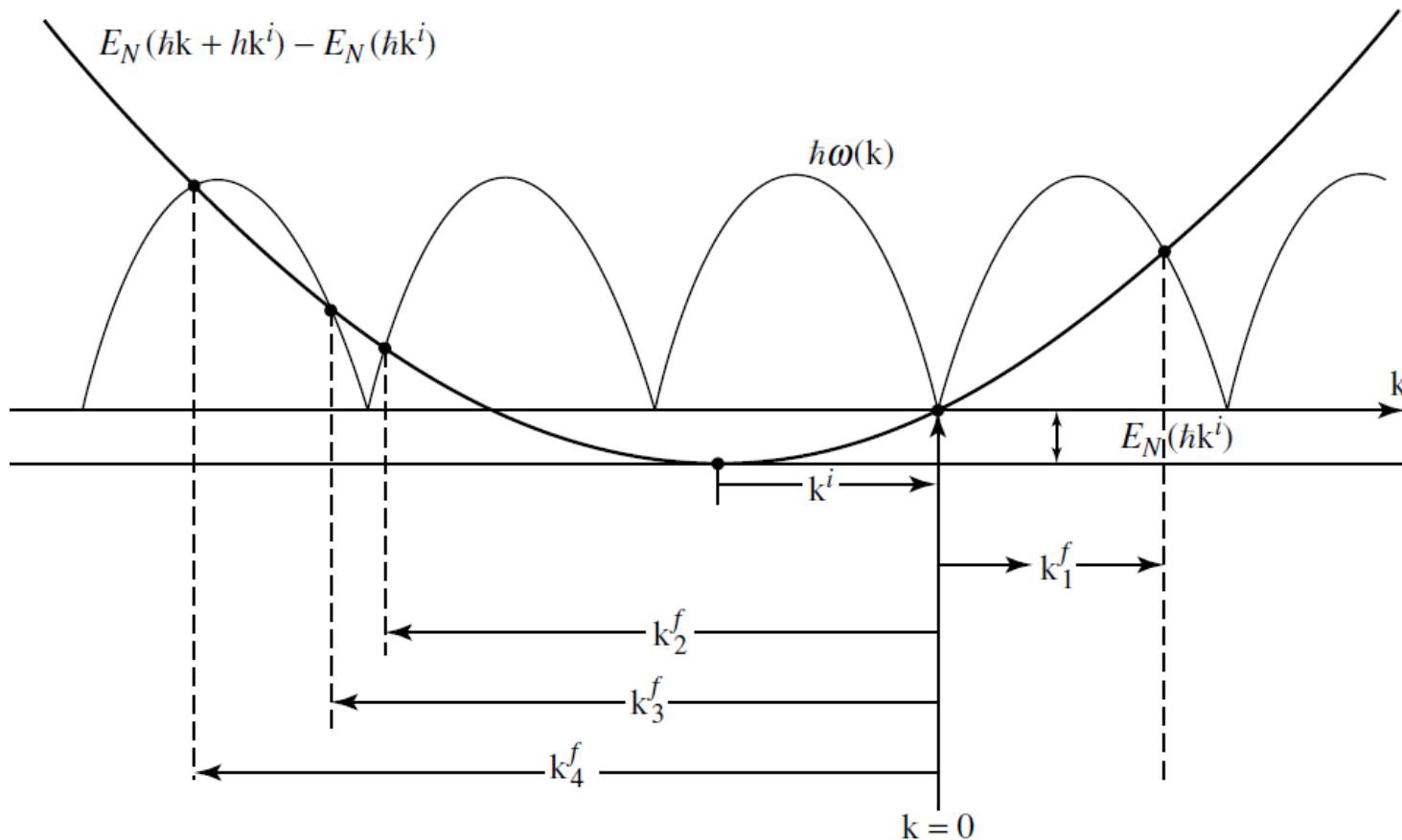
Fig. 10.1 Representation of the two types of one-phonon scattering process, drawn here for neutron scattering, but the same diagrams are also applicable to photon scattering (X-ray or light).

DOVE

CONSERVATION LAWS AND ONE-PHONON SCATTERING

Graphical solution to the one-phonon conservation laws when the incident neutron has wave vector \vec{k}^i . The conservation law for phonon absorption can be written $E_n(\hbar\vec{k} + \hbar\vec{k}^i) - E_n(\hbar\vec{k}^i) = \hbar\omega(\vec{k})$, where $\hbar\vec{k}^i$ is the momentum of the scattered neutron, and $E_n(\vec{p}) = p^2/2M_n$. To draw the left-hand side of the conservation law, one

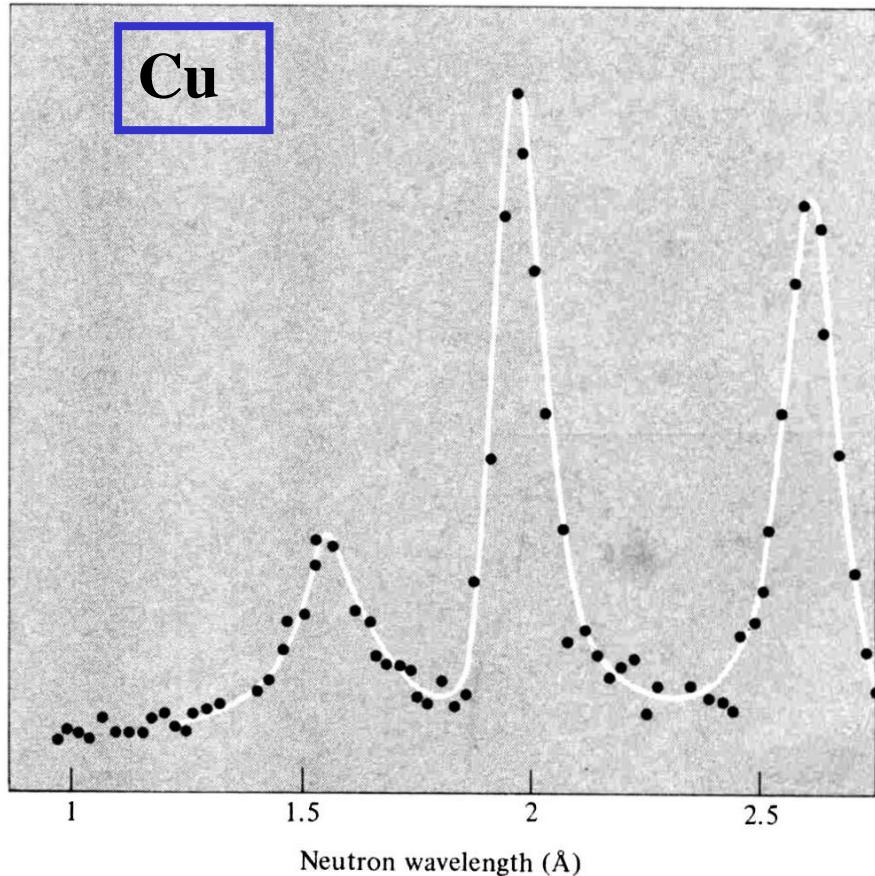
displaces the neutron energy-momentum curve horizontally, so that it is centered at $\vec{k} = -\vec{k}^i$ rather than $\vec{k} = 0$, and displaces it downward by an amount $E_n(\hbar\vec{k}^i)$. Solutions occur wherever this displaced curve intersects the phonon dispersion curve $\hbar\omega(\vec{k})$. In the present case, there are solutions for four different scattered neutron wave vectors, $\vec{k}_1^f \dots \vec{k}_4^f$.



Neutron Scattering : Cu Ge

Cu

Intensity



(b)

Ge

Intensity

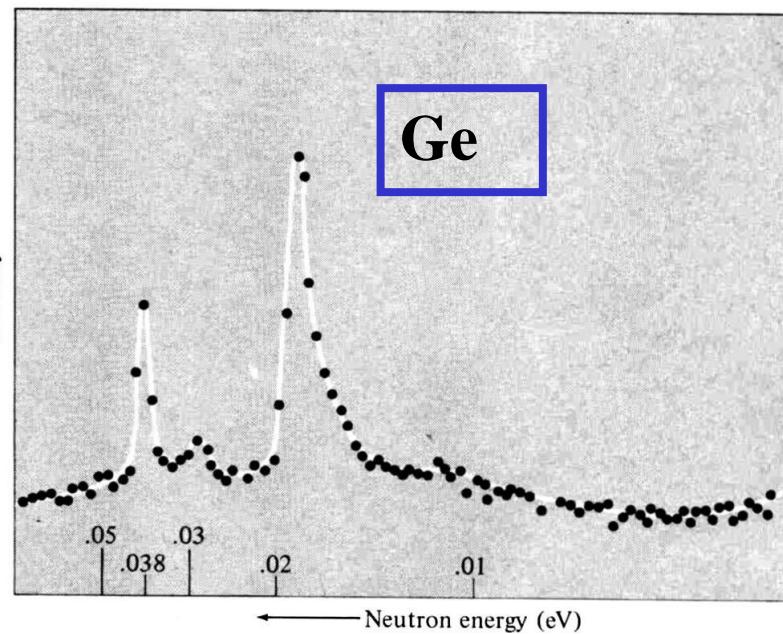


Figure 24.4

Some typical experimental neutron groups. In all cases the number of neutrons emerging in a fixed direction for a fixed incident energy is plotted against a variable that distinguishes scattered neutron energies. (a) Copper. (G. Gobert and B. Jacrot, *J. Phys. Radium* **19** (1959).) (b) Germanium. (I. Pelah et al., *Phys. Rev.* **108**, 1091 (1957).) Ashcroft

Raman and Brillouin scattering

Grosso_Parravicini

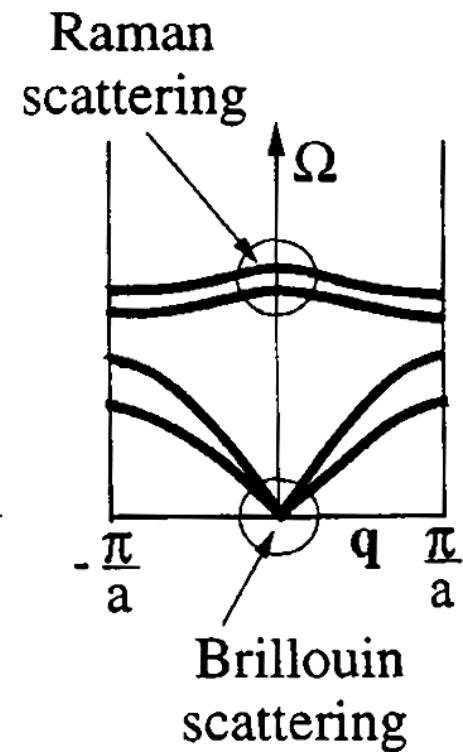
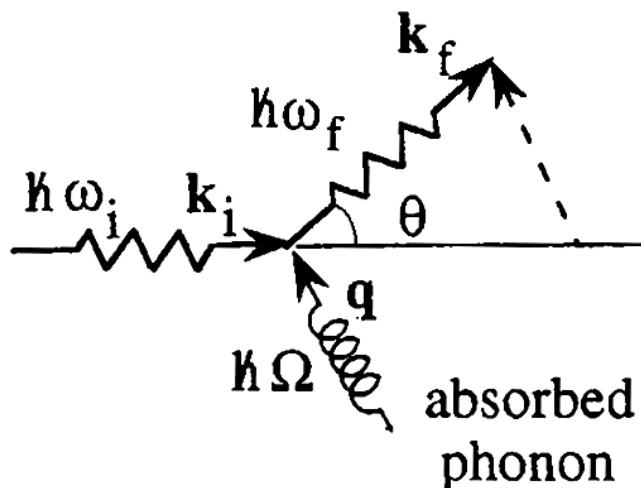
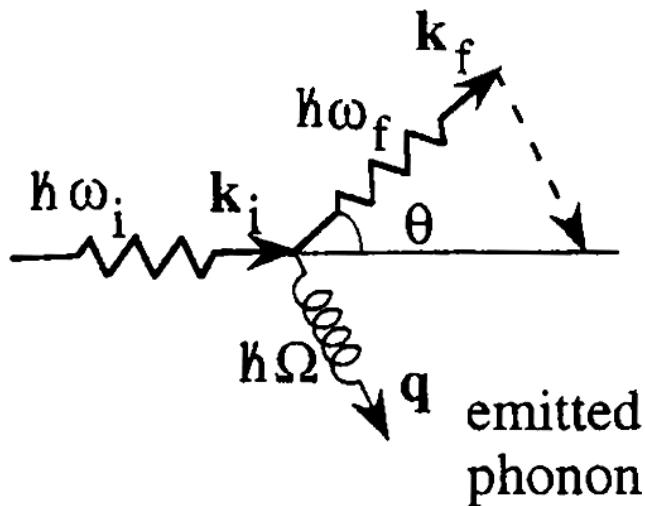


Fig. 8 Scattering of a photon through an angle θ with creation of a phonon (Stokes process) or annihilation of a phonon (anti-Stokes process); \mathbf{k}_i and \mathbf{k}_f denote the propagation wavevectors of the photon in the medium, before and after the scattering process. For photons in the visible region, a very small part of the phonon dispersion curves can be explored.

Raman and Brillouin scattering

Grosso_Parravicini

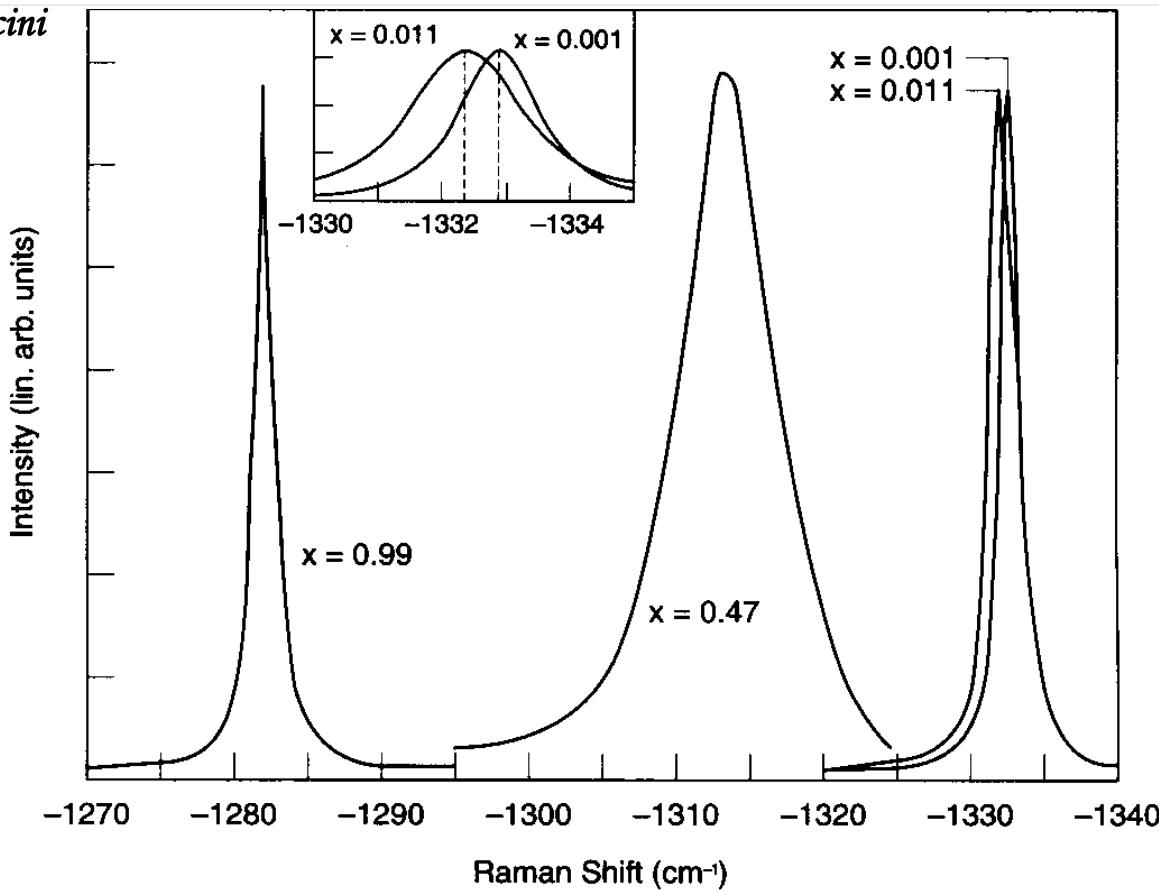
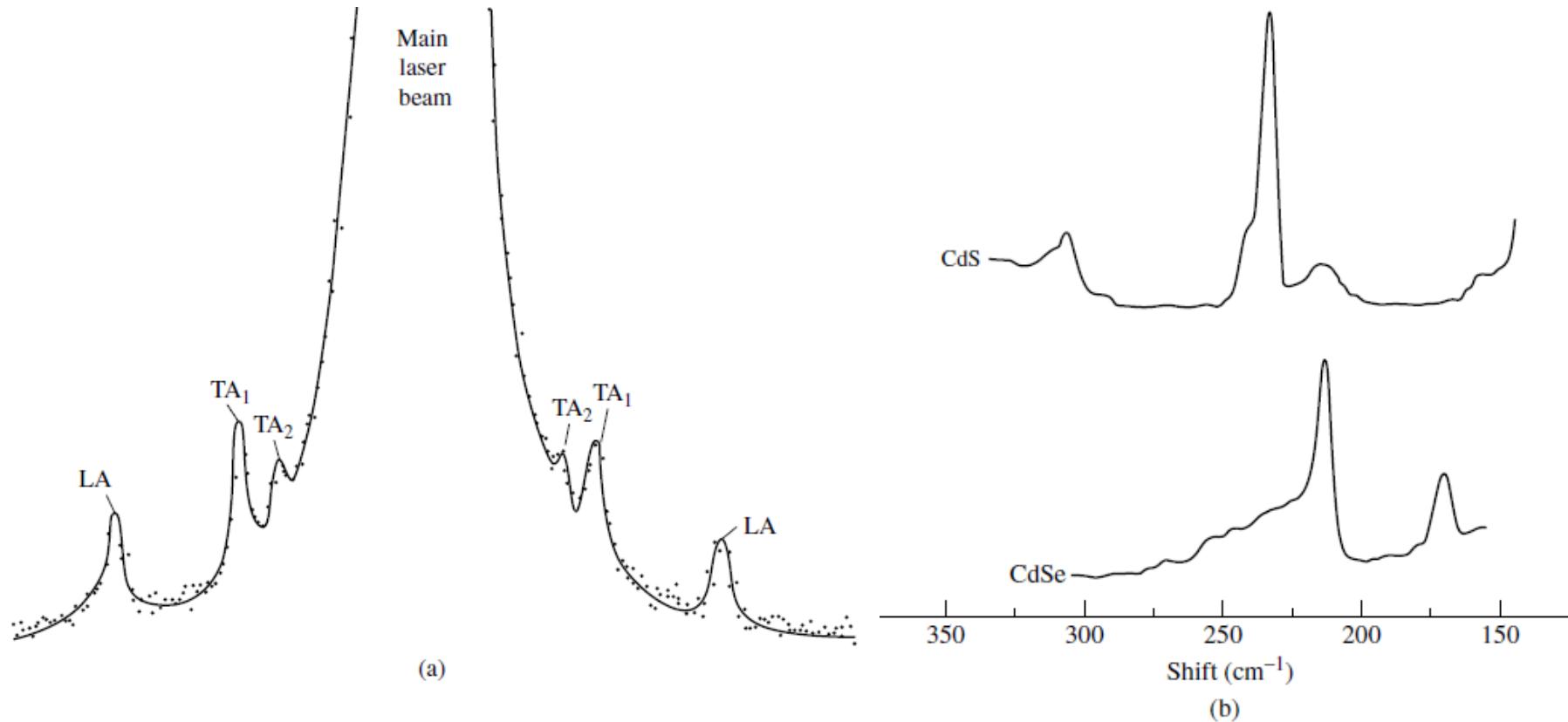


Fig. 9 Raman spectra of diamond specimens $^{12}\text{C}_{1-x}^{13}\text{C}_x$ for $x = 0.001$, $x = 0.011$ (natural composition), $x = 0.47$ and $x = 0.99$; the change of the optical mode frequency ω_0 with the isotopic composition x follows approximately the $M^{-1/2}$ dependence, where M is the average atomic mass [from R. Vogelgesang, A. K. Ramdas, S. Rodriguez, M. Grimsditch and T. R. Anthony, Phys. Rev. B54, 3989 (1996); copyright 1996 by the American Physical Society].

Brillouin and Raman Spectra

OPTICAL MEASUREMENTS OF PHONON SPECTRA

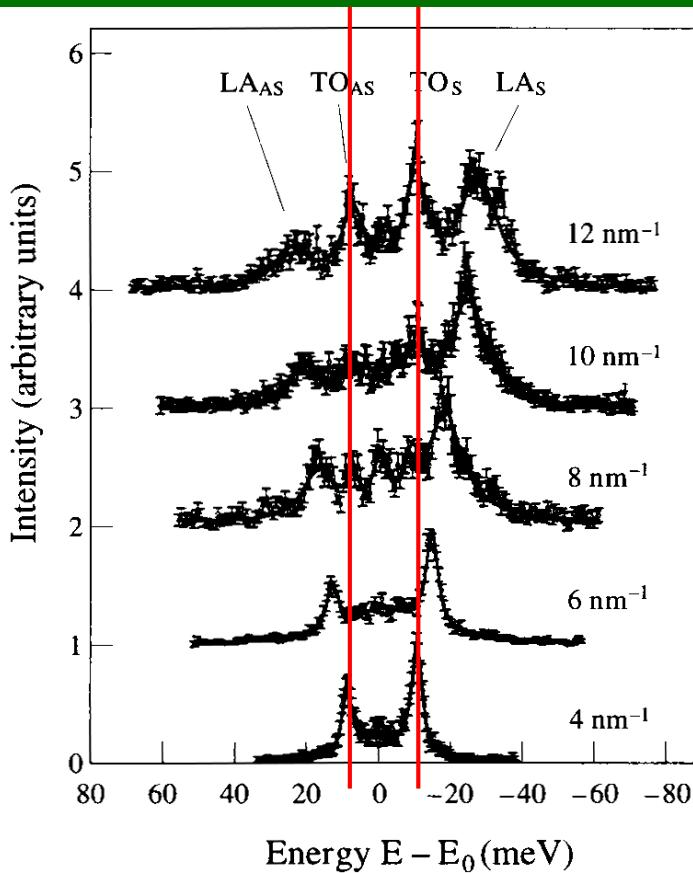


(a) Characteristic structure of a Brillouin spectrum. Intensity is plotted versus frequency. There are clearly identifiable peaks at frequencies above and below the frequency of the main laser beam, corresponding to one longitudinal and two transverse acoustic branches. (b) The Raman spectra of CdS and CdSe revealing peaks are determined by the longitudinal and transverse optical phonons.

Inelastic X-ray scattering

Grosso_Parravicini

$$h\nu=18\text{keV}$$



$$v_s = \hbar\omega / \hbar q \approx 3200 \text{m/s}$$

Fig. 7 Inelastic X-ray scattering spectra of polycrystalline H₂O ice at -20 °C. The reference energy E_0 is that of the incident beam; the intensity of the scattered beam versus E is reported at the indicated values of the wavevector transfer. The labels TO, LA, S and AS stand for transverse optical, longitudinal acoustic, Stokes and anti-Stokes, respectively [from G. Ruocco, F. Sette, U. Bergmann, M. Krisch, C. Masciovecchio, V. Mazzacurati, G. Signorelli and R. Verbeni, Nature **379**, 521 (1996); reprinted with permission from Nature, copyright 1996 Macmillan Magazines Limited].

Infrared absorption

- ◆ Raman active : atomic displacements change the crystal polarizability -- A_{1g}
- ◆ Infrared active : a change in the dipole moment –
 A_{2u} E_{1u}

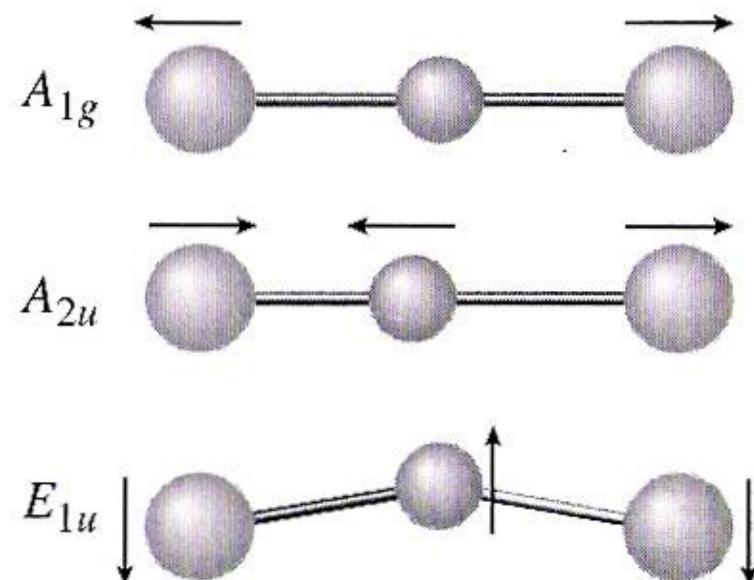
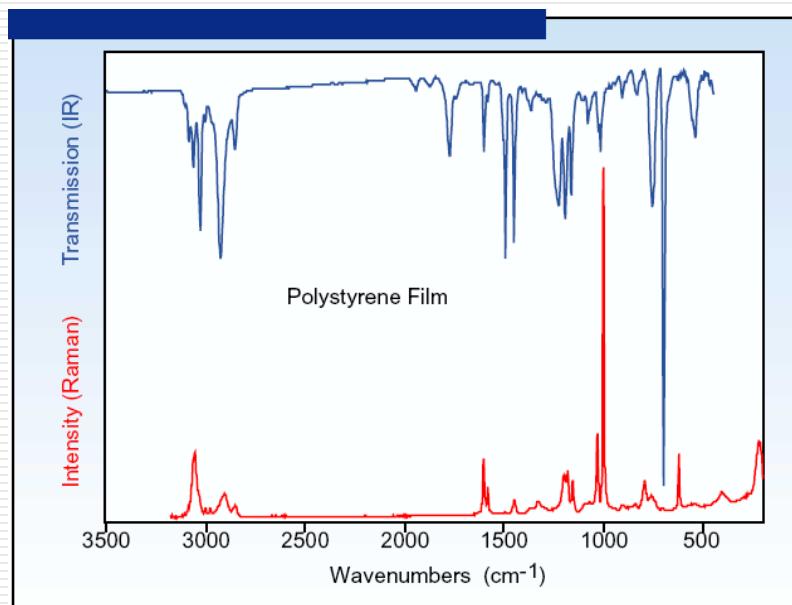


Fig. 10.7 The three normal modes of the CO_2 molecule.
DOVE

<http://www.inphotonics.com/raman.htm>

Anharmonic interactions

What physical properties require descriptions beyond harmonic interaction?

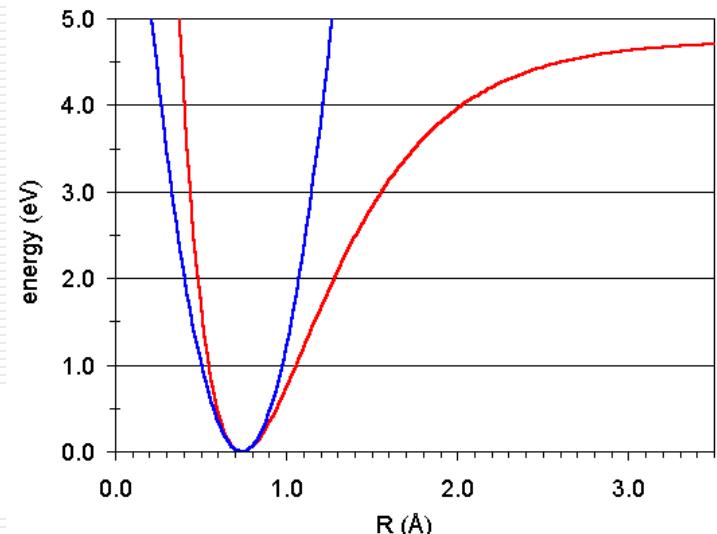
- ◆ Thermal expansion
- ◆ Thermal conductivity
- ◆ Temperature dependence of phonon frequencies

Anharmonic interactions

$u_{j,x} u_{j,y} u_{j,z} \rightarrow u_{j,\alpha}$ atomic displacement

$$E = E_0 + \sum_{\substack{j, \\ \alpha}} \frac{\partial E}{\partial u_{j,\alpha}} u_{j,\alpha} + \frac{1}{2} \sum_{\substack{j,j' \\ \alpha,\alpha'}} \frac{\partial^2 E}{\partial u_{j,\alpha} \partial u_{j',\alpha'}} u_{j,\alpha} u_{j',\alpha'} + \dots$$

$$+ \frac{1}{n!} \sum_{\substack{j^{(1)}, \dots, j^{(n)} \\ \alpha^{(1)}, \dots, \alpha^{(n)}}} \frac{\partial^n E}{\partial u_{j^{(1)}, \alpha^{(1)}} \cdots \partial u_{j^{(n)}, \alpha^{(n)}}} u_{j^{(1)}, \alpha^{(1)}} \cdots u_{j^{(n)}, \alpha^{(n)}}$$



<http://www.files.chem.vt.edu/chem-ed/quantum/harmonic-oscillator.html>

Thermal expansion

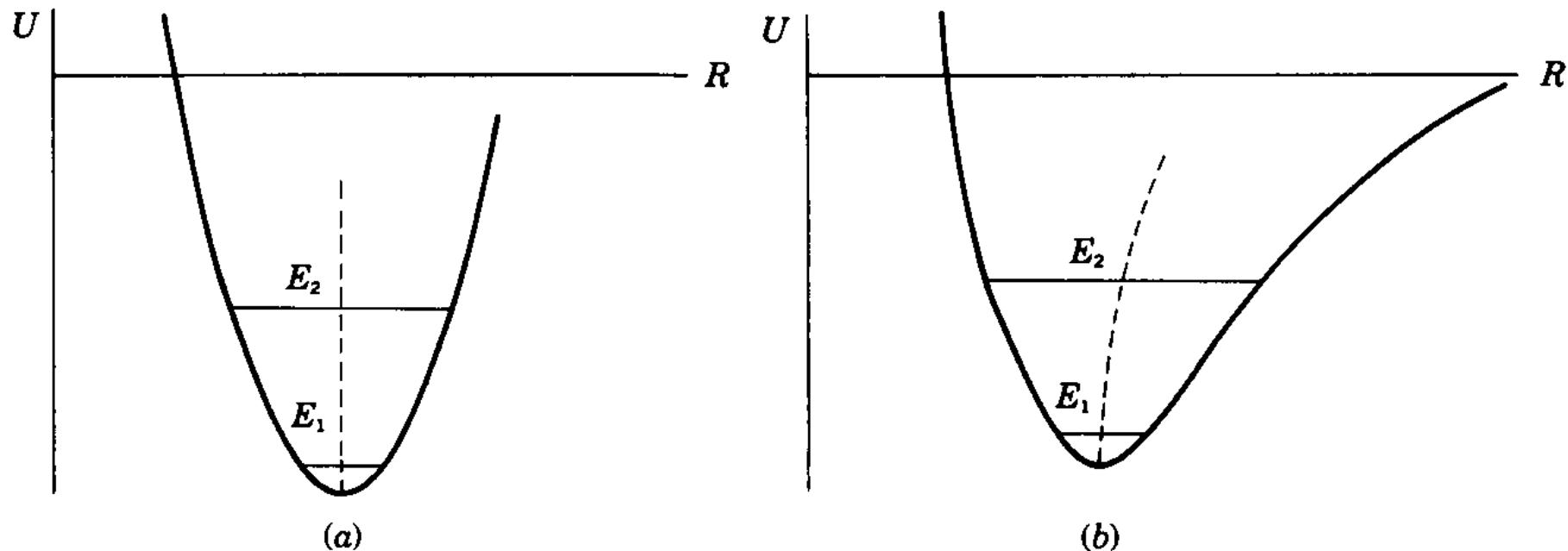


FIGURE 6-2 (a) Harmonic and (b) anharmonic potential energy functions for the interaction of two atoms. R is the atomic separation, while E_1 and E_2 represent two possible vibrational energies. For (a) an increase in energy does not result in a change in the average atomic separation, given by the midpoints of constant energy lines. For (b) an increase in energy results in an increase in average separation.

Christman

EQUATION OF STATE AND THERMAL EXPANSION IN A HARMONIC CRYSTAL

- To calculate the equation of state we write Pressure as $P = -(\partial F / \partial V)_T$, the Helmholtz free energy F is given by $F = U - TS$ (S – Entropy, U – Internal Energy). The relation between T and S

$$T \left(\frac{\partial S}{\partial T} \right)_V = \left(\frac{\partial U}{\partial T} \right)_V,$$

- So, the Pressure is

$$P = - \left(\frac{\partial F}{\partial V} \right)_T = - \frac{\partial}{\partial V} \left[U - T \int_0^T \frac{dT'}{T'} \frac{\partial}{\partial T'} U(T', V) \right].$$

- and internal energy is

$$U = U^{\text{eq}} + \sum_{\vec{k}s} \frac{1}{2} \hbar \omega_s(\vec{k}) + \sum_{\vec{k}s} \frac{\hbar \omega_s(\vec{k})}{e^{\beta \hbar \omega_s(\vec{k})} - 1}.$$

- Finally, Pressure,

$$P = - \frac{\partial}{\partial V} [U^{\text{eq}} + \sum_{\vec{k}s} \frac{1}{2} \hbar \omega_s(\vec{k})] + \sum_{\vec{k}s} \left(- \frac{\partial}{\partial V} \hbar \omega_s(\vec{k}) \right) \frac{1}{e^{\beta \hbar \omega_s(\vec{k})} - 1}.$$

- This result has a very simple structure: The first term (which is all that survives at $T = 0$) is the negative volume derivative of the ground-state energy.

EQUATION OF STATE AND THERMAL EXPANSION IN A HARMONIC CRYSTAL

- In a rigorously harmonic crystal, the pressure required to maintain a given volume does not vary with temperature

$$\left(\frac{\partial V}{\partial T}\right)_P = -\frac{(\partial P/\partial T)_V}{(\partial P/\partial V)_T} \equiv 0, \quad P = P^{\text{harm}} = -\frac{\partial}{\partial V} U^{\text{eq}}$$

- the coefficient of thermal expansion α must vanish.

$$\alpha = \frac{1}{l} \left(\frac{\partial l}{\partial T}\right)_P = \frac{1}{3V} \left(\frac{\partial V}{\partial T}\right)_P = \frac{1}{3B} \left(\frac{\partial P}{\partial T}\right)_V,$$

So,

$$c_p = c_v - \frac{T(\partial P/\partial T)_V^2}{V(\partial P/\partial V)_T}$$

and

$$\frac{c_p}{c_v} = \frac{(\partial P/\partial V)_S}{(\partial P/\partial V)_T}.$$

$$B = -V(\partial P/\partial V)_T = 1/K$$

THERMAL EXPANSION; THE GRÜNEISEN PARAMETER

- The coefficient of thermal expansion may be written as

$$\alpha = \frac{1}{3B} \sum_{\vec{k}s} \left(-\frac{\partial}{\partial V} \hbar \omega_{\vec{k}s} \right) \frac{\partial}{\partial T} n_s(\vec{k}),$$

where

$$n_s(\vec{k}) = [e^{\beta \hbar \omega_s(\vec{k})} - 1]^{-1}.$$

- The specific heat can be written as

$$c_v = \sum_{\vec{k}s} \frac{\hbar \omega_s(\vec{k})}{V} \frac{\partial}{\partial T} n_s(\vec{k}),$$

THERMAL EXPANSION; THE GRÜNEISEN PARAMETER

- The Grüneisen parameter

$$\gamma_{\vec{k}s} = -\frac{V}{\omega_s(\vec{k})} \frac{\partial \omega_s(\vec{k})}{\partial V} = -\frac{\partial(\ln \omega_s(\vec{k}))}{\partial(\ln V)}$$

$$\gamma = \frac{\sum_{\vec{k},s} \gamma_{\vec{k}s} c_{vs}(\vec{k})}{\sum_{\vec{k},s} c_{vs}(\vec{k})} \quad \alpha = \frac{\gamma c_v}{3B}$$

- In a Debye model

$$\gamma_{\vec{k}s} \equiv -\frac{\partial(\ln \omega_D)}{\partial(\ln V)}$$

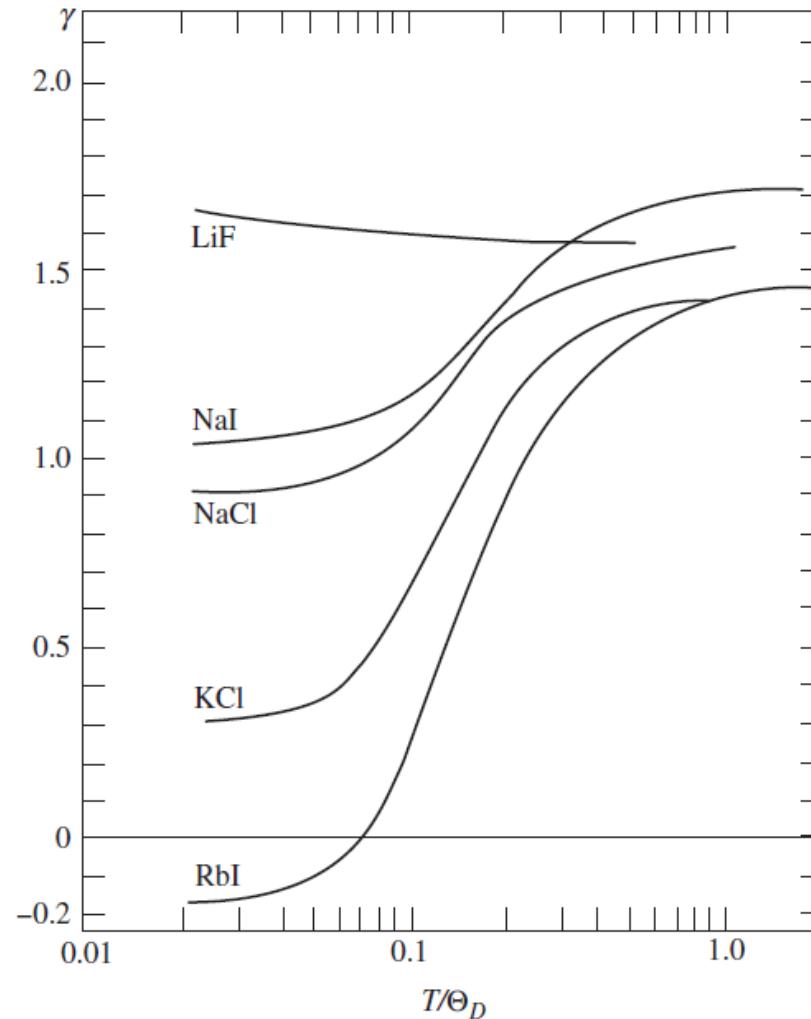
- The normal-mode frequencies scale linearly with the cutoff frequency ω_D

THERMAL EXPANSION; THE GRÜNEISEN PARAMETER

Linear Expansion Coefficients and Grüneisen Parameters for Some Alkali Halides

T(K)		LiF	NaCl	NaI	KCl	KBr	KI	RbI	CsBr
0	α	0	0	0	0	0	0	0	0
	γ	1.70	0.90	1.04	0.32	0.29	0.28	-0.18	2.0
20	α	0.063	0.62	5.1	0.74	2.23	4.5	6.0	10.0
	γ	1.60	0.96	1.22	0.53	0.74	0.79	0.85	—
65	α	3.6	15.8	27.3	17.5	22.5	26.0	28.0	35.2
	γ	1.59	1.39	1.64	1.30	1.42	1.35	1.35	—
283	α	32.9	39.5	45.1	36.9	38.5	40.0	39.2	47.1
	γ	1.58	1.57	1.71	1.45	1.49	1.47	—	2.0

THERMAL EXPANSION; THE GRÜNEISEN PARAMETER



Grüneisen parameter versus T/Θ_D for some alkali halide crystals.

THERMAL EXPANSION OF METALS

- The free electron gas equation of state is:

$$P = \frac{2}{3} \frac{U}{V}$$

$$\left(\frac{\partial P^{\text{el}}}{\partial T} \right)_V = \frac{2}{3} c_v^{\text{el}}$$

- The coefficient of thermal expansion in a metal:

$$\alpha = \frac{1}{3B} \left(\gamma c_v^{\text{ion}} + \frac{2}{3} c_v^{\text{el}} \right).$$

- The difference between the expansion coefficient of metals and insulators is that at very low temperatures, α should vanish linearly in T in metals but as T^3 in insulators.

Thermal expansion

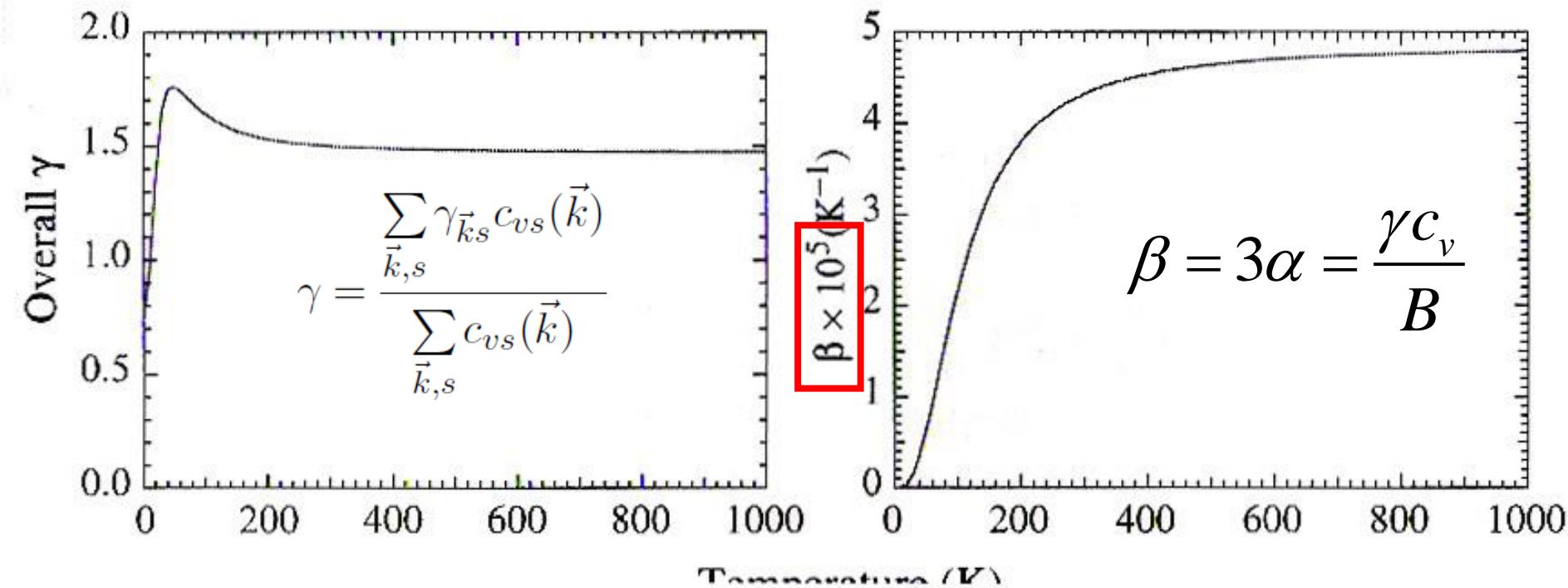


Fig. 11.6 Temperature dependence of the overall Grüneisen parameter (left) and coefficient of volume thermal expansion (right) for fluorite, CaF_2 , calculated using a simple model set of interatomic interactions (Chapter 5).

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Thermal expansion

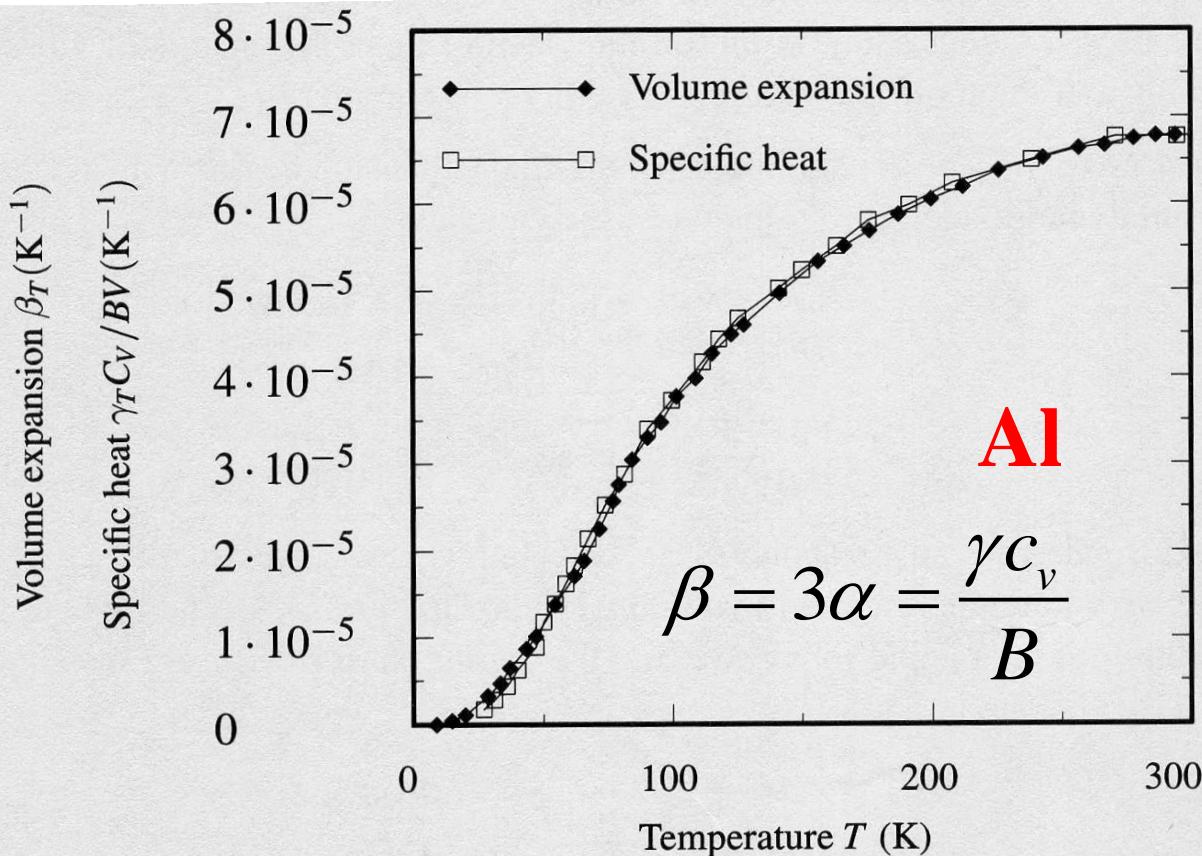
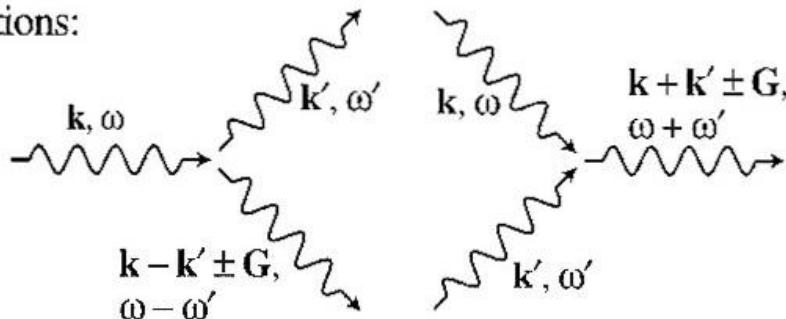


Figure 13.12. Comparison of specific heat C_V and volume expansion coefficient β_T for aluminum using Eq. (13.85). The comparison employs a bulk modulus B of 77 GPa from Eq. (12.19) and Table 12.1, uses a Grüneisen parameter γ_T of 2.2, obtained by matching specific heat and expansion at 300 K, and obtains the coefficient of bulk expansion from linear expansion data through $\beta_T \approx 3\alpha_T$. [Source: Touloukian and Buyco (1970a) and Touloukian et al. (1975).]

Marder

Anharmonic interactions

Cubic interactions:



Quartic interactions:

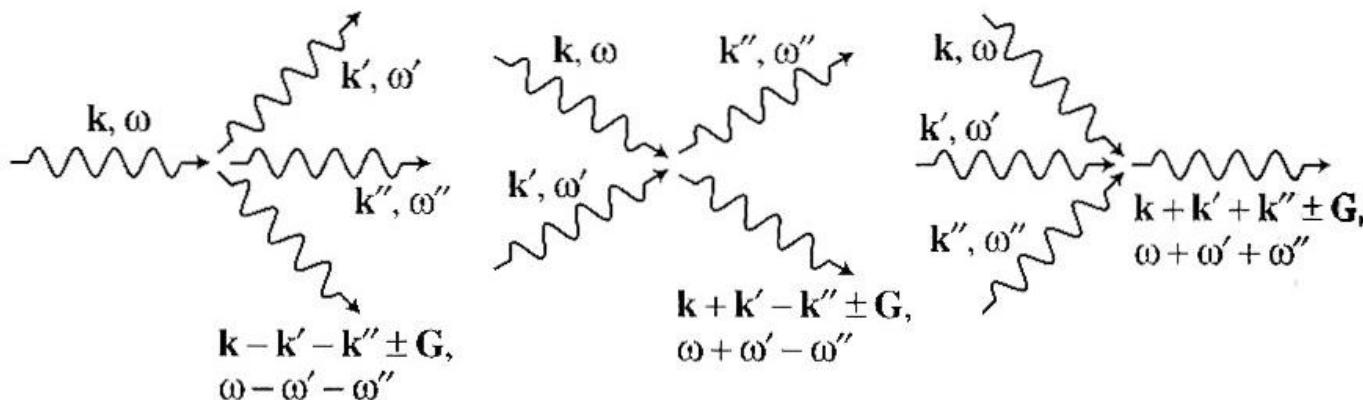
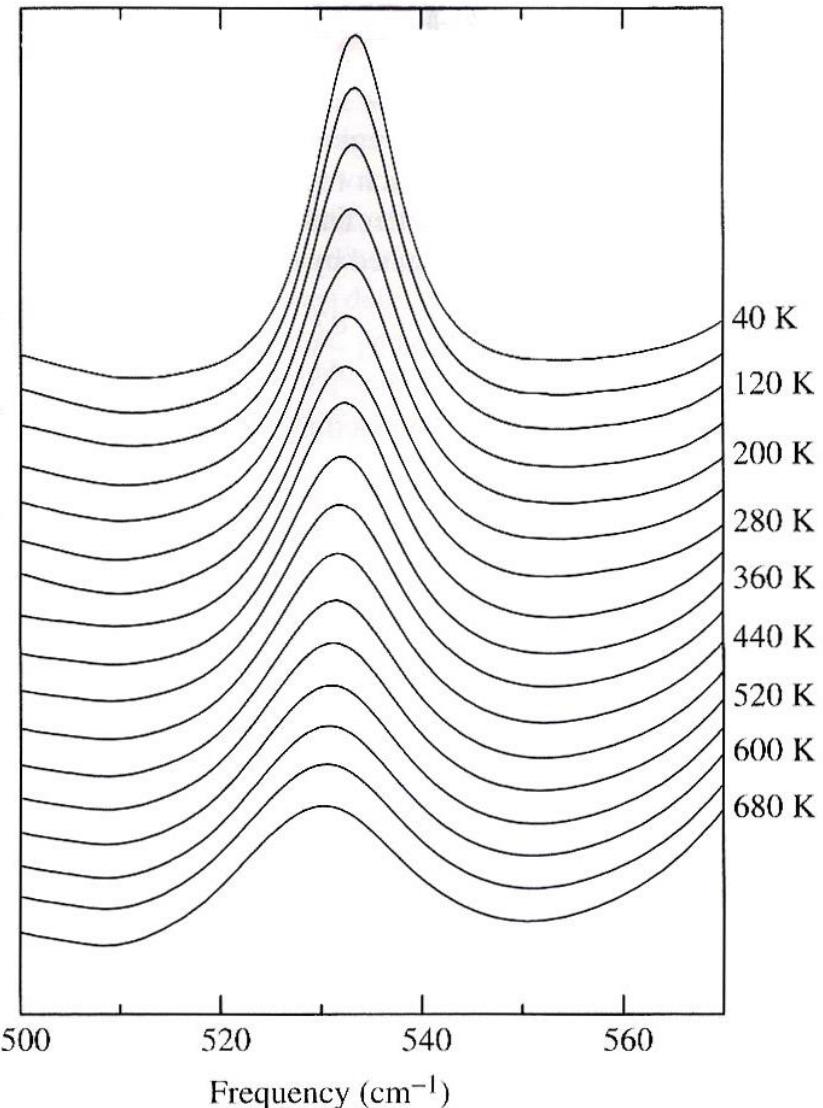


Fig. 11.1 Third- and fourth-order anharmonic phonon interactions represented as collisions between phonons with conservation restrictions. The phonons are represented by waves with arrows.

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Phonon life time

Absorbance (arbitrary units)



ccheng@phys.ncku.edu.tw

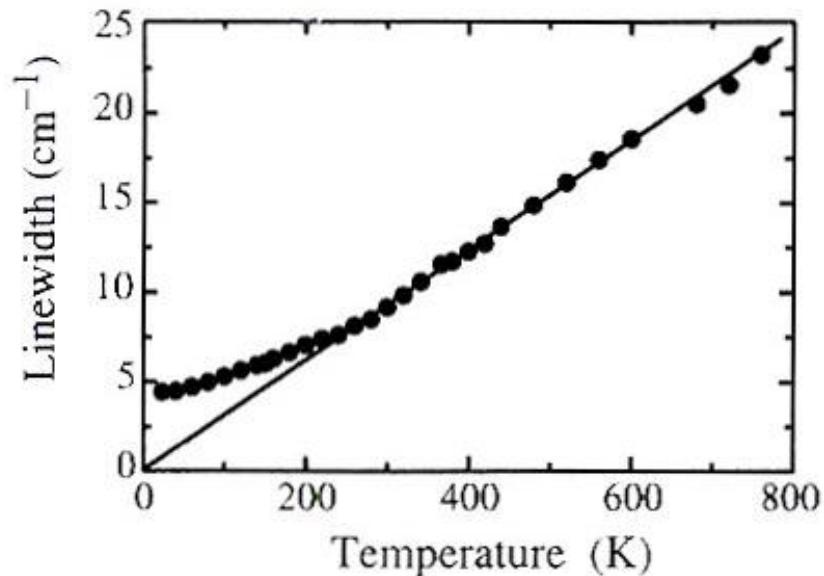


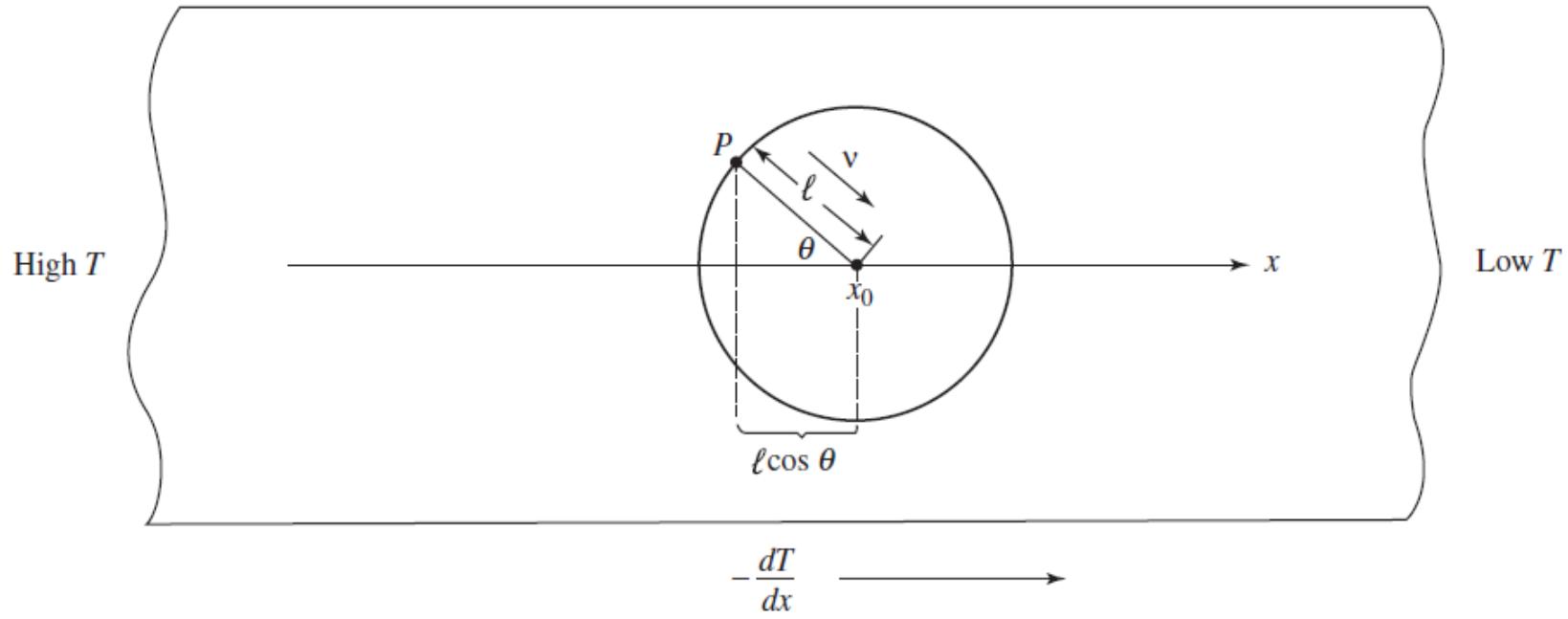
Fig. 11.3 Temperature dependence of the width of the phonon peak shown in Fig. 11.2. Note that quantum effects come into play for temperatures below 250 K.

DOVE

Fig. 11.2 Example of temperature dependence of one of the phonon spectra in the mineral albite, $\text{NaAlSi}_3\text{O}_8$, measured in an infrared spectroscopy experiment (Chapter 10). (Data courtesy of Ming Zhang, University of Cambridge.)

DOVE

LATTICE THERMAL CONDUCTIVITY: ELEMENTARY KINETIC THEORY



Heat propagation by phonons in the presence of a uniform temperature gradient along the x -axis. The thermal current at x_0 is carried by phonons whose last collision was, on an average, a distance $\ell = v\tau$ away from x_0 . Phonons with velocities making an angle θ with the x -axis at x_0 collided last at a point P a distance $\ell \cos \theta$ up the temperature gradient, and therefore carry an energy density $u(x_0 - \ell \cos \theta)$ with x -velocity $v \cos \theta$. The net thermal current is proportional to the product of these quantities averaged over all solid angles.

LATTICE THERMAL CONDUCTIVITY: ELEMENTARY KINETIC THEORY

- Assuming, in the spirit of the Drude model, that the collision occurred a distance $\ell = v\tau$ from the point x_0 , in a direction making an angle to the x -axis, we have

$$\begin{aligned} j &= \langle v_x u(x_0 - \ell \cos \theta) \rangle_\theta = \int_0^\pi v \cos \theta u(x_0 - \ell \cos \theta) \frac{2\pi d\theta}{4\pi} \sin \theta, \\ &= \frac{1}{2} \int_{-1}^1 \mu d\mu v u(x_0 - \ell \mu). \end{aligned}$$

- To linear order in the temperature gradient, we then have

$$j = -v\ell \frac{\partial u}{\partial x} \frac{1}{2} \int_{-1}^1 \mu^2 d\mu = \frac{1}{3} v\ell \frac{\partial u}{\partial T} \left(-\frac{\partial T}{\partial x} \right)$$

where the thermal conductivity is given by

$$j = \kappa \left(-\frac{\partial T}{\partial x} \right), \quad \kappa = \frac{1}{3} c_v v \ell = \frac{1}{3} c_v v^2 \tau.$$

- Here, c_v is the specific heat of the phonons and is one of the quantities that determines the temperature dependence of κ . The other is the phonon collision rate, τ^{-1} .

Thermal conductivity

No anharmonicity
 $\rightarrow \lambda = \infty \rightarrow K = \infty$

$$j = \kappa \left(-\frac{\partial T}{\partial x} \right), \quad \kappa = \frac{1}{3} c_v v \ell = \frac{1}{3} c_v v^2 \tau.$$

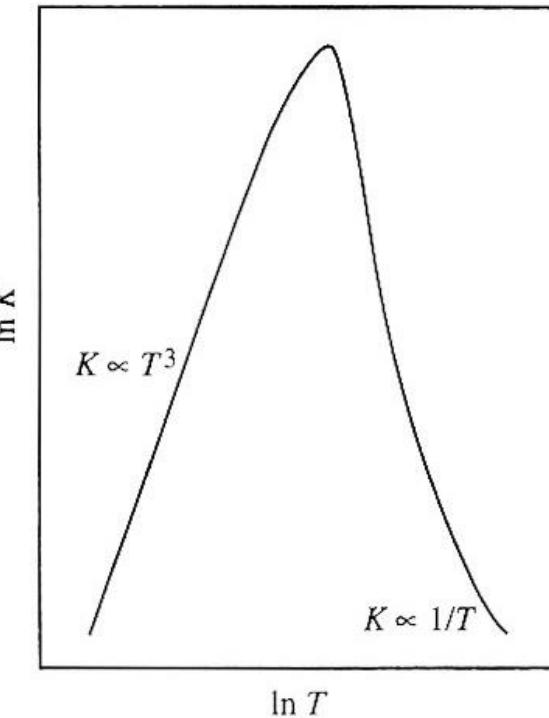
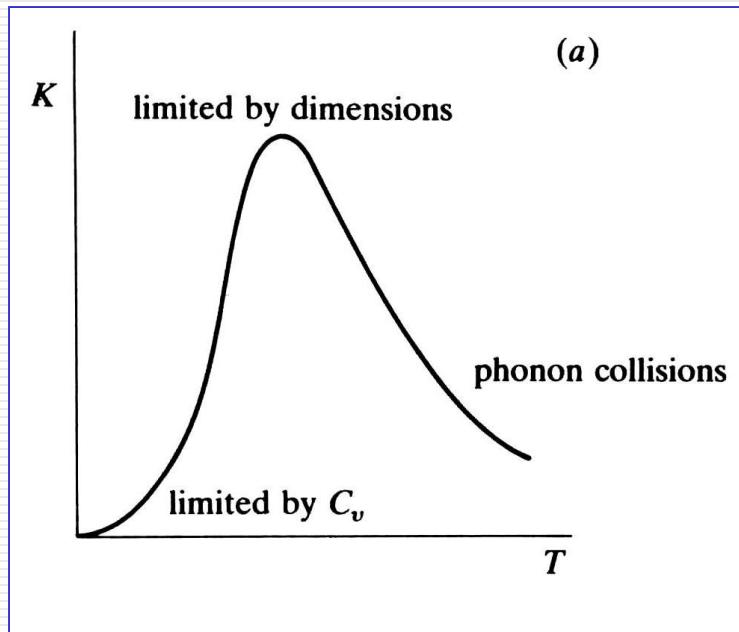
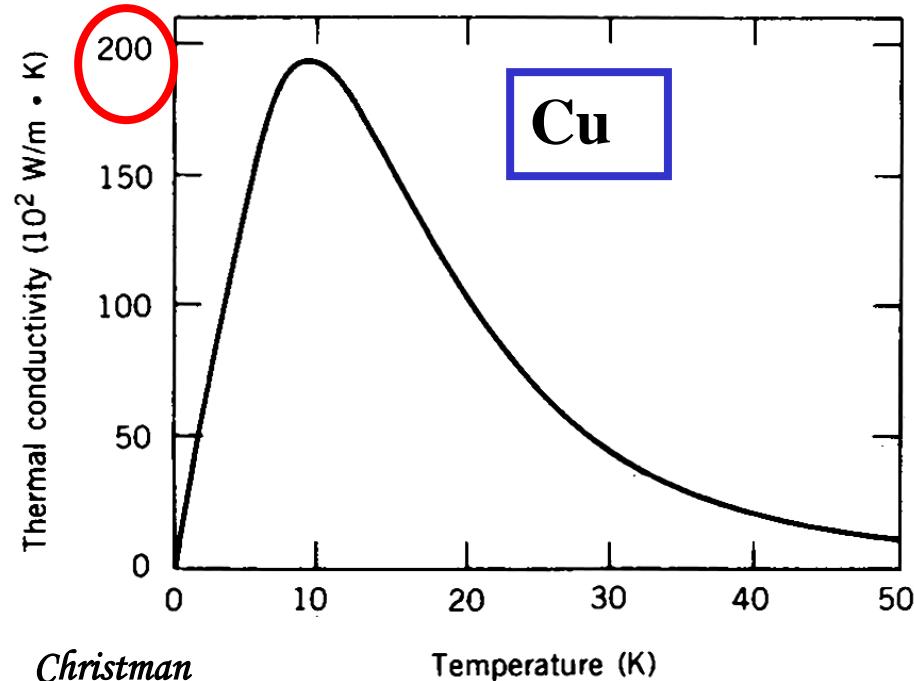
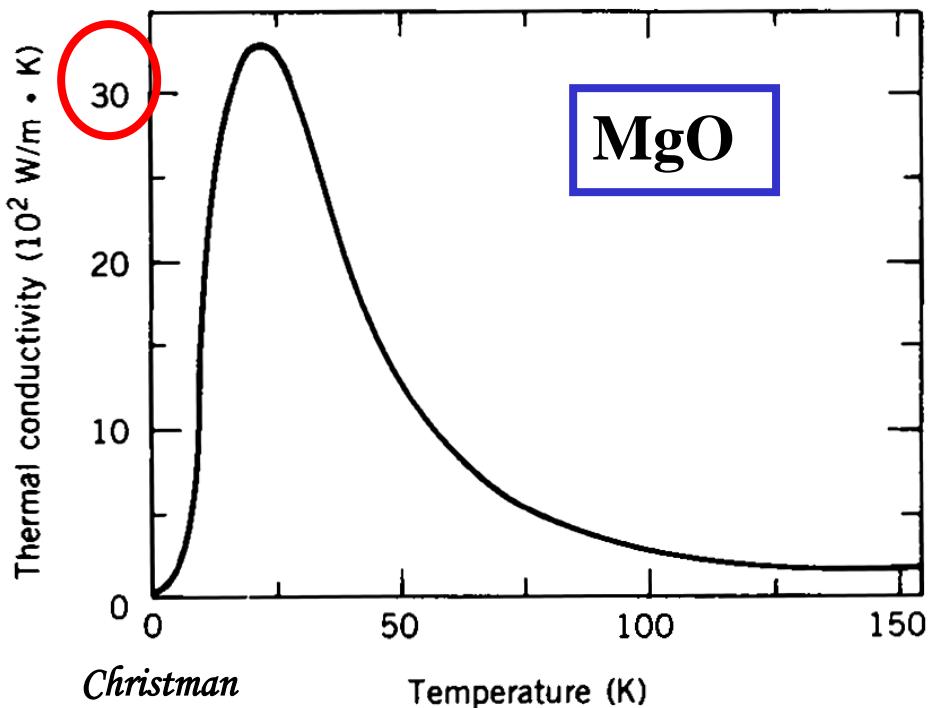


Fig. 11.5 Schematic representation of the temperature dependence of the thermal conductivity.

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Thermal conductivity



Lattice dynamics from DFT methods

How is DFT applied to study lattice dynamics and thermodynamical properties of materials?

- ◆ Frozen Phonons
- ◆ Direct Approach
- ◆ Linear Response Theory

Frozen Phonons

- ◆ Frozen Phonons : Wendel_Martin PRL 1978
- ◆ FROZSL

TABLE I. Comparison of calculated and experimental harmonic force constants for $\text{TO}(\Gamma)$, $\text{TA}(X)$, and $C_{11} - C_{12}$ modes in Si (in eV/ \AA^2). Also given is the cubic anharmonic force k_{xyz} (in eV/ \AA^3) for $\text{TO}(\Gamma)$. It is compared with a value derived from Ref. 11. II, BS, and EE correspond to the separation of terms in Eqs. (2) and (3). C is the correction discussed in the text.

	$M\omega_{\text{TO}(\Gamma)}^2$	$2a(C_{11} - C_{12})$	$M\omega_{\text{TA}(X)}^2$	k_{xyz}
II	21.56	- 29.25	- 24.35	- 69.92
BS	- 5.76	27.62	20.70	18.62
EE	2.71	16.26	15.45	- 1.16
C	- 4.66	- 6.98	- 6.98	0
Total	13.85	7.65	4.82	- 52.46
Expt.	14.00	7.32	2.33	(- 40.51)

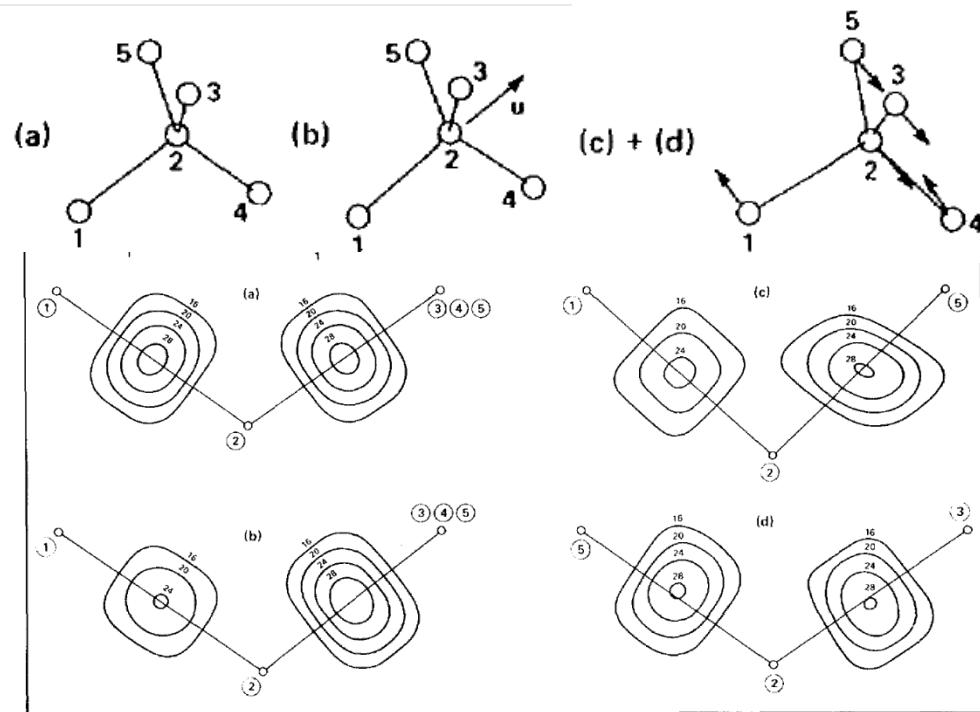
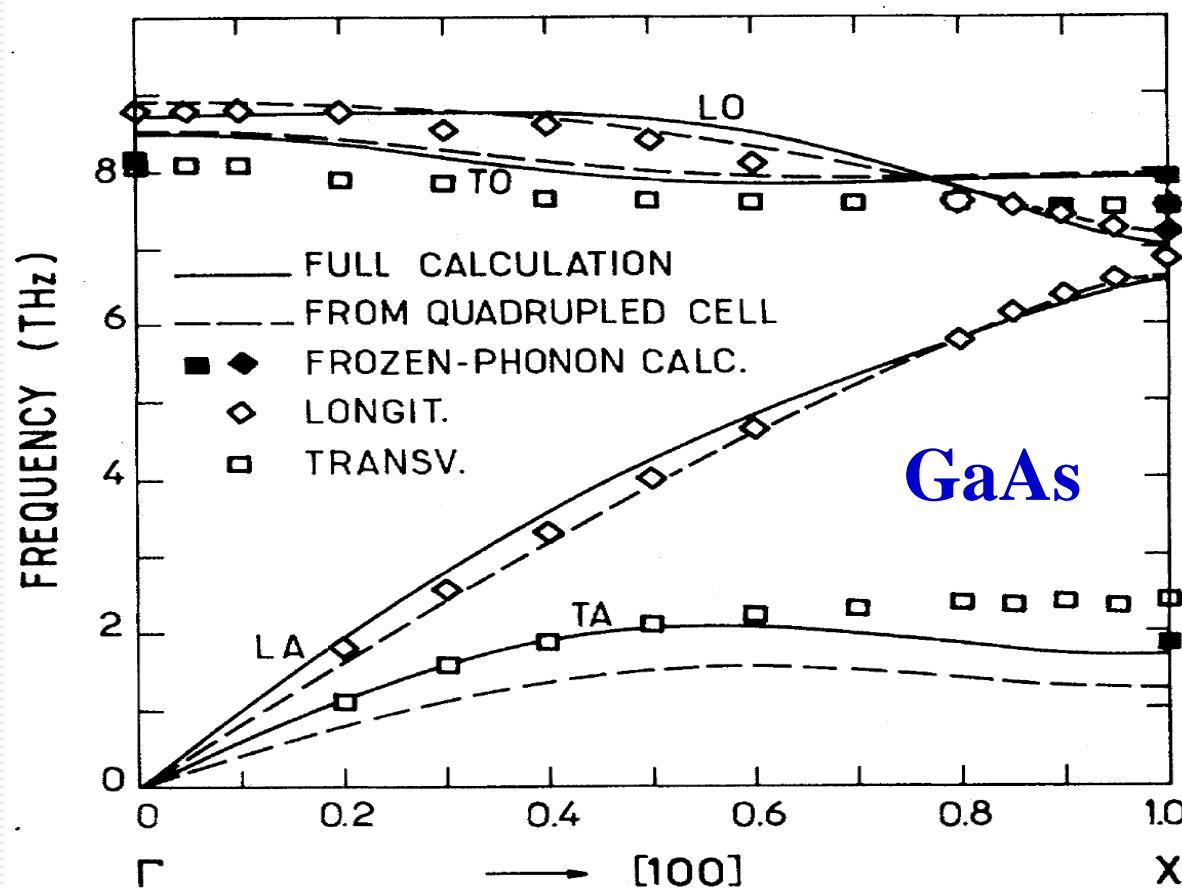


FIG. 1. Pseudo charge density in the bond region of crystalline Si: (a) undistorted lattice, (b) $\text{TO}(\Gamma)$ phonon, and (c), (d) $\text{TA}(X)$ phonon.

Direct Approach for Dispersion Curve

- ◆ Direct Approach : Kunc_Martin PRL 1981
- ◆ PHON

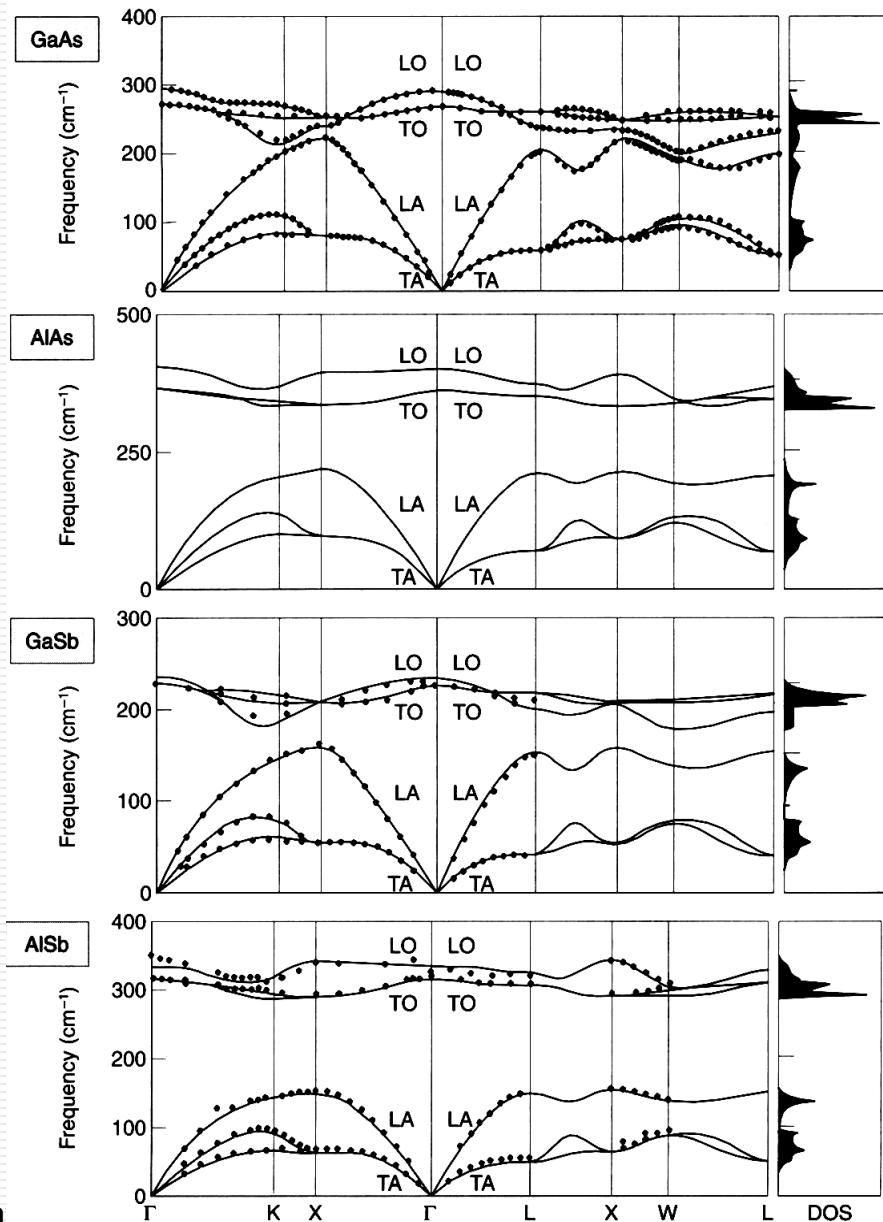


Linear Response Theory

- ◆ Baroni, Giannozzi, Testa
PRL 1987
- ◆ Giannozzi, Gironcoli,
Pavone, Baroni PRB 1991

TABLE I. Equilibrium lattice parameter [a , (a.u.)] used in the present calculations, calculated Born effective charges (Z^*), and static dielectric constants (ϵ_∞). Parentheses denote experimental data.

	Si	Ge	GaAs	AlAs	GaSb	AlSb
a	10.20 (10.26)	10.60 (10.68)	10.605 (10.68)	10.605 (10.69)	11.40 (11.49)	11.51 (11.58)
Z^*				2.07 (2.07)	2.17 (2.18)	1.73 (1.88) 1.91 (2.18)
ϵ_∞	13.6 (12.1)	18.7 (16.5)	12.3 (10.9)	9.2 (8.2)	18.1 (14.4)	12.2 (10.2)



Outline of the Lecture

- ◆ Description of lattice dynamics
- ◆ Thermodynamic properties ← Lattice dynamics
- ◆ Experimental methods → vibration frequencies
- ◆ Anharmonicity
- ◆ DFT approaches

Hands-on session

- ◆ DFT bulk Al: primitive cell; MP=(4 4 4)
- ◆ Generate supercell $2 \times 2 \times 2$
- ◆ Calculate DFT atomic forces: MP=(2 2 2)
- ◆ Calculate phonon dispersion curve -- plot
- ◆ Calculate thermodynamical properties – plots
- ◆ Numerical errors in dispersion curve: try MP(3 3 3) MP(4 4 4)
- ◆ Similarly for thermodynamical properties
- ◆ Plot the classic internal energy for comparison
- ◆ Low-T T-dep specific heat
- ◆ Try larger supercell