MSE

Phonon Excitations as Emergent Phenomena & *`Mode Softening' of Ferroic States in Displacive Phase Transitions*

Presented by: Caroline S. Gorham, Ph.D.

topologylab.com

Email: caroling@cmu.edu

Special Topics: Ferroic and Multiferroic Materials (Prof. David E. Laughlin)

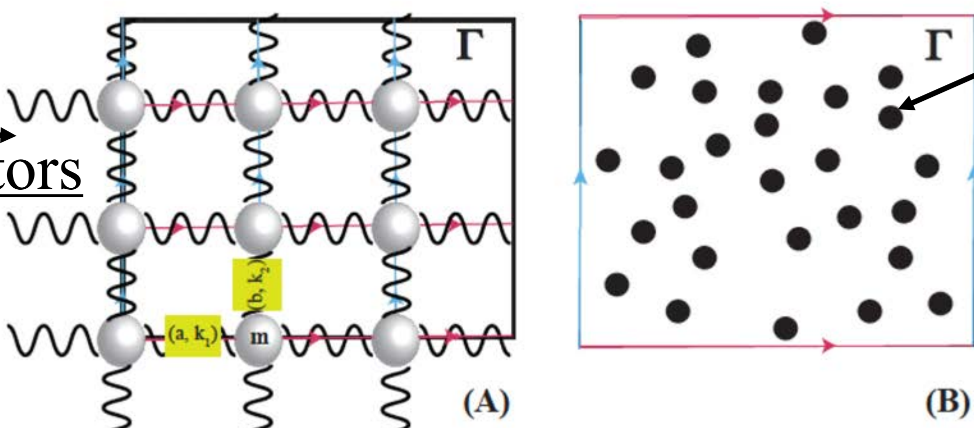
Carnegie Mellon University

What is a Phonon?

***Phonon: comes from Greek word* φωνή (*phonē*), which translates to *sound* or *voice* because long-wavelength phonons give rise to sound.**

Phonons are collective excitations (bosons) of a lattice of atoms (orientationally-ordered, elastic arrangement) – an emergent phenomena.

Elastic solid comprised of harmonic oscillators (Hookean)

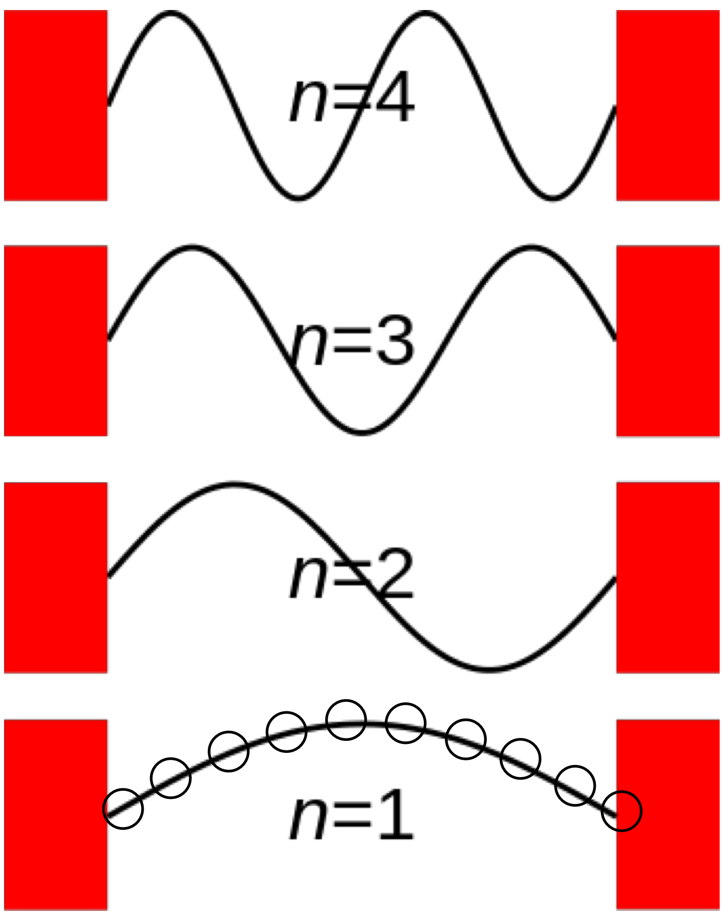


Vibrational modes (phonons) are quantized.

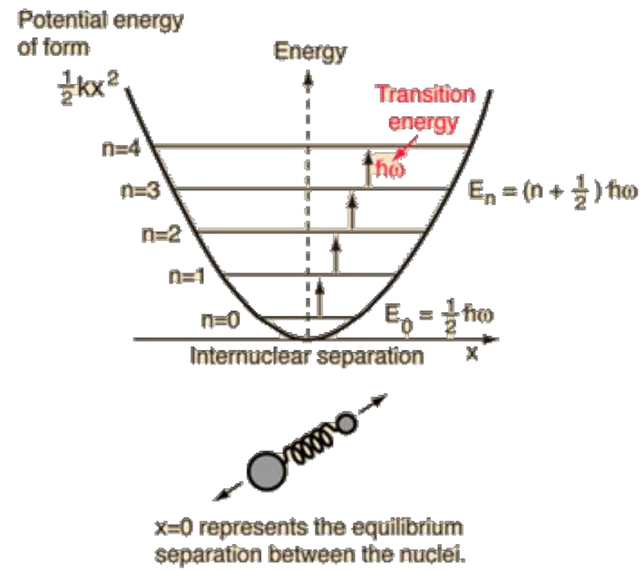
REAL SPACE (x, t) ⟷ RECIPROCAL SPACE (q, ω)

What are Phonon energy levels? Heat Particles in a Box

phonons are particles of heat “in a box”.

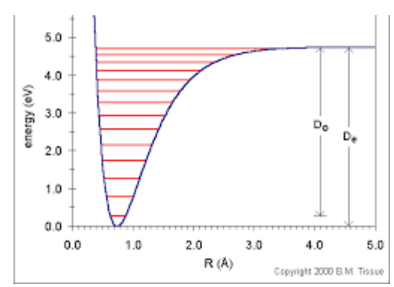


Harmonic



Anharmonic

$$E_v = \left(v + \frac{1}{2}\right) v_e - \left(v + \frac{1}{2}\right)^2 v_e x_e + \left(v + \frac{1}{2}\right)^3 v_e y_e + higher\ terms$$



Phonon dispersion:

Relationship between Phonons and Photons

(*sound*): Propagation of sound through a solid, by phonons, is described by the wave-equation!

(*light*): Propagation of light through vacuum, by photons, is also described by the wave-equation!

wave-equation:

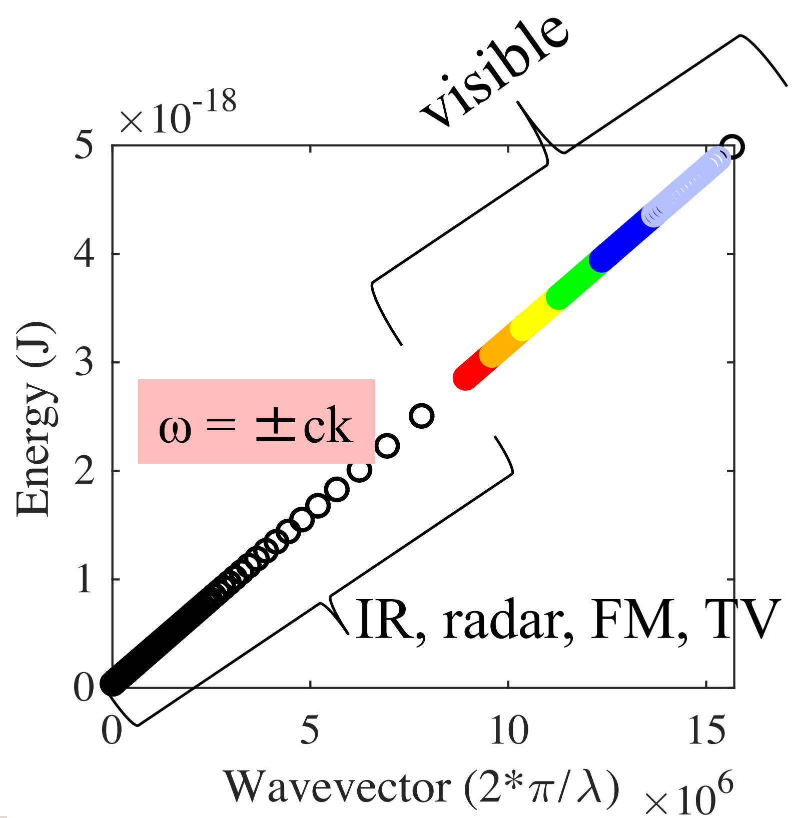
$$\psi(x,t) = Ae^{i(kx-\omega t)}$$

$$\boxed{\frac{\partial^2\psi}{\partial t^2} = c^2\frac{\partial^2\psi}{\partial x^2}},$$

$$\omega^2 = c^2k^2.$$

where $k = 2\pi/\lambda$

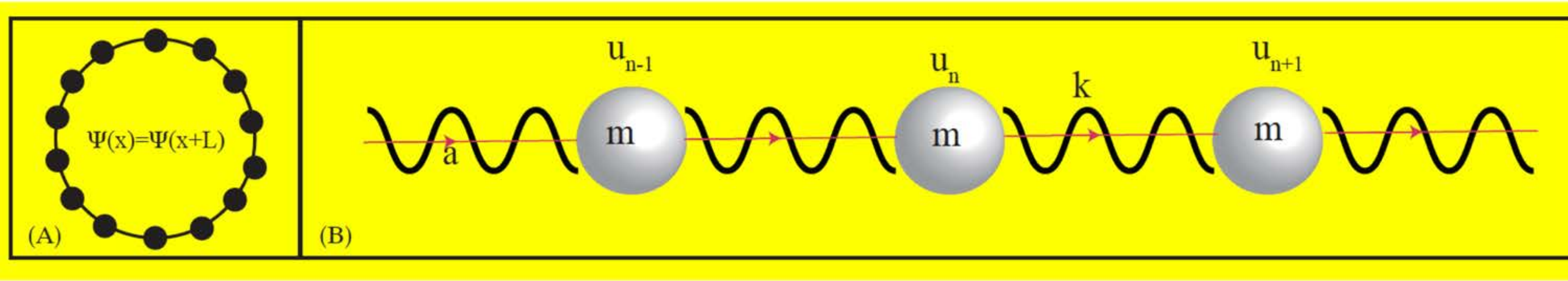
- Photons travel at the speed of light



Phonon Dispersion: Acoustic modes

Without loss of generality, consider a 1D monoatomic lattice:

- *Global translational order* leads to periodic Born von Karman boundary conditions.



Harmonic Springs: $V(r) = \frac{1}{2}Kx^2$

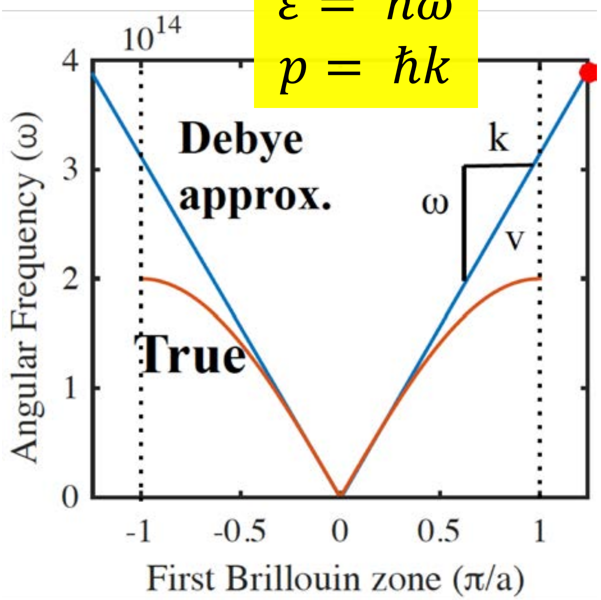
Equation of Motion:

$$F = m\ddot{u} = -\nabla V(r) = K[u_{n+1} + u_{n-1} - 2u_n]$$

Bloch wave-like displacement: $u_n \propto e^{i(kx-\omega t)}$

vibrational dispersion: $\omega(k) = \sqrt{\frac{4K}{m}}\left|\sin\left(\frac{ka}{2}\right)\right|$

Topology: 1st Brillouin Zone

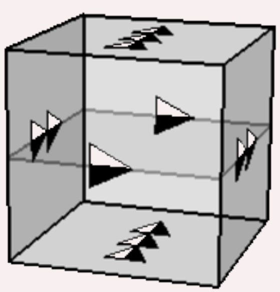


1st Brillouin zone $-\frac{\pi}{a} \leq k_x \leq \frac{\pi}{a}$

Born-von Karman periodic boundary conditions give D-dimensional torus:

$$T^D \approx \overbrace{S^1 \times \cdots \times S^1}^{D}$$

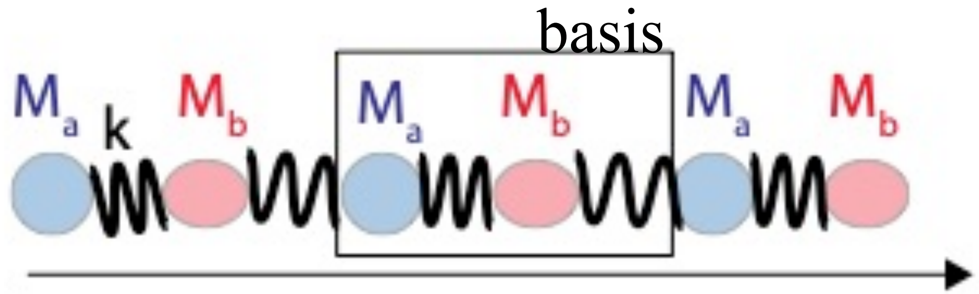
$(k_x, k_y, k_z) \sim T^3$



In 3D, there are 1L and 2T *__acoustic__ phonon polarizations*

Diatomic Chain: Optical Branches

*If lattice basis consists of two or more atoms, **optical branches appear**.*



Equations of Motion:

$$F_a = M_a \ddot{u}_{a,n} = K(u_{b,n} + u_{b,n-1} - 2u_{a,n})$$
$$F_b = M_b \ddot{u}_{b,n} = K(u_{a,n} + u_{a,n-1} - 2u_{b,n})$$

Dispersion Relation:

$$\omega(k) = \sqrt{\frac{K(M_a + M_b)}{M_a M_b} \pm K\sqrt{\frac{(M_a + M_b)^2}{M_a^2\, M_b^2} - \frac{4}{M_a M_b}\sin^2\left(\frac{ka}{2}\right)}}$$

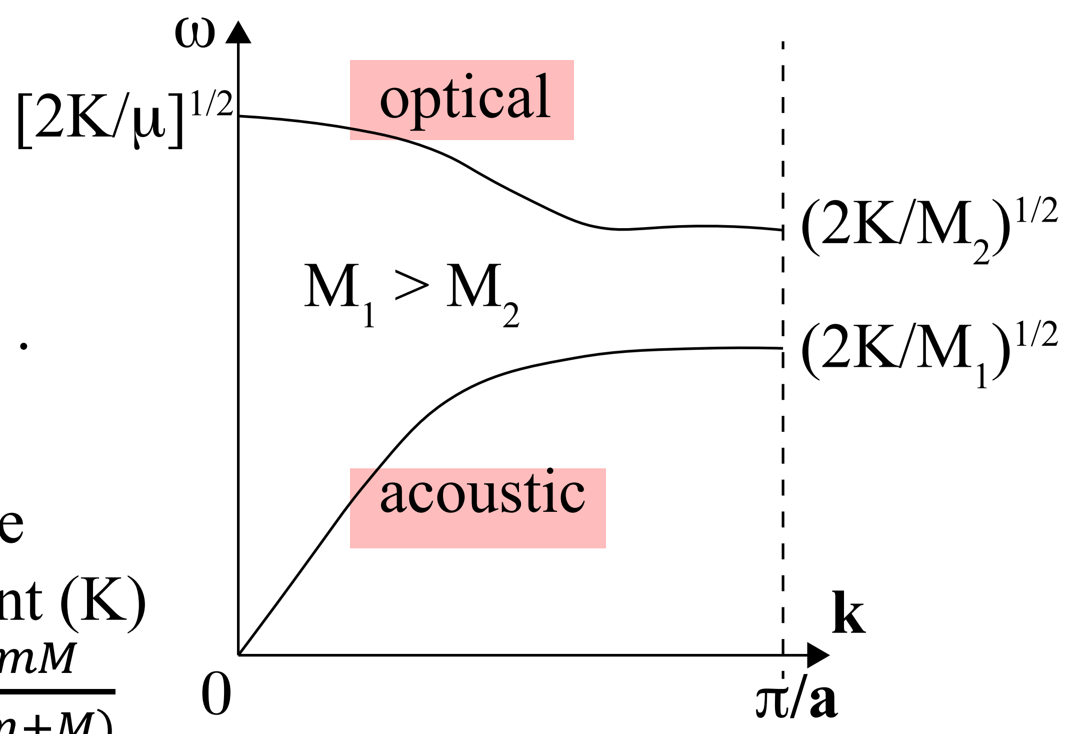
This dispersion relation admits 2 solutions for $\pm$ under outer root, an *optical* and an *acoustical* branch. Separation occurs for 1L and 2T.

Optical Dispersion: Mass Gap

For p atoms in the cell, there are $3p$ branches in the dispersion relation: $3p$-3 are optical branches.

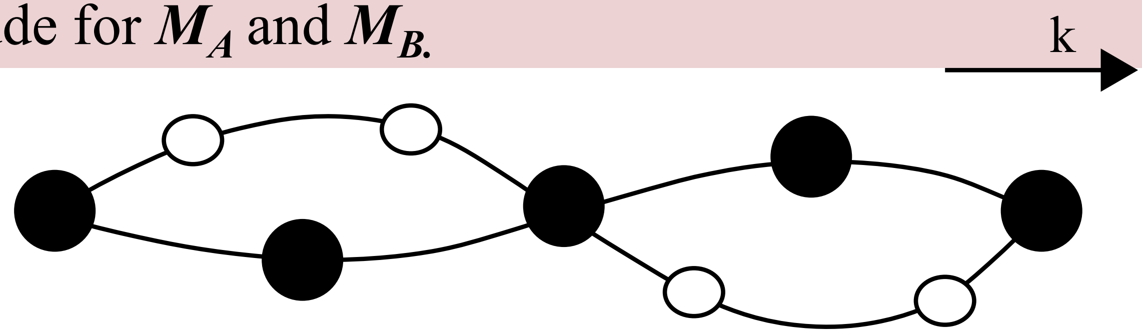
- Gap at zone edge is due to mass difference $\boldsymbol{M_A}$ and $\boldsymbol{M_B}$.

- ω of zone-center optical mode depends on the spring constant (K) and the reduced mass: $\mu = \frac{mM}{(m+M)}$

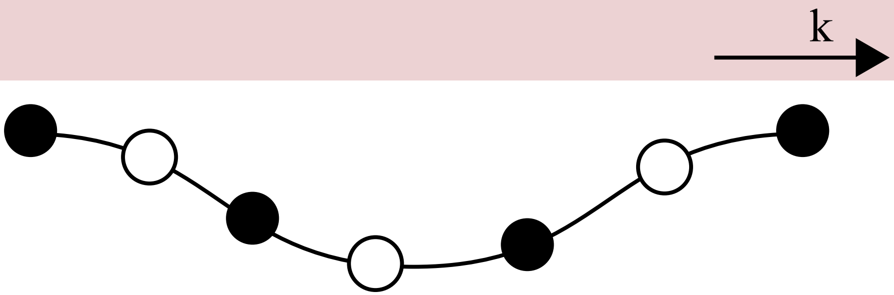


Acoustical and Optical: Atomic Motion

Optical modes: atoms move in different directions, and have different atomic displacement amplitude for M_A and M_B.

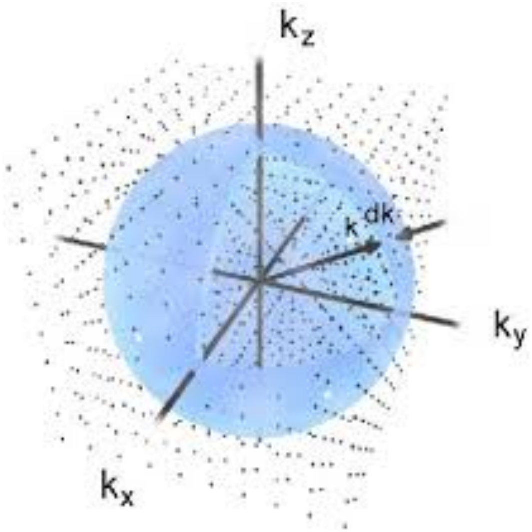


Acoustic modes: atoms move in the same direction, and same atomic displacement amplitudes.



Optical phonons are involved in the Raman scattering process and *acoustic phonons* in the Brillouin scattering.

Emergent thermal properties: Phonon Density of States



In general, allowed values of $\boldsymbol{k}=(k_x, k_y, k_z)$

$$k_i = \frac{n\pi}{L}, \ldots \frac{(n-1)\pi}{L}$$

n =unit cells

L = crystal size

In 3D, there is one allowed value of $\boldsymbol{k}$ in each $(\frac{2\pi}{L})^3$ volume of k-space:

$$\boxed{D(\omega) = \frac{1}{L^D}\frac{dN}{d\omega} = \frac{1}{V}\frac{dN}{dK}\frac{1}{d\,\omega/d\,K}}$$

3D Density of States:

$$N \sim \frac{\frac{4}{3}\pi K^3}{\left(\frac{2\pi}{L}\right)^3} = \frac{VK^3}{6\pi^2}$$

$$D(\omega) = \frac{K^2}{2\pi^2 v_g} = \frac{\omega^2}{2\pi^2 v_p^2 v_g}$$

Alternatively, phonon density of states is equivalent to the *<u>Fourier Transform of the Velocity Autocorrelation Function (i.e., FT{VACF}).</u>*

Emergent thermal properties: Heat Capacity and Thermal Conductivity

At 0 K, atoms are not vibrating and so *phonons* (*bosons*) do not exist.

The change in **internal energy** of the phonon system (δU) given arbitrary change in temperature (δT) depends on (δf_{BE}).

Heat Capacity

$$C(\omega) = \frac{\mathrm{dU}}{dT} \sum_{i}^{3} \int_{0}^{\omega max} \hbar\omega \frac{df_{BE}}{dT} D(\omega) d\omega$$

$$\frac{\hbar\omega}{k_B T} = x$$

Populated Bose-Einstein distribution function:

$$\frac{df_{BE}}{dT} = \frac{\exp[x]}{(\exp[x] - 1)^2}$$

Thermal Conductivity

$$\kappa = \frac{1}{3} C v \Lambda$$

Phonon mean free path:

$$\Lambda = v\tau$$

Emergent thermal properties: Einstein and Debye Heat Capacity

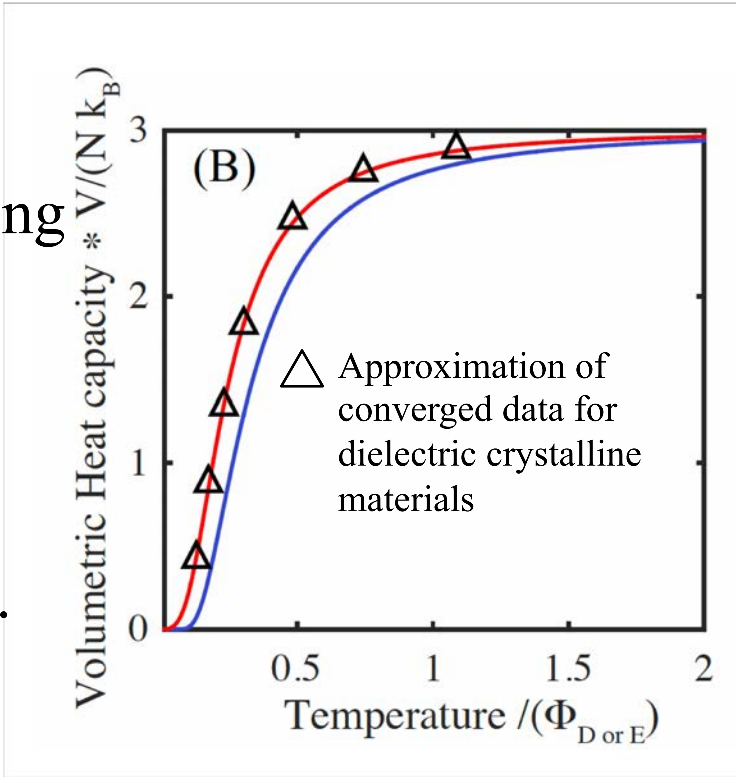
Dulong-Petit limit: $k_B T \to \hbar\omega_{MAX}, \qquad C \to 3R$

1 Einstein (1906): All atoms vibrate independently, with frequency ω_E – correlations between motions of neighboring atoms are ignored.

$$k_B T \to 0, \qquad C \to \exp(-\Theta_E/T)$$

2 Debye (1912): For the acoustic branch, $\omega \to 0$ *as* $k \to 0$, and Einstein model fails. That is, atoms in a crystal *do* interact with each other.

$$k_B T \to 0, \qquad C \to T^3 \ (Debye\ law)$$



Symmetry Breaking: Phonon Mode Softening in Ferroic Transitions

Symmetry Breaking:
Importance of Point Groups

During phase transitions, *the point group of the crystal changes.*

point group changes are extremely important to monitor:
they allow new macroscopic physical phenomena.

e.g.,

$\bar{3}m$ → 3m

Cannot support electric polarization

Can support electric polarization

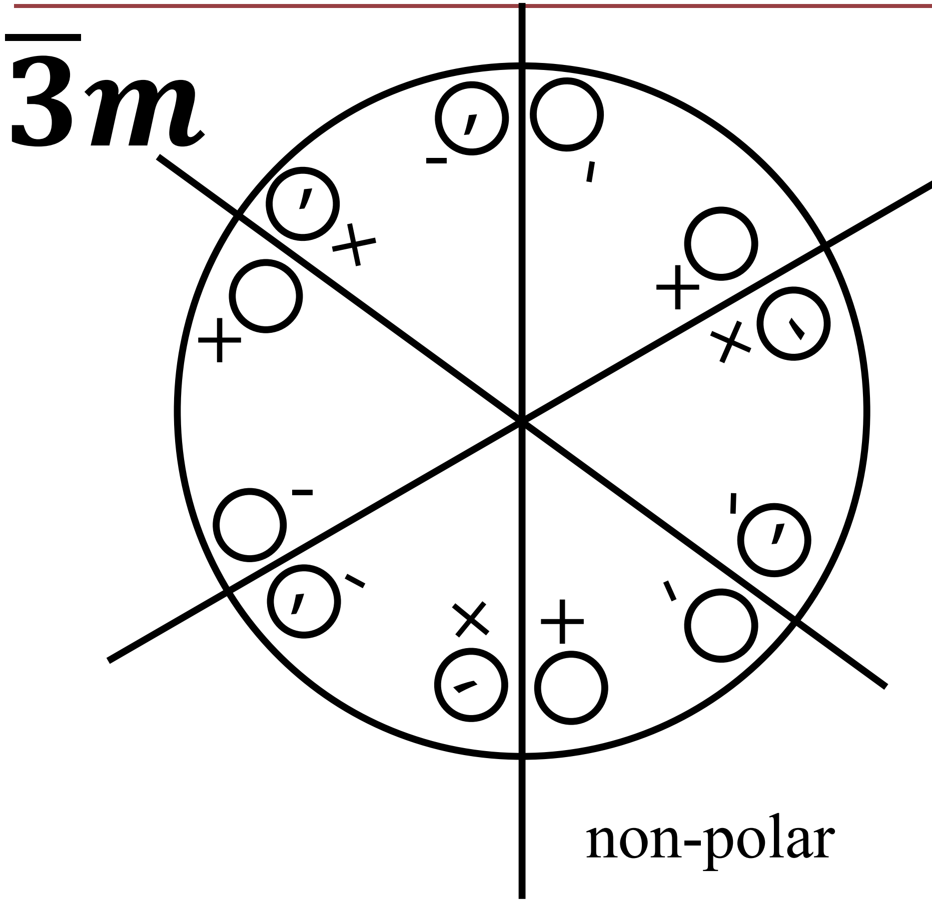
Curie Principle: "the symmetries of the causes are to be found in effects"

$G_{new} = G_{polar} \cap G_{crystal}$

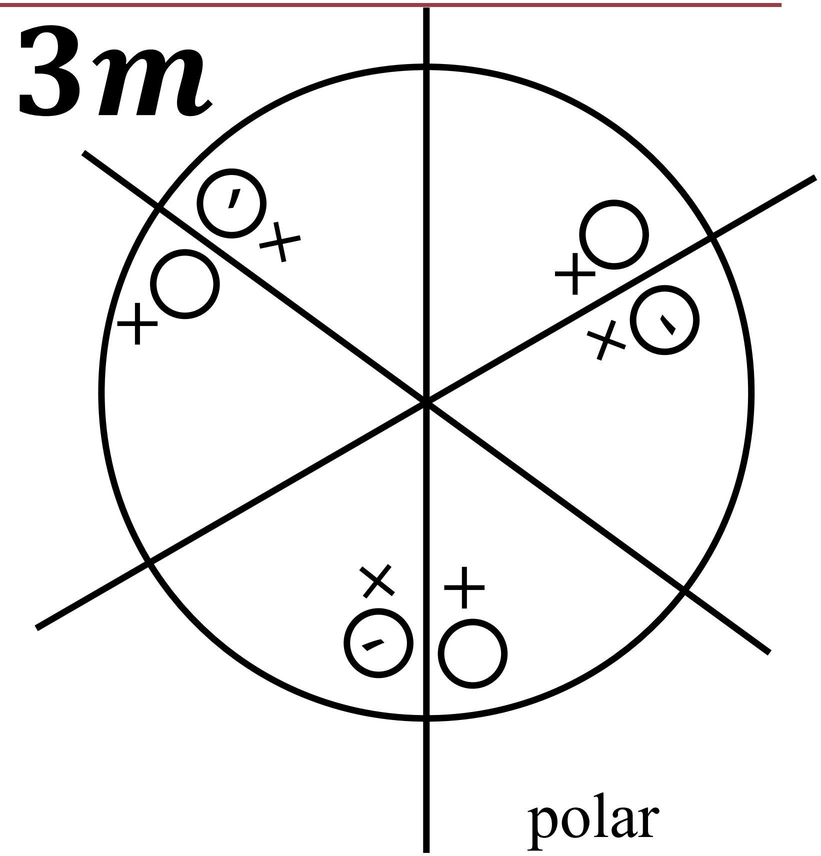
e.g.,

$3m = \infty m \cap \bar{3}m$

Neumann Principle: *"Symmetry elements of any physical property include the symmetry elements of the point group of the crystal."*



PARAELECTRIC



FERROELECTRIC

Ferroic Transitions: *Polarization*

New lower symmetry describes the crystal "below" the phase transition.

Measured as changes in free energy (ΔF) upon ordering: $\Delta F = \underbrace{-\eta H}_{\textbf{explicit}} + \overbrace{\frac{a}{2}\eta^2 + \frac{c}{3}\eta^3 + \frac{b}{4}\eta^4}^{\textbf{Landau expansion}} + o(\eta^5)$

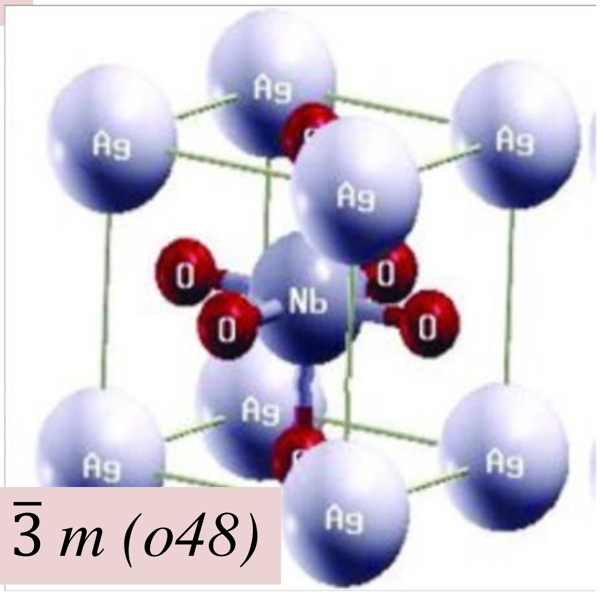
Ferromagnetic, *ferroelectric* and *ferroelastic* transitions can occur **spontaneously** or **explicitly,** and can be changed by applied fields (electric field , magnetic field, stress)

<u>*P* is polarization</u>
(e.g., electric, magnetization, strain): $P = -\frac{\partial F}{\partial H} = \eta$

Ferroelectric Phase Transitions: $AgNbO_3$ (Perovskites)

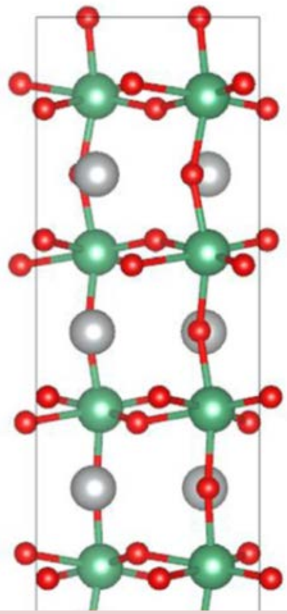
$T > T_C$

Paraelectric



Cubic: Pm $\bar{3}$ *m (o48)*

$T < T_C$



Ferroelectric

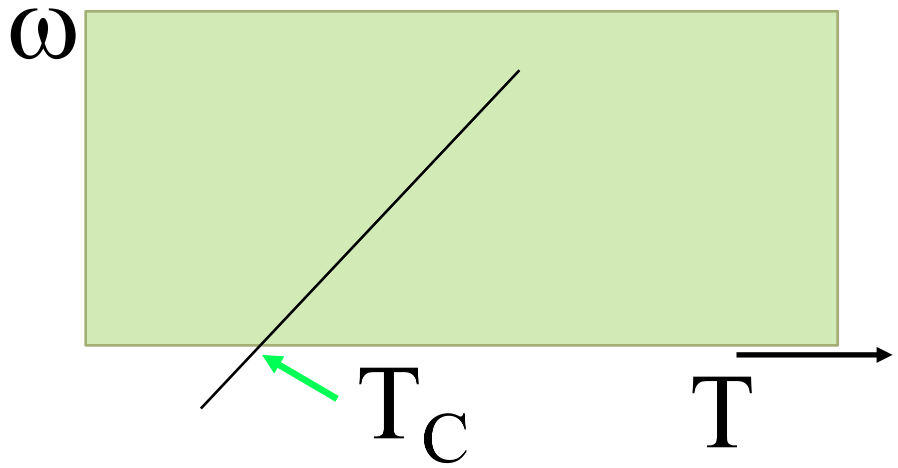
Orthorhombic: Pmc2_1 *(o4)*

Most displacive phase transitions are caused by *softening and "freezing" of particular phonon modes*.

Which *phonon modes* must "soften" (i.e., $\omega \rightarrow 0$) to give rise to the ferroelectric $AgNbO_3$ transition?

Lattice instability and Soft Modes in Displacive Transitions

During displacive ferroic transitions, specific phonon modes have a temperature dependence of their frequency on temperature:



The result is a softening of the phonon dispersion, i.e., a *softening* of velocity ($v_g = \left(\frac{\partial \omega}{\partial k}\right)$) in specific crystallographic directions.

These softened modes enable lowering of symmetry at phase transition.

Ferroelectric Phase Transitions: Optical Phonon Mode Softening

That is, as the free energy develops a set of minima, what happens to the phonon modes?

1. Replace the internal energy (U) with the Landau free energy, polarization (P) is the order parameter:

$$\mathcal{F} = \frac{\alpha(T)}{2} P^2$$

2. Polarization (P) is clearly related to the displacement of the optical amplitude (u_{opt}). For rigid charge ions $+Ze$:

$$\mathrm{P} = Zeu_{opt}/\mathrm{V}$$

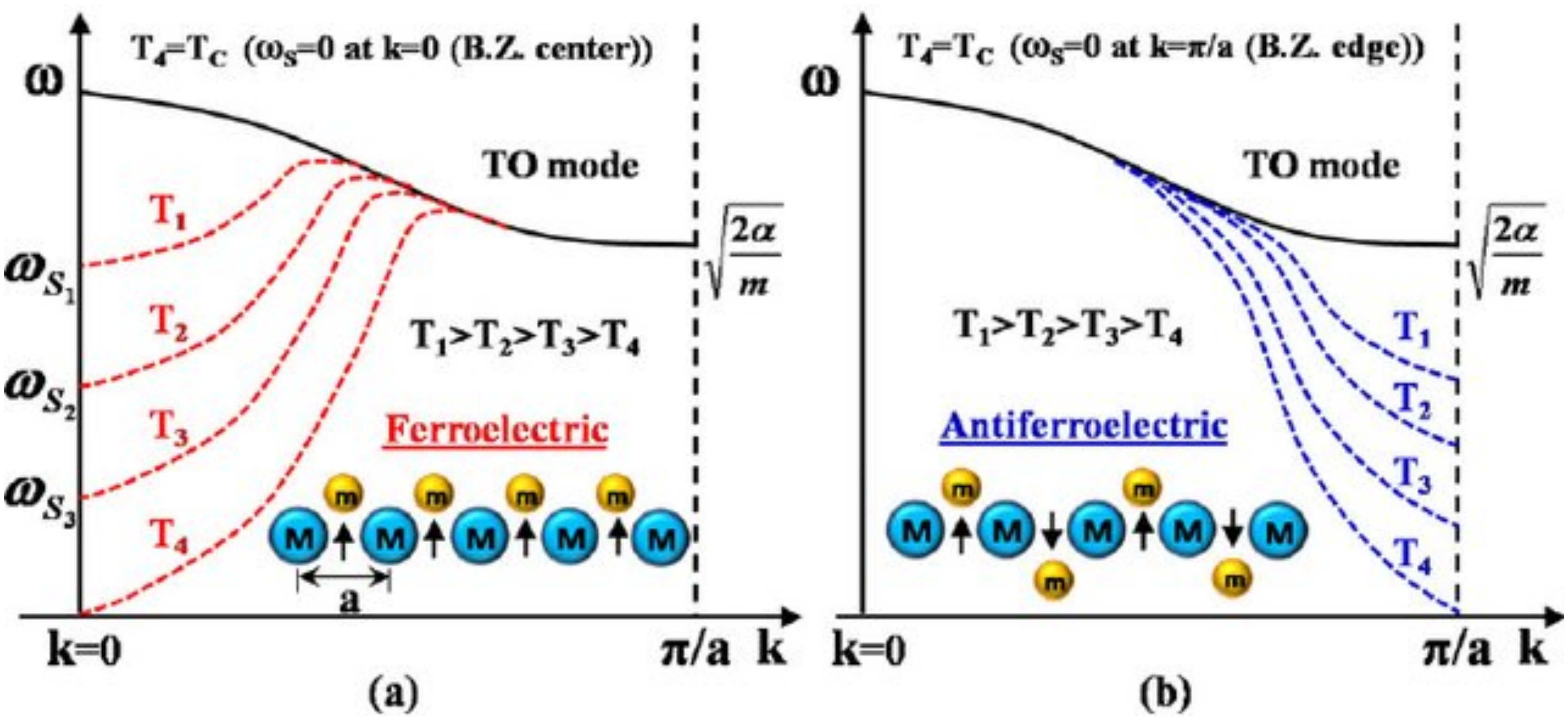
The relevant optical phonon displacement amplitude is:

$$u_{opt} = u_A - u_B$$

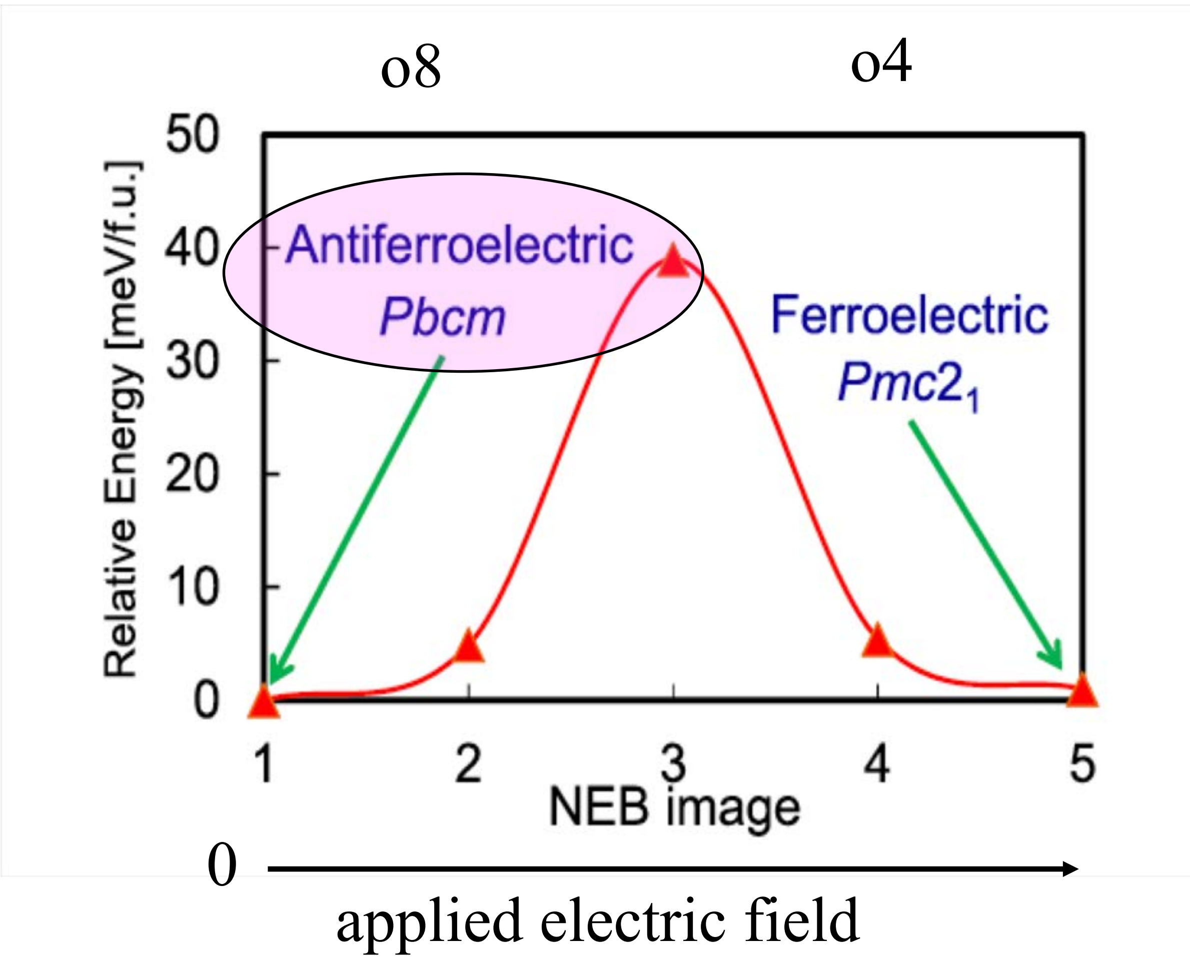
3. $\alpha(T) = a(T - T_C)$ is like the stiffness constant (K). $K \sim \omega_O$ goes to zero at the zone-center ($q \rightarrow 0$) as $T \rightarrow T_C$.

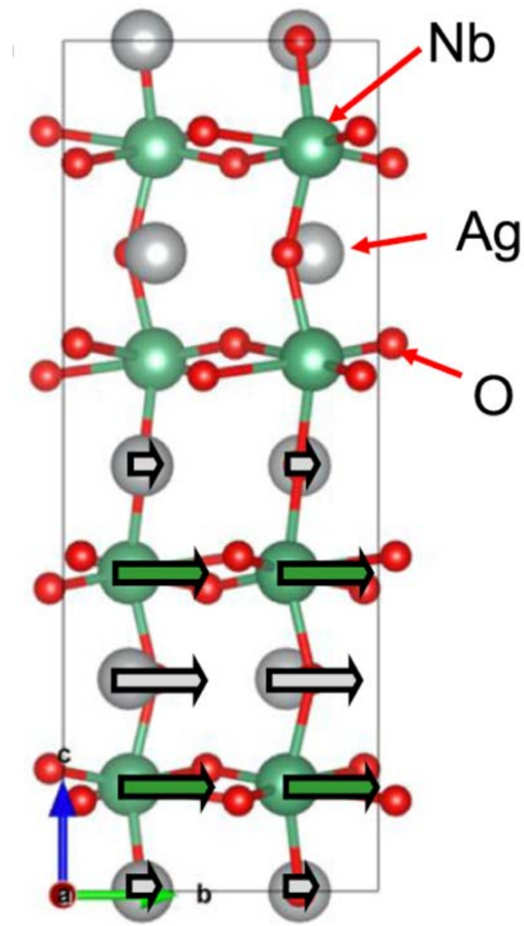
Ferroelectric Phase Transitions: Optical Phonon Mode Softening

- **Ferroelectric:** Zone-center ($q = 0$) optical phonon mode vanishes
- **Antiferroeelctric:** Zone-edge ($q = \pi/a$) optical phonon mode vanishes



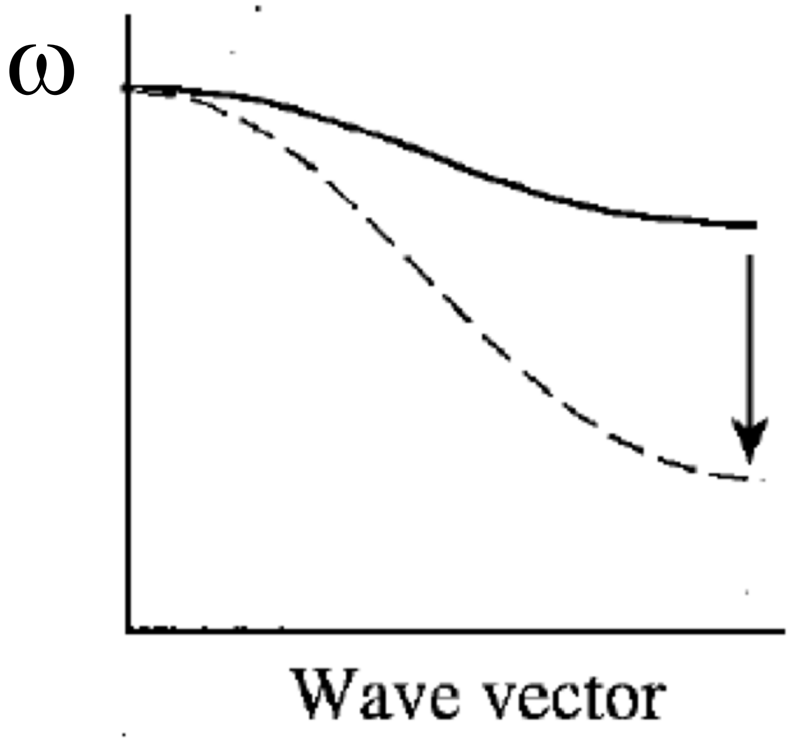
AntiFerroelectric Phase Transitions: Zone-Boundary Optical Mode Softening



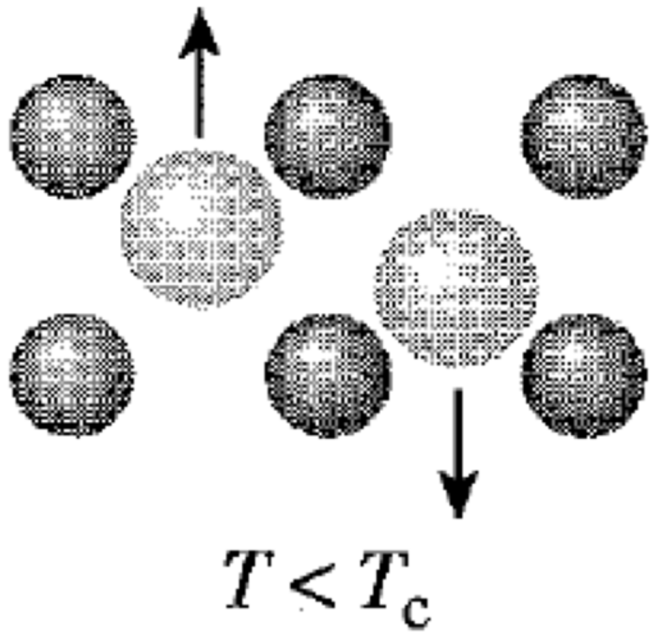


J. Appl. Phys. 119, 064102 (2016)

AntiFerroelectric Phase Transitions: Zone-Boundary Optical Mode Softening



There is a doubling of the unit cell.



Role of phonon softening in phase transitions may be obtained using first principles DFT calculations: (1) Zone-center polar ferroelectric mode & (2) Zone-boundary non-polar antiferro-distortive modes.

Ferroelastic Phase Transitions:
Acoustic Phonon Mode Softening

In *ferroelastic transitions*, strain is the order parameter:

$$\frac{\partial e_{ij}}{\partial \sigma_{kl}} = s_{ijkl} = \frac{1}{c_{ijkl}}$$

s: *compliance*
c: stiffness

At ferroelastic transitions, the stiffness goes to zero

$$\frac{1}{s} = c \to 0 \quad \text{as} \quad T \to T_C$$

The speed of sound is influenced by two properties of matter: the elastic constants (C_{ij}) and density (ρ).

$$v_g = \sqrt{\frac{C_{ij}}{\rho}}$$

Ferroelastic Phase Transitions:

Phase transition occurs and the ferroelasticity is displayed.

Orthorhombic (Pbnm) ⟶ Monoclinic ($P2_1/n$)

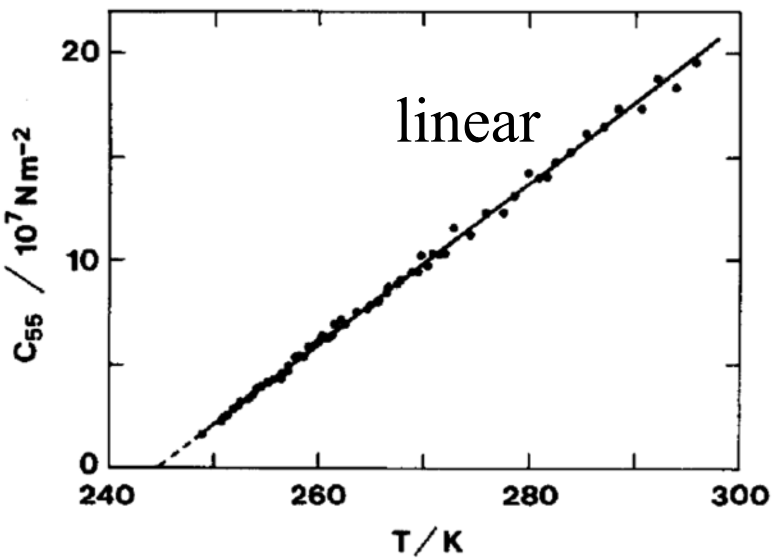
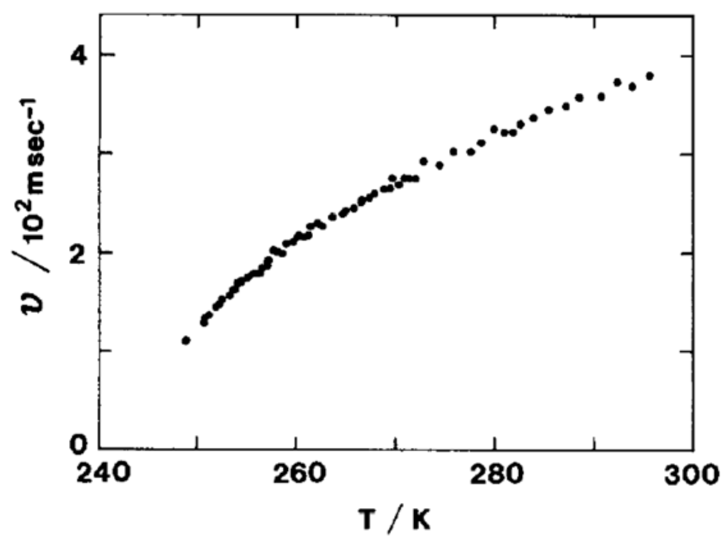


Fig. 2. Temperature dependence of the elastic constant C_{55}. The solid line represents the least-square fit by equation (6).



Transverse wave propagating with along the orthorhombic direction [001] with polarization along the orthorhombic [100] direction (v_{zx}).

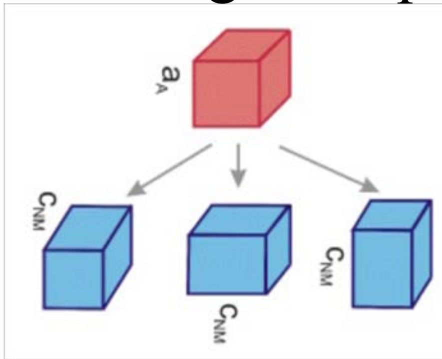
Nakayama, Ishii, Sawada, "Softening of acoustic phonon in the phase transition of the phenothiazine crystal," Solid State Comm., v67n2, 1988.

Ferroelastic Phase Transitions: Martensitic transitions (A15 Nb_3Sn, V_3Si)

Martensitic transitions (volume-conserving) are associated with spontaneous homogeneous strain -- and are accompanied by a so-called shuffle that results in a *softening of the shear modulus*, (C_{11}-C_{12}).

Such an effect is observed in single crystals of A15 V_3Si and Nb_3Sn as T→ T_C.

(Cubic to tetragonal upon cooling)



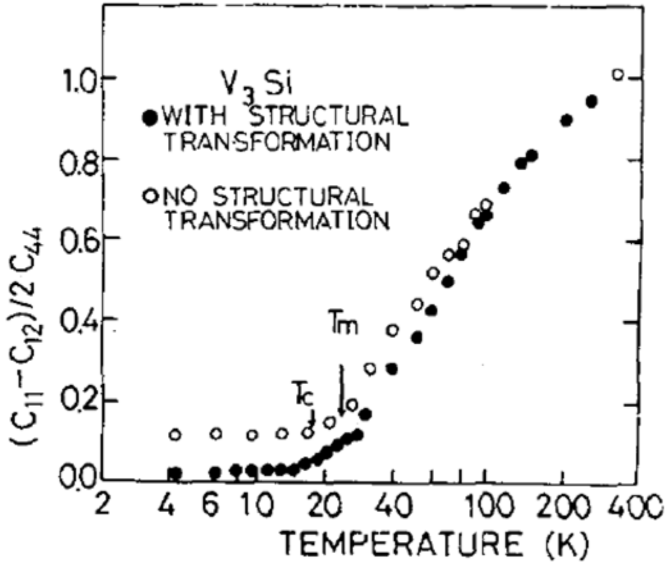


Fig. 8 Temperature dependence of $(C_{11}-C_{12})/2C_{44}$ for a single crystal V_3Si (19).

N. Nakanishi, A. Nagasawa, Y. Murakami. LATTICE STABILITY AND SOFT MODES. J. Physique Colloques, 1982.

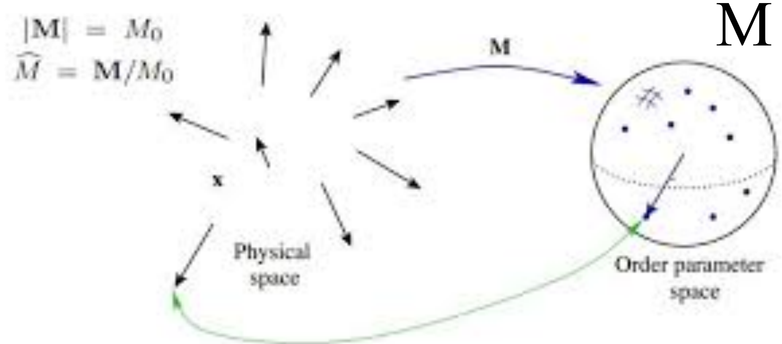
The end!

Extra slides

Ferromagnetic Phase Transitions: Magnon Mode Softening

Magnons in magnetically ordered systems are like
phonons of lattice of nuclei.

$M = S^2$

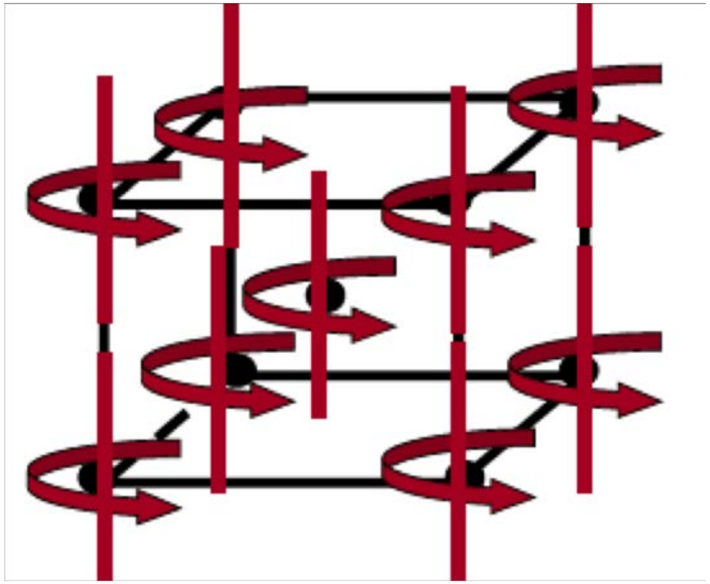


Ferromagnetic Phase Transitions:

Curie Principle: "the symmetries of the causes are to be found in effects" $G_{new} = G_{axial} \cap G_{spin-lattice}$

$$\text{e.g., } 4/m = \frac{\infty}{m} \cap m\bar{3}m$$

$$M = -\frac{\partial F}{\partial H} = \eta$$



What needs to happen to the magnon modes in order to allow for the ferromagnetic phase transition?

Ferromagnetic Phase Transitions: Magnon Mode Softening

Consider the *antiferromagnet*: $ErFeO_3$ (Rare-Earth Orthoferrites)

Softening of the magnon spectrum at the zone-edge, when crossing the acoustic branches. This suggests an interaction with the lattice modes.

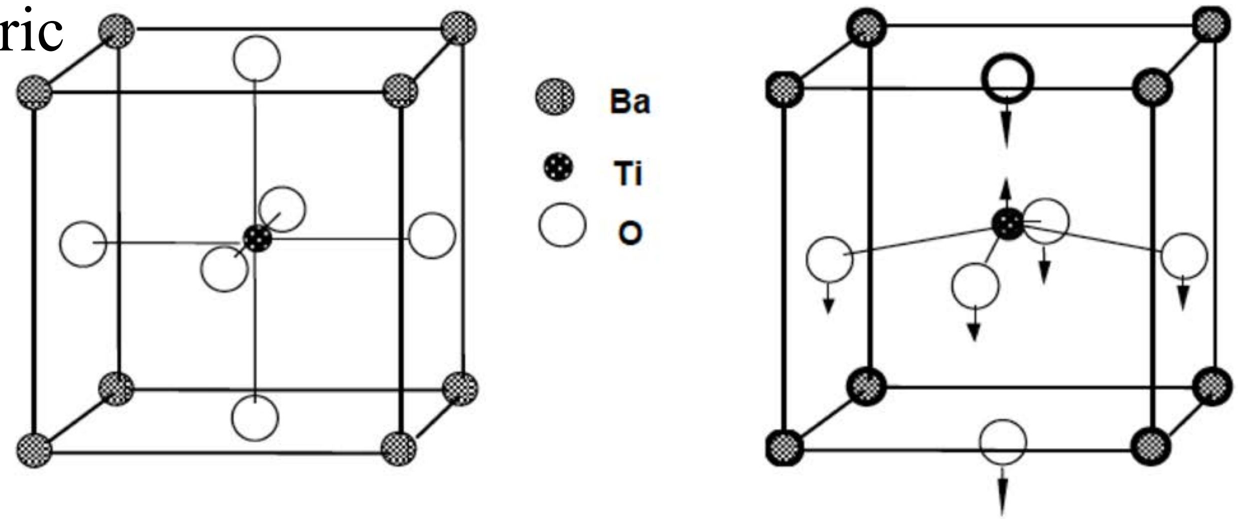
Ferroelectric Phase Transitions: $BaTiO_3$ (Perovskites)

$T > T_C$

$T < T_C$

Paraelectric

Ferroelectric



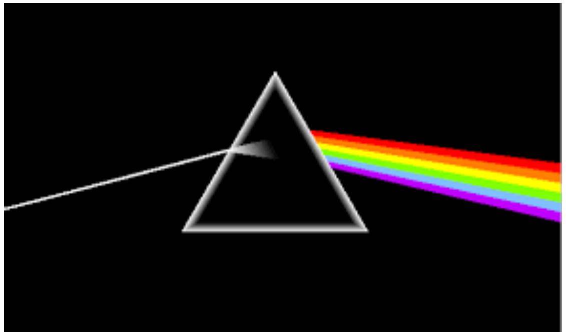
Cubic: Pm3m (o48)

Tetragonal: P4mm (o8)

Most displacive phase transitions have a dynamical character, and are caused by *softening and "freezing" of particular phonon modes*.

Phonon dispersion:
Dispersion of Light in Media

(*light*): Propagation of light has a dispersion in medium



- Dispersion (in medium): $v_g = \left(\frac{\partial k}{\partial \omega}\right)^{-1} = \frac{c}{n_g(\omega)}$

$n_g(\omega) = n(\omega) + \omega \frac{\partial n}{\partial \omega}$ is the group refractive index
$n(\omega)$ is the refractive index