UES022
Thermal properties of solids

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Basics of Solid-State Physics

Introduction to Solids: Structure and bonding in solids: Overview of crystal lattices and their role in defining material properties. Classification of solids into metals, semiconductors, and insulators based on bonding and electron behavior.

Electronic Properties of Materials: Band theory explaining conduction, valence bands, and energy gaps in different material types. Detailed examination of Fermi level, density of states, and their implications for electronic behavior.

Phonons and Thermal Properties: The role of lattice vibrations (phonons) in thermal and electronic properties. Concepts like specific heat and thermal conductivity in relation to material structure and temperature.

Introduction to Solid state Physics, Charles Kittel: Ch 5
Elementary Solid State Physics, M. A. Omar: Ch 3

Thermal Properties of Solids

Molar Specific Heat: the amount of energy required to produce a unit temperature rise in 1 mole of material while maintaining a constant volume

$$C_v = \frac{dE}{dT}, \text{dE is the energy required to raise the temperature by dT}$$

- What is the physical meaning of C_v?

- Is C_v constant for all temperatures?

As heat energy flows into the solid: Vibrational energy of the atoms in the solid increases.

Classical Theory

- Atom is bound at its site by harmonic force

- As the solid is heated,
  atoms vibrate around their sites like harmonic oscillators
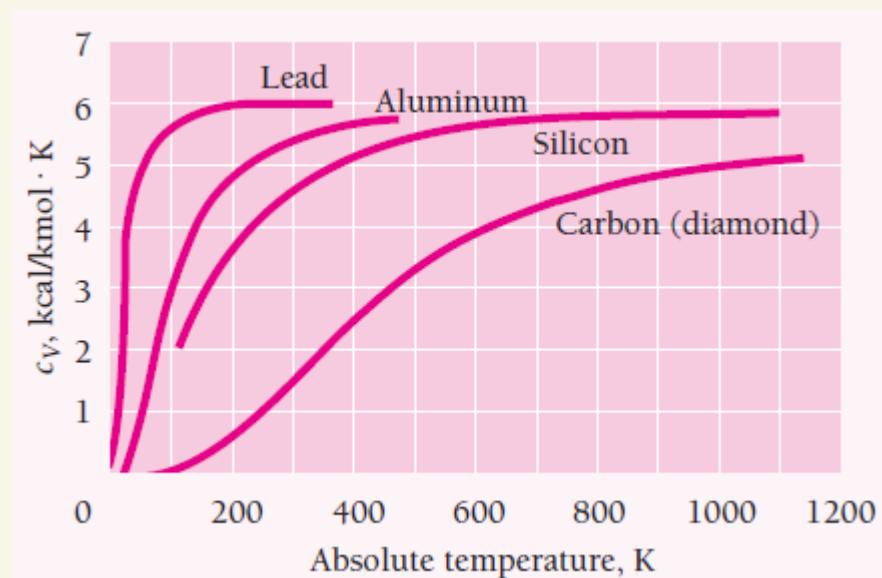
    Average energy of 1-D oscillator = $k_B T$

    Average energy per atom (3-D oscillator) = $3k_B T$
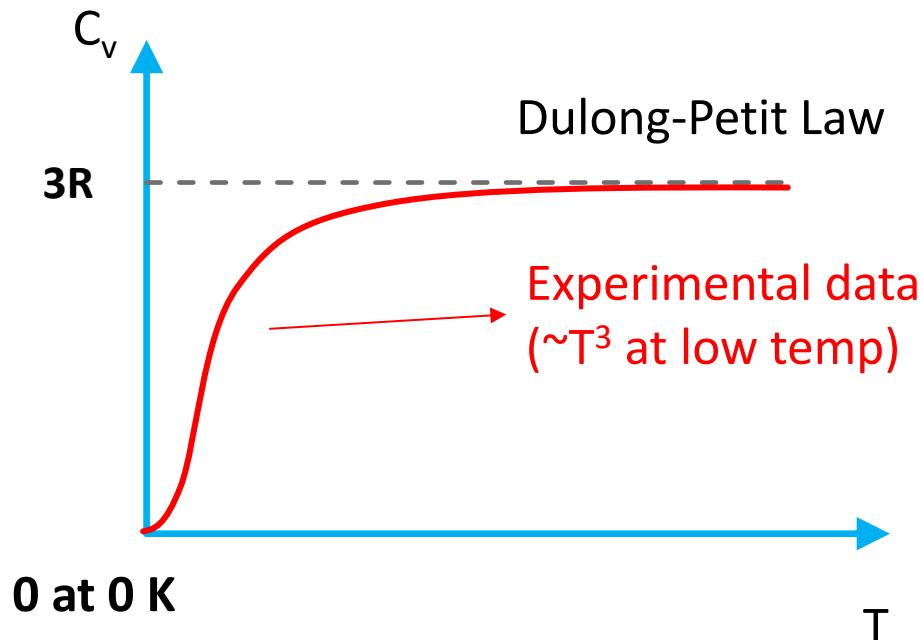
    Energy per mole: $E = 3N_A k_B T = 3RT$

    Molar Specific Heat = 3R

    → *Dulong-Petit Law*

Thermal Properties of Solids

C_v

3R ----------------------------------

Dulong-Petit Law

Experimental data
(~T^3 at low temp)

0 at 0 K

T

- Dulong-Petit law is valid for high temperatures.
- **Classical theory fails at low temp.**

Einstein Theory
- Oscillators (atoms) are independent oscillators
- **C_v decreased with Temp, but not as T^3**

In a solid the atoms cannot vibrate independently of each other.

The vibration of each atom is coupled to neighbours (because of bonds).

Debye Model

→ Vibrations are coordinated: *Collective modes of lattice vibrations* **(Each mode has energy $k_B T$)**

→ Travelling lattice waves are produced

Solid/crystal vibrations are in long-wave length limit (λ_{min} >> *a* (inter atomic distance))

→ Solid can be treated as a continuous medium

→ Sound waves / Elastic waves propagating through the solid

Debye Theory of Molar Specific Heat

q: Wave vector of the wave, ***each wave vector has 3 modes*** (1 longitudinal and 2 transverse)

Dispersion relation, $\omega = v_s\, q,\quad q = 2\pi / \lambda$

v_s: velocity of propagating wave = velocity of sound in solid

Highest frequency is determined from the lower limit on the wavelength/continuum nature of the solid:

ω_D = **Debye Frequency**

$\quad = v_s\, (6\pi^2 N_d)^{1/3}$
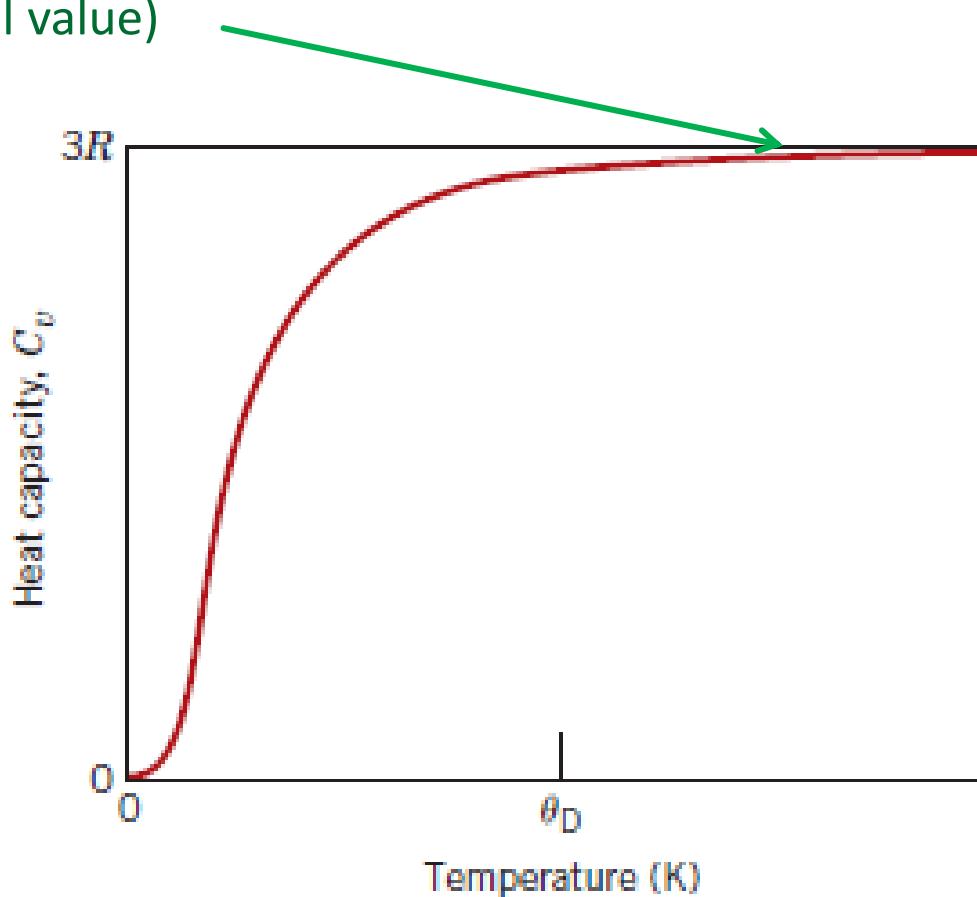
N_d: Number density
$\quad \equiv$ No. of atoms/Volume
$\quad = (\text{density} \bullet N_A)/ \text{Atomic mass}$
$\quad \sim 10^{28}/m^3$ (for solids)

N_A: Avogadro's Number = 6.023×10^{23}/mole

Debye Theory of Molar Specific Heat

- At any given temperature in a solid multiple modes of oscillations with different ω (ranging up to $ω_D$) are excited.

- Each mode is an independent harmonic oscillator. *(Modes are independent, but atoms interact)*

- At high temp, every mode of oscillation is completely excited and has energy = k_BT

  - E = 3RT

 - C_v = 3R (Matches the classical value)

  High Temp: T > $θ_D$
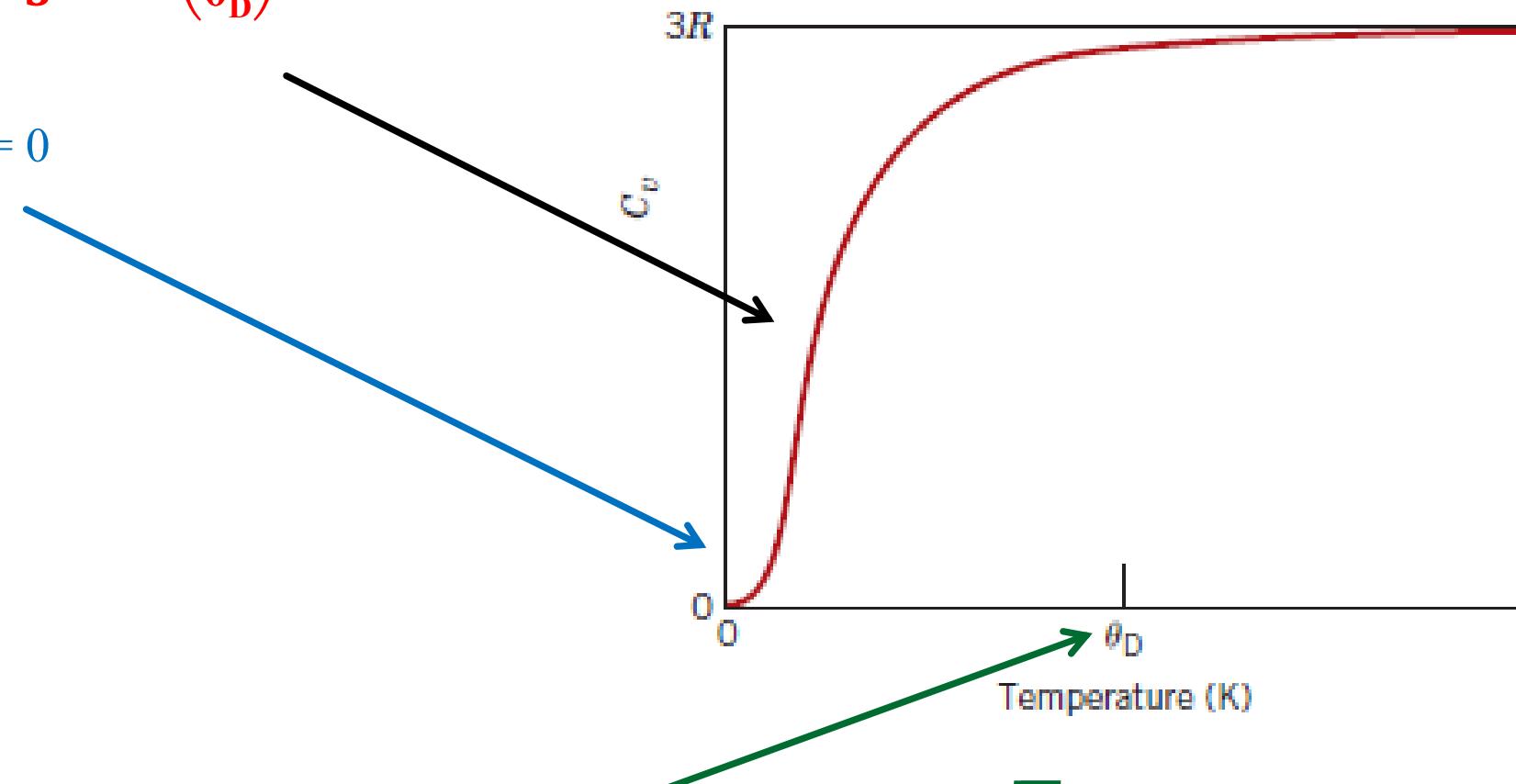
Debye Theory of Molar Specific Heat

Low Temp $T << \theta_D$:

$$C_v = \frac{12}{5}\pi^2 R \left(\frac{T}{\theta_D}\right)^3$$

At $T = 0$ K : $C_v = 0$

θ_D : Debye Temperature $\sim \sqrt{\dfrac{Y}{M}}$; M: Atomic mass

Origin: $k_B \theta_D = \hbar \omega_D$

Phonons

- **Debye considered a solid as a continuous elastic body.**
    - Internal energy of the solid resides in elastic standing waves instead of the vibrations of individual atoms.
    - The elastic waves in a solid are of two kinds, longitudinal and transverse, and range in frequency from 0 to a maximum v_m. (The interatomic spacing in a solid sets a lower limit to the possible wavelengths and hence an upper limit to the frequencies.)

- These waves, like EM waves, have energies quantized in units of h (Energy = $\hbar\omega$) .
- A quantum of acoustic energy in a solid is called a **phonon**, and it travels with the speed of sound since sound waves are elastic in nature.
- Elastic wave = Stream of phonons: these phonons carry the energy and momentum of the wave
- Average number of phonons in a mode, $\bar{n} = \dfrac{1}{e^{\frac{\hbar\omega}{kT}}-1}$

    At T= 0 K, $\bar{n}$ = 0.

    As T increases, $\bar{n}$ increases. At High Temp, $\bar{n} \cong \dfrac{kT}{\hbar\omega}$

Phonons are created by simply raising the temperature, the number is not conserved

Specific Heat: Metals

Atoms are present in all solids →Debye model is true for all materials → Phononic contribution.

If there are more energy adsorption processes/mechanisms present in a solid → Adds to Specific heat.

Metals also have conduction electrons:

$$C_{metal} = C_e + C_{ph}$$

contributed by only a small fraction of electrons
(lie within ~ $k_B T$ of E_f)

value will be small, and becomes important only at low temperature (~ 0-20 K, At these low temperatures, the phononic modes excited are very less)

At higher temperatures Debye Model will work even for metal.

$$C_e = \frac{\pi^2}{2} n k_B \left(\frac{T}{T_F}\right)$$

n = electron density, TF = Fermi Temp = E_F/kB

Thermal Conductivity of Solids

Thermal conduction is the phenomenon by which heat is transported from high to low temperature regions of a substance.

Thermal Conductivity is a measure of the ability of a material to transfer heat.

Power transferred per unit area

$$\frac{\Delta Q}{\Delta t \, A} = -\boldsymbol{\kappa} \frac{dT}{dx}$$

thermal conductivity   temperature gradient

- Unit of $\boldsymbol{\kappa}$: W/m-K
- Minus sign indicates that the direction of heat flow is from hot to cold, or down the temperature gradient.

Thermal Conductivity

Possible Conduction Processes:

- Lattice Vibrations/ Lattice waves/Phonons (All solids)
- Free electrons (Metals)

$$\kappa_{metal} = \kappa_e + \kappa_{ph}$$

thermal energy transport by conduction electrons.

- phonons transport thermal energy in the direction of their motion.
- There is net movement of phonons from high temp to low temperature (*on high temp side there will be more phonons*)

For metals

$\kappa_e \gg \kappa_{ph}$: electrons have higher efficiency for conducting thermal energy than phonons:

  i) electrons are less easily scattered,

  ii) have higher velocities,

  iii) electron density, n is very large.

Thermal Conductivity of metals

In metals, electron contribution dominates thermal conductivity.

$$\kappa_{\textbf{metal}} \approx \kappa_e = \frac{\pi^2 n\, T\, k_B^2\, \tau}{3m}$$

When we make alloys:
Impurities $\uparrow$: Scatterings $\uparrow$: $\kappa_e \downarrow$

Electrical Conductivity of a metal,

$$\sigma = \frac{ne^2\tau}{m}$$

Lorenz Number = 2.44×10^{-8} Ω W/K^2

$$\frac{\text{Thermal Conductivity}}{\text{Electrical conductivity}} = \frac{K}{\sigma} = \frac{\pi^2\, k_B^2}{3\, e^2} T = L\, T$$

Wiedemann-Franz Law

Thermal Conductivity of poor conductors

If no free electrons are available,

$$\kappa = \kappa_{ph}$$

$$\kappa = \frac{1}{3}{C'}_v\, v\, l$$

C_v' = Specific heat per unit volume

v = velocity

l = mean free path

Mean free path: distance travelled between scatterings

Phonon scattering Interactions:
- Phonon-Phonon
- Phonon-Imperfection (scattering of phonons from a defect)
- Phonon-Boundary (scattering of phonons from surface)

$$\frac{1}{l} = \frac{1}{l_p} + \frac{1}{l_i} + \frac{1}{l_b}$$

Mean free path

Phonon scattering Interactions:

- Phonon-Phonon
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$$\frac{1}{l} = \frac{1}{l_p} + \frac{1}{l_i} + \frac{1}{l_b}$$

Phonon-Boundary scattering

- temperature independent
- Limited by dimension of the solid

Phonon-Imperfection scattering

- temperature dependent.

- Strength of scattering $\propto \dfrac{\text{diameter of the scattering center}}{\text{Wavelength of the entity scattered}}$

- As the temperature decreases,
  - only phonons with small **q** (large wavelength) are excited $\rightarrow$ strength of scattering is decreased.

At low temperatures phonon-boundary scattering will dominate.

Phonon-phonon scatterings
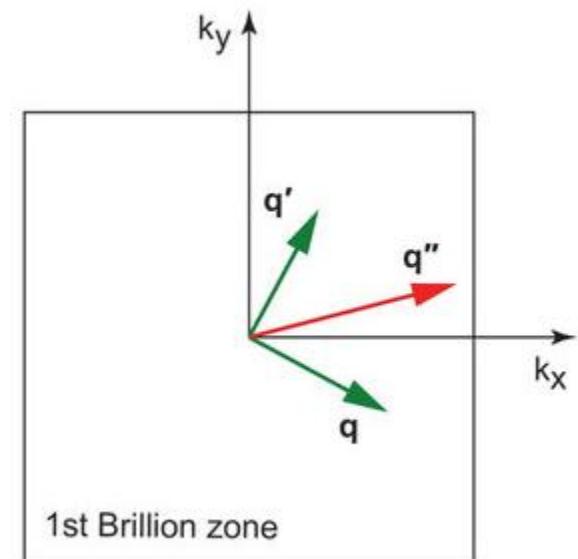
A phonon alters the local atomic spacing, so that another phonon sees a difference in the crystal structure and is scattered by it.

Lattice has a periodicity of: **a**

So momentum space will be periodic in: $\frac{2\pi}{a}$

E(q) = E(q + $\frac{2\pi}{a}$), q = wave vector for a phonon

Consider the first Brillouin Zone (phonons in $\frac{-\pi}{a}$ to $\frac{\pi}{a}$)

1st Brillion zone

Energy is conserved: $\hbar\omega + \hbar\omega' = \hbar\omega''$

Momentum is conserved: q + q' = q''
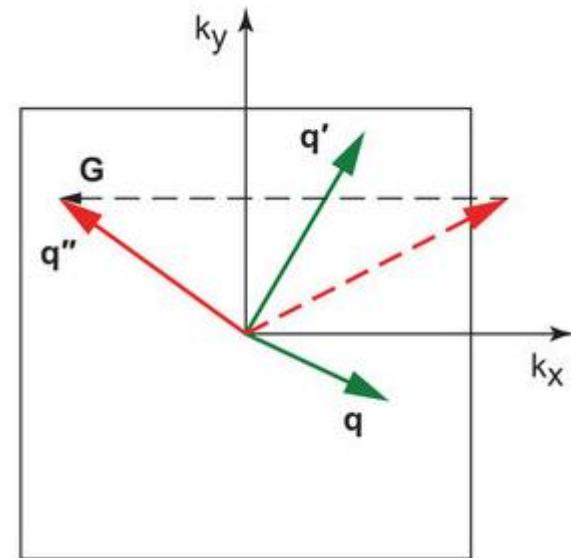
The initial and final directions of the phonons are the same

- No randomization
- will not contribute to resistivity

Normal Process/Scattering – does not contribute to thermal conductivity

Umklapp scattering process

If the two initial wavevectors add to a new wavevector, which is outside the Brillouin zone, they give a new wave with a group velocity in the opposite direction.

$q'' = q + q' - G$

Usually, a reciprocal lattice vector G is subtracted , to get back into the Brillouin zone

$$G = \frac{2\pi}{a}$$
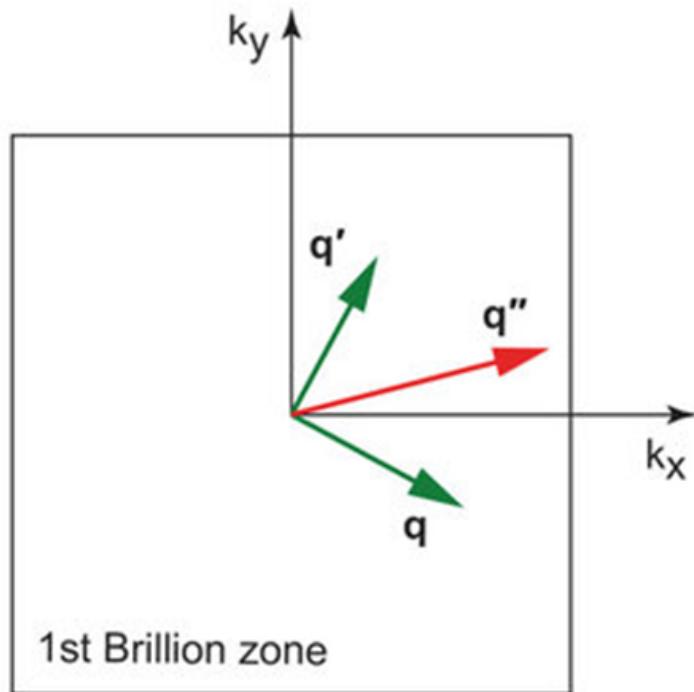
Such a process is called an Umklapp process (German: flip-over) or U-process.

Processes in which G = 0 are called N-processes.
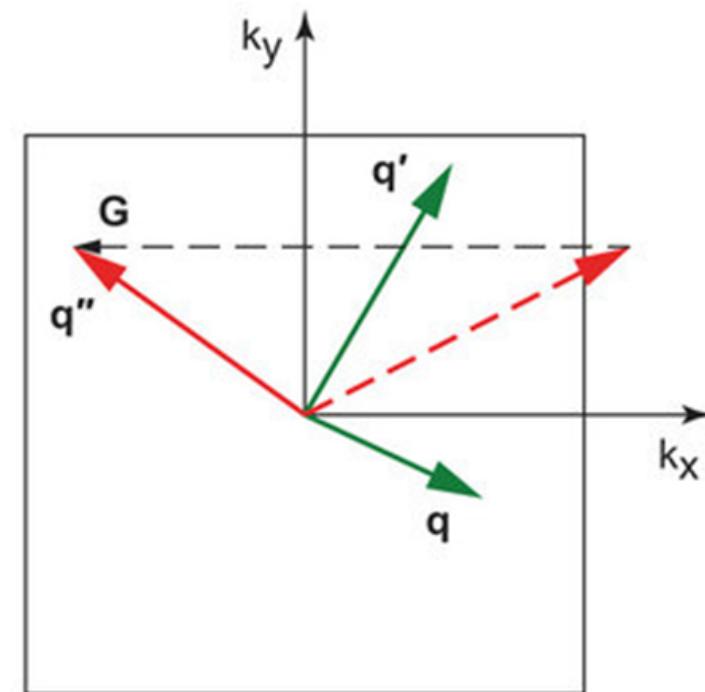
Note that for a U-process at least one of the phonons must have $|q| > \pi/(2a)$ – so very rare at low T.

In U-process, energy is conserved, but momentum is not.

Phonon-phonon scattering process
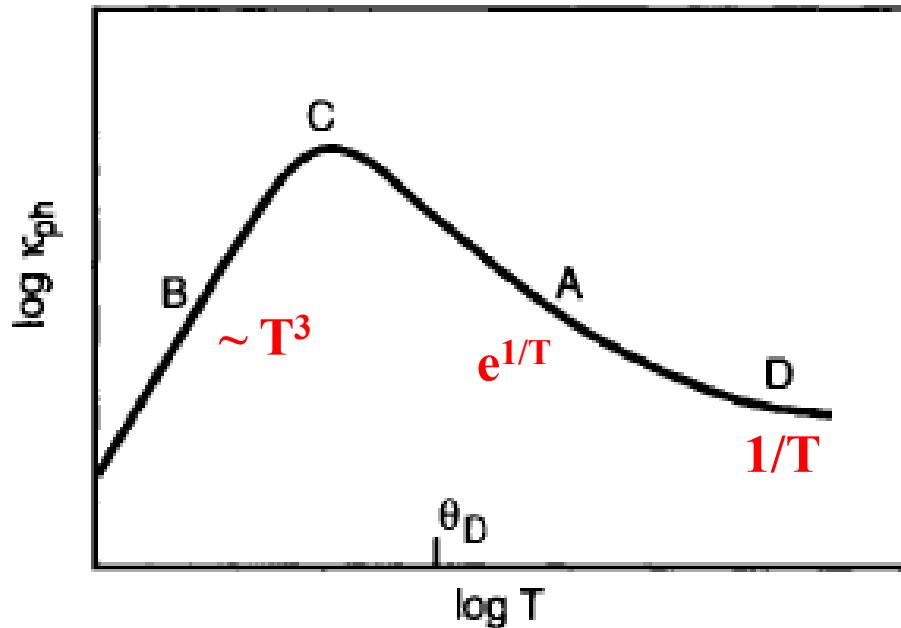
Normal process
(N-process)
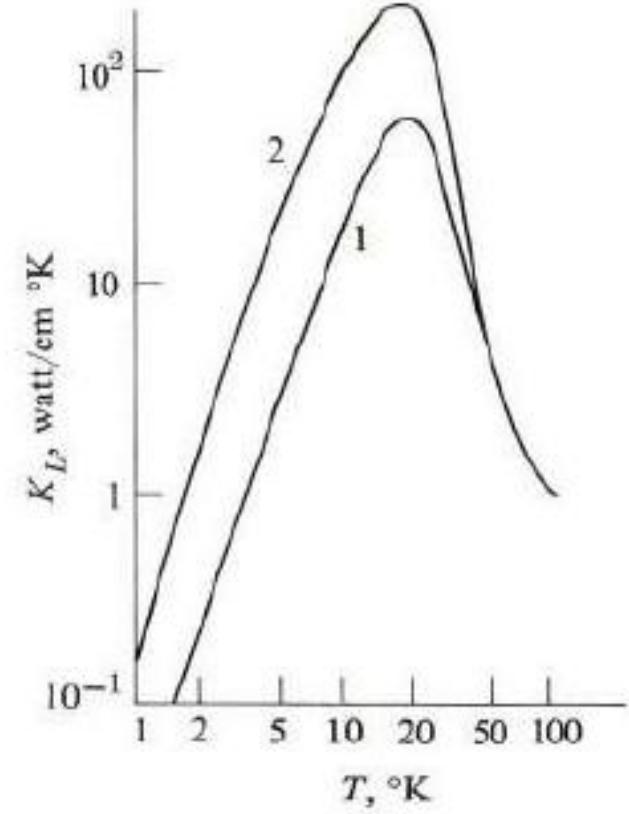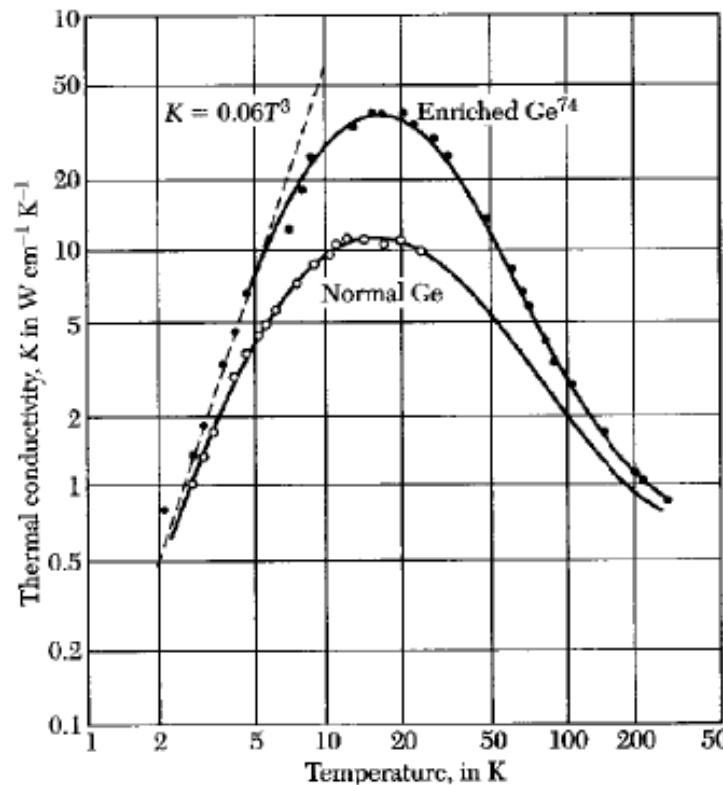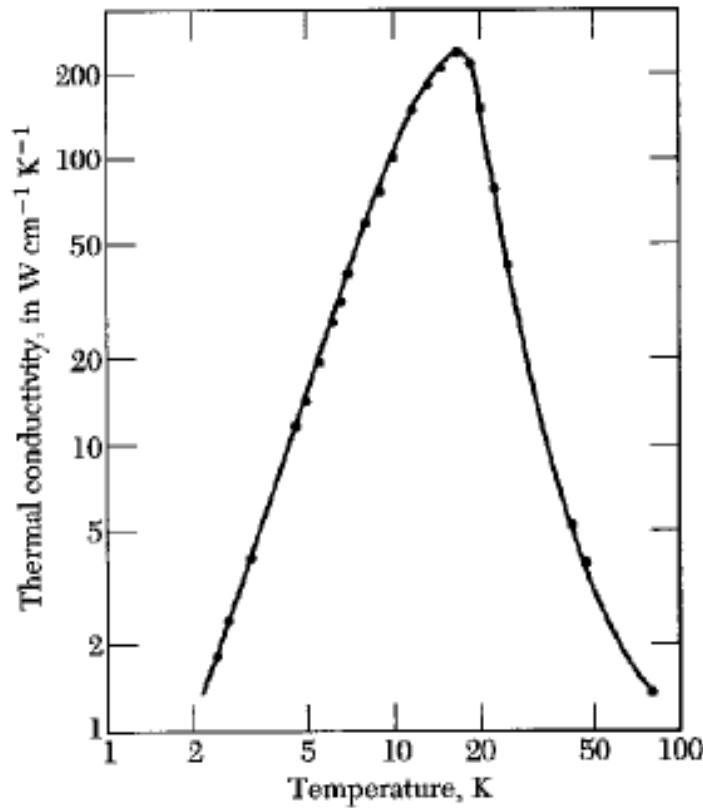
Umklapp process
(U-process)

Thermal Conductivity – mean free path

- At high temperature most phonon-phonon scatterings will be U-process.

    $\kappa \propto 1/T$

- As temperature decreases the phonon-phonon scatterings will become more and more N-process and finally become completely N-process at very low temperatures.

    $\kappa \propto e^{1/T}$

- At very low temperatures boundary scatterings become constant and $l \sim L$

    $\kappa \propto C'_v \propto T^3$

Enriched Sample has less impurity,
and hence less phonon-impurity scattering.
Same cross-sectional area so graphs meet at low
temperatures

Sample 2 has higher Cross-
sectional Area