

Solid State Physics Phys(471)







Having studied the dispersion relation of phonons in solids, we now turn to main properties of solids that arise from those collective lattice vibrations . In specific, we will discuss;

1- Heat Capacity

#### 2- Thermal conductivity

#### HEAT CAPACITY OF LATTICE



General definition of **heat capacity** is; **the amount of heat** required to change one mole of body's temperature by a given amount

$$C = \frac{\Delta Q}{\Delta T}$$



Where  $\triangle Q$  is the heat required to increase the temperature of one mole by  $\triangle T$ .

At constant volume all internal energy E converts to heat, i.e.  $\Delta Q = \Delta E$ , then one can define the **specific heat** at constant volume as;

$$C_{v} = \left(\frac{\partial E}{\partial T}\right)_{v}$$
(1)



Second band -----

**A- Classical Theory:** 



Vibration of lattice may be treated as that of a harmonic oscillator. Thus, the average energy for **1D** oscillator is

 $\overline{\varepsilon}=kT$ 

Therefore, the total thermal energy per mole in **3D** is

 $E = 3N_A kT = 3RT$ 

 $C_{v} = 3R$ 

where  $N_A \& R$  are **Avogadro's no**. and *the universal gas constant* respectively. Substituting into (1), we find

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This law of Dulong and Petit (1819) predicts a constant value to  $C_v$ , and it is approximately obeyed by most solids at high T ( > 300 K).

But by the middle of the 19<sup>th</sup> century it was clear that  $C_V \rightarrow 0$  as  $T \rightarrow 0$  for solids.



Second band

#### **B- Einstein Model:**

> Considering the atoms as **independent oscillators**, vibrating with **a common frequency**.

> Treating the oscillator quantum mechanically, where the average energy for 1D oscillator is

$$\overline{\varepsilon} = \frac{\hbar\omega}{e^{\hbar\omega/kT} - 1}$$

 $\succ$  At high T,

 $\overline{\varepsilon} = kT$  (and the classic value is reached)

Third band

> At low 
$$T$$
, the total energy is;

$$E = 3N \frac{\hbar \omega_E}{e^{\hbar \omega_E / kT} - 1}$$

Where the common frequency of the oscillators,  $\omega_{\rm E}$  , is known as **Einstein frequency**.





Substituting into (1), we find

$$C_{v} = 3R \left(\frac{\hbar\omega_{E}}{kT}\right)^{2} \frac{e^{\hbar\omega/kT}}{\left(e^{\hbar\omega_{E}/kT} - 1\right)^{2}}$$

> Introducing *Einstein temperature*,

$$\theta_E = \hbar \omega_E / k$$

the above expression can be reduced to

$$C_{v} = 3R \left(\frac{\theta_{E}}{T}\right)^{2} \frac{e^{\theta_{E}/T}}{\left(e^{\theta_{E}/T} - 1\right)^{2}}$$









Second hand

#### **C- Debye Model:**

> Treating the atoms as **coupled dependent oscillators** vibrating collectively as sound wave follows the *dispersion relation:* 

Total energy in such system is ,

$$E = \int \overline{\varepsilon}(\omega) \frac{g(\omega)}{g(\omega)} d\omega$$

 $\omega = v_{s}q$ 

$$\Rightarrow g(\omega) = \frac{3V}{2\pi^2} q^2 \frac{dq}{d\omega}$$

where  $g(\omega)$  is the density of state, and hence the integration is taken over all allowed frequencies.

Or;

Or:

$$E = \frac{3V}{2\pi^2 v_s^3} \int \omega^2 \frac{\hbar\omega}{e^{\hbar\omega/kT} - 1} d\omega$$

Third band —

First band

Debye stated the integral limit : (from 0 to 
$$\omega_D$$
), where  $\omega_D$  is the cut off frequency which is known as **Debye frequency** and given by

$$3N_A = \int_{0}^{\omega_D} g(\omega) d\omega$$
$$\omega_D = v_s (6\pi^2 n)^{1/3}$$







## THERMAL CONDUCTIVITY



In metals, the heat is carried both by electrons and by lattice waves (phonons), although the contribution of the electrons is much the larger.

In insulators, on the other hand, heat is transmitted totally by phonons.

When thermal energy propagates through a solid, it is carried by lattice waves or phonons from the hotter to the cooler end.

The *thermal energy flux* (J/m<sup>2</sup>s) is proportional to the *temperature gradient* as:

$$J = -\kappa \frac{dT}{dx}$$



Where  $\kappa$  is thermal conductivity, since

$$\kappa = \frac{1}{3}C_V v l$$
 and

 $C_v$  heat capacity per unit volume

*v* wave velocity

*l* mean free path of scattering



## THERMAL CONDUCTIVITY

#### Temperature-Dependence of $\boldsymbol{\kappa}$



There are three basic mechanisms to consider:

- 1. Impurities or grain boundaries in polycrystalline sample
- 2. Sample boundaries (surfaces)
- 3. Other phonons (deviation from harmonic behavior)

To understand the temperature dependence of  $\kappa$ , let us consider the limiting values of  $C_v$  and l (since v does not vary much with T).



$$\begin{cases} \propto T^3 \ low T \\ 3R \ high T \end{cases}$$

$$\propto \frac{1}{n_{ph}} = e^{\hbar \omega / kT} - 1$$



### **THERMAL CONDUCTIVITY**







Having studied the **structural arrangements** of atoms in solids, and the **thermal** and **vibrational** properties of the lattice, we now consider the **electronic properties** of solids in terms of a very simple model.

#### Free Electron (FE) Model :



**FE** is a simple model for *the behaviour of valence electrons in a crystal structure of a metallic solid*. It was developed principally by **Sommerfeld** who combined the classical **Drude** model with quantum mechanical **Fermi-Dirac** statistics and hence it is also known as the **Drude–Sommerfeld model**.

#### **Main Assumptions:**



Electrons free to move in a background of uniform (+ve) charge provided by ions (*jellium model*), i.e. electrons behave like a gas.

- No interactions between electrons, because of:
- **1.** Pauli exclusion.
- 2. To minimize the system energy, electrons tend to stay away of each other.



#### **Conduction Electrons**

≻A valence electron in a free atom, becomes a conduction electron in a solid.

The core electrons **do not** contribute anything to the electric current.
Hence, No. of conduction electrons = No. of atoms × atomic valence

$$N = Z_v \frac{\rho_m N_A}{M'}$$

Where M is the molar mass of the element (gm/mole).

#### **Electrical Conductivity**



Apply external electric field (ε) on a wire has a length L and cross section A, we find:

$$J = \frac{I}{A}$$
  $\varepsilon = \frac{V}{L}$  and  $R = \frac{L}{A}$ 



Where **J** is the **current density**, and  $\rho$  is the **electrical resistivity** =1/ $\sigma$  ( $\sigma$  is the **electrical conductivity**).



- $\blacktriangleright \text{ According to Ohm's Law: } J = \sigma \varepsilon$  (1)
- > When external electric field is applied two main things happen:
- 1. Coulomb force causes electrons to accelerate with  $\frac{dv_d}{dt}$ , where  $v_d$  is the **drift velocity**.
- 2. Scattering (with other electrons, ions, impurities etc) produces a decay of  $v_d$  back to zero. This retardation is represented by: - $v_d/\tau$ , where  $\tau$  is the *relaxation time*.

Adding up total force on electron, we get:

$$m^* \frac{dv_d}{dt} = -e\varepsilon - m^* \frac{v_d}{\tau}$$

In steady state, **dv/dt=0**, and hence

$$v_d = -\frac{e\,\tau}{m^*}\varepsilon$$

But since *J* represents the amount of charge crossing a unit area per unit time, then

$$J = (-Ne)v_d = \frac{Ne^2\tau}{m^*}\varepsilon$$
 (2)





Comparing (1) with (2) leads to;

$$\sigma = \frac{Ne^2\tau}{m^*}$$

Since  $\tau$  is the time between two following collisions, it can be expressed as; l

$$\tau = \frac{l}{v_r}$$

(~10<sup>-14</sup> s in metals)

Where *l* is distance between two following collisions (**electron's mean free path**) and  $v_r$  is the **random velocity**. Using these terms ( $\sigma$ ) can be rewritten as

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**In semiconductors:** 

$$\sigma = \frac{Ne^2l}{m^* v_r}$$

 $N \sim 10^{29} \text{ m}^{-3} \& v_r \sim 10^6 \text{ m.s}^{-1} \Rightarrow \sigma \sim 10^7 \text{ W}^{-1} \text{.m}^{-1}$  $N \sim 10^{20} \text{ m}^{-3} \& v_r \sim 10^4 \text{ m.s}^{-1} \Rightarrow \sigma \sim 1 \text{ W}^{-1} \text{.m}^{-1}$ 





The mean free path, l, for electrons in metals may be estimated via:  $v_r \tau = l$ . This give  $l \sim 10^{-8} \text{ m} \sim 10^2 \text{ A}^{\circ}$ , which is **20 times** larger than the interatomic spacing.

**i.e.**, electrons can **move freely in a perfect periodic structure**. scattering occurs when periodicity is interrupted by phonons or impurities.







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#### **Temperature dependence of Electrical Resistivity**



In metals, the temperature dependence of  $\rho$  is determined by  $\tau$ , according to the relation:

$$\rho = \frac{m}{Ne^2} \frac{1}{\tau}$$

But total scattering rate  $\tau$  given by addition of two individual scattering rates:

$$\frac{1}{\tau} = \frac{1}{\tau_{ph}} + \frac{1}{\tau_i}$$
 Matthiesens' Rule.

Therefore;







#### **Temperature dependence of Electrical Resistivity**

#### **1-** Impurity Scattering

Causes **the residual resistivity**,  $\rho_i$ , which is independent of *T*. It is determined by distance between impurities.

#### 2- Electron-phonon scattering

Causes **the ideal resistivity**,  $\rho_{ph}$ , which is dependent of *T*.

At very low temperature, scattering by phonons is negligible. So

 $\tau_{ph} \Rightarrow \infty \& \rho_{ph} \Rightarrow 0$  and hence  $\rho = \rho_i$ 

> At high temperature, no. of phonons increases, hence scattering, as *T* increases.  $\tau$  proportional to 1/T(true for  $T > \frac{1}{4}\theta_{\rm D}$ ).



Fhird band



#### HEAT CAPACITY OF CONDUCTION ELECTRONS

1.5

Based on Drude model, the average energy of electrons per mole is :  $\langle E \rangle = \frac{3}{2} N_A kT = \frac{3}{2} RT$ Hence, the electrons heat capacity is  $C_{e} = \frac{3}{2}R$ The total heat capacity in metals should then be;  $C = C_{nh} + C_e$ This means that at high temperature  $C=4.5 R \sim 9$  cal/mole K 0.8 Debye But experiments show that the total  $C_{V}$ Einstein *C* for metals is only slightly higher than for insulators, which conflicts 0.4 with the classical theory! 0.2 In specific,  $C_{\rho}$  should be **smaller** than the 0 classical value by **tow order magnitude**. 0.3 0.6 0.9 1.2 0  $T/T_{\rm D}$ 



Second band —

#### **Quantum explanation**

> **Pauli's exclusion** principle implies that **only 2** electrons of opposite spin orientation are allowed in each state.

> At T = 0K, electrons occupy all energy levels from the ground state upward. The energy of the highest filled state is known as the *Fermi energy*. All the levels above are empty.

➢ In metals the value of the Fermi energy is of the order of 5 eV.

#### What happens if the temperature is increased?

Third band Second band First band ➤ The kinetic energy of the electron gas increases with temperature.

> Electrons with energy ~  $E_{\rm F}$  can gain thermal energy and occupy energy states > $E_{\rm F}$ .

#### It is the electrons near E<sub>F</sub> that dominate the properties of the metal.





#### The Fermi distribution

> The distribution of electrons among the levels is usually described by the **distribution function**, f(E), which is defined as the probability that the level E is occupied by an electron.

> Thus if the level is certainly **empty**, then, f(E) = 0, while if it is certainly **full**, then f(E) = 1.

> At T = 0K, the distribution function is

$$f(E) = \begin{cases} 0, & E > E_F \\ 1, & E < E_F \end{cases}$$

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#### THERMAL CONDUCTIVITY OF METALS

In metals, the electronic contribution to  $\kappa$  far outweighs the contribution of the lattice. So we can write:

$$\kappa \cong \kappa_e = \frac{1}{3}C_e v l$$

Since electrons that can absorb thermal energy and therefore contribute to the heat capacity have energies very near  $E_F$ , so they essentially all have velocity  $v_F$ . This gives:

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Now the thermal conductivity per unit volume is:

$$\kappa = \frac{\pi^2 k^2 n \tau}{3m^*} T$$

(3)





# Do the electrons or the phonons carry the greater part of the heat current in a metal?

In pure metals the electronic contribution is dominant at all temperatures. -212 -

$$\kappa = \frac{\pi^2 k^2 n \tau}{3m^*} T$$

In impure metals or in disordered alloys, the electron mean free path is reduced by collisions with impurities, and the phonon contribution may be comparable with the electronic contribution.

$$\kappa = \frac{1}{3}C_V v l$$

