

HOMEWORK - June 2023

1

• Problem I

$$\textcircled{1} \quad C = \underbrace{\alpha T}_{\text{Electrons}} + \underbrace{\beta T^3}_{\text{Phonons}} = C_{el} + C_{ph}$$

$C/T = \alpha + \beta T^2$ Then $C/T = f(T^2)$ is a linear expression.

② Potassium: $K: [Ar] 4d^1$

$$C_{el} = \frac{\pi^2}{2} N k_B \left(\frac{T}{\Theta_F} \right) = 1,668 \times 10^{-3} T$$

$$\text{So } \Theta_F^K = \underline{\underline{24598 \text{ K}}}$$

Sodium: $Na: [Ne] 3d^1$

$$C_{el} = \frac{\pi^2}{2} N_A k_B T / \Theta_F^{Na} = 1,094 \times 10^{-3} T$$

$$\text{So } \Theta_F^{Na} = \underline{\underline{37474 \text{ K}}}$$

③ Number of quantum states below energy E :

$$\phi(E) = 2 \times \frac{\frac{4}{3} \pi \left(\frac{\sqrt{2mE}}{\hbar} \right)^3}{\left(\frac{2\pi}{L} \right)^3} = \frac{V}{3\pi^2} \times \left(\frac{\sqrt{2mE}}{\hbar} \right)^3$$

Then density of states: $g(E) = \frac{d\phi}{dE} = \frac{V}{2\pi^2} \left(\frac{\sqrt{2m}}{\hbar} \right)^{3/2} E^{1/2}$

④ The fermi energy (E_F) corresponds to the energy of highest occupied state, then:

$$\phi(E_F) = N \quad \text{if } N \text{ is the total number of electrons.}$$

$$\phi(E_F) = \frac{V}{3\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} E_F^{3/2} = N$$

$$\Rightarrow \boxed{E_F = \frac{\hbar^2}{2m} \left(3\pi^2 \frac{N}{V} \right)^{2/3} = k_B \Theta_F}$$

• Potassium: $\frac{N}{V} = \frac{2}{a_K^3}$ with 2 atoms (electrons) per cubic cell in Bcc.

$$\Theta_F^K = \frac{\hbar^2}{2mk_B} \left(3\pi^2 \times \frac{2}{a_K^3} \right)^{2/3} = \underline{\underline{23679 \text{ K}}}$$

$$\text{Error} = \frac{\Delta \Theta_F^K}{\Theta_F^K} \times 100\% = \underline{\underline{3,6\%}}$$

This small discrepancy between experimental and theoretical value comes from the "Fermi gas" approximation made on valence electrons.

• Sodium: $\Theta_F^{\text{Na}} = \underline{\underline{36552 \text{ K}}}$

$$\frac{\Delta \Theta_F^{\text{Na}}}{\Theta_F^{\text{Na}}} \times 100\% = \underline{\underline{2,5\%}}$$

Same remark.

⑤ The Debye temperature of Solids can be deduced from the expression of phononic contribution to the heat capacity:

$$C_{ph} = \frac{12\pi^4}{5} N k_B \left(\frac{T}{\Theta_D}\right)^3$$

Potassium:

$$C_{ph} = 2,75 \times 10^{-3} T^3$$

then $\Theta_D^K = \underline{\underline{89\text{ K}}}$

Sodium: $\Theta_D^{Na} = \underline{\underline{153\text{ K}}}$

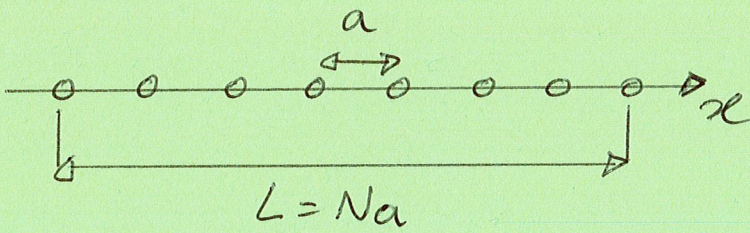
⑥ The highest is the Debye temperature, (= highest is the Debye frequency since $\omega_D = k_B \Theta_D / \hbar$), the highest is the strength of the interatomic bonds. So the "hardest" is the Solid.

Then a so-called "soft" solid is characterized by a low Debye freq. and temperature.

As an example, the C-diamond considered as part of the hardest materials is charact. by a Debye temp. of about 1900 K.

As a result, the heat capacity rises very quickly with increasing temperature for the case of "soft" materials (low Θ_D) and rises very slowly for "harder" materials (high Θ_D). 4

Problem II:



① free electrons along this line of atoms are described by wave-functions of type: $\psi(x) = Ae^{ikx}$

Then, by applying cyclic boundary conditions:

$$\psi(0) = \psi(L) = Ae^{ikL} = A$$

$$\Rightarrow kL = n2\pi$$

$$\Rightarrow \boxed{k = \frac{n2\pi}{L}}$$

Quantization of wave-vector.

Application of Schrödinger equation gives the energy of any electron described by a given quantum state $\psi_k(x)$.

$$\boxed{E_k = \frac{\hbar^2 k^2}{2m}}$$

Dispersion relation

Since 2 electrons can be accommodated on one quantum state, the highest occupied state corresponds to $k = \frac{N}{2} \times \frac{2\pi}{L} = \frac{N\pi}{L}$

5

Then: $E_F = \frac{\hbar^2}{2m} \times \left(\frac{N\pi}{L}\right)^2 = \frac{\hbar^2}{2m} \left(\frac{\pi}{a}\right)^2 = \underline{\underline{4.18 \text{ eV}}}$

$\Theta_F = \frac{E_F}{k_B} = \underline{\underline{48550 \text{ K}}}$

example: Li ($Z=3$) $E_F = 4.74 \text{ eV}$ $a_{Li} = 3.25 \text{ \AA}$
 $\Theta_F = 55100 \text{ K}$

② Number of quantum states below a given value of k : $\phi(k) = \frac{k}{\frac{2\pi}{L}} = \frac{Lk}{2\pi} = \frac{Na k}{2\pi}$

Then $g(k) = \frac{d\phi(k)}{dk} = \frac{aN}{2\pi}$

$g(E) dE = g(k) dk$

(\Rightarrow) $g(E) = g(k) \frac{dk}{dE} = \frac{aN}{2\pi} \times \frac{d}{dE} \left(\sqrt{\frac{2mE}{\hbar^2}} \right)$

(\Rightarrow) $g(E) = \frac{aN}{2\pi} \times \frac{1}{\hbar} \sqrt{2m} \times \frac{1}{2\sqrt{E}}$

(\Rightarrow) $g(E) = \frac{Na}{2\pi} \times \frac{1}{\hbar} \sqrt{\frac{m}{2E}} \times 2$ if ~~spin~~ spin and Pauli principle is used.
 $g(E) = A E^{-1/2}$

(3)

$$U_0 = \int_0^{E_F} E g(E) dE = A \int_0^{E_F} E^{1/2} dE$$

6

$$\Rightarrow U_0 = \frac{2}{3} A E_F^{3/2}$$

with

$$N = \int_0^{E_F} A E^{-1/2} dE = 2 A E_F^{1/2}$$

$$\Rightarrow A = \frac{N}{2} E_F^{-1/2}$$

$$\text{So } U_0 = \frac{N}{3} E_F$$

(4)

$$U_T = \int_0^{+\infty} E g(E) f(E) dE$$

Using Sommerfeld approximation:

$$U_T = \int_0^{\mu} E g(E) dE + \frac{\pi^2}{6\beta^2} \left(\frac{A}{2} E_F^{-1/2} \right)$$

$$\text{with } \phi(E) = E g(E) = A E^{1/2}$$

$$\phi'(E) = \frac{A}{2} E^{-1/2}$$

$$\text{Then: } U_T = U_0 + \int_{E_F}^{\mu} A E^{1/2} dE + \frac{\pi^2}{6\beta^2} \left(\frac{A}{2} E_F^{-1/2} \right)$$

$$U_T \approx U_0 + A E_F^{1/2} (\mu - E_F) + \frac{A \pi^2}{12\beta^2} E_F^{-1/2}$$

$$\text{At low } T: \quad \mu - E_F \approx 0 \quad \text{and } U_T \propto T^2$$

and heat capacity C proportional to T

$$C = \frac{dU}{dT} \propto T$$

Problem III :

7

3D semi-metal DOS :

$$\begin{cases} g(E) = A \sqrt{E_F - E} & \text{for } E < E_F \\ g(E) = A \sqrt{E - E_F} & \text{for any } E > E_F \\ g(E) = 0 & \text{at } E = E_F \end{cases}$$

$$\textcircled{1} \quad N = \int_0^{E_F} g(E) dE = A \int_0^{E_F} \sqrt{E_F - E} dE$$

$$\Rightarrow N = A \left[-\frac{2}{3} (E_F - E)^{3/2} \right]_0^{E_F} = \frac{2}{3} A E_F^{3/2}$$

$$\text{Then } \boxed{A = \frac{3N}{2} E_F^{-3/2}}$$

$$\textcircled{2} \quad U_0 = \int_0^{E_F} E g(E) dE = A \int_0^{E_F} E \sqrt{E_F - E} dE$$

change in variables:

$$\begin{cases} x = E_F - E \\ E = E_F - x \\ dE = -dx \end{cases}$$

$$\begin{aligned} U_0 &= -A \int_{E_F}^0 (E_F - x) \sqrt{x} dx = A \int_0^{E_F} (E_F - x) \sqrt{x} dx \\ &= A \int_0^{E_F} E_F \sqrt{x} dx - A \int_0^{E_F} x^{3/2} dx \end{aligned}$$

$$U_0 = \frac{2}{3} A E_F \left[x^{3/2} \right]_0^{E_F} - \frac{2A}{5} \left[x^{5/2} \right]_0^{E_F}$$

8

$$\Leftrightarrow U_0 = \frac{2}{3} A E_F^{5/2} - \frac{2}{5} A E_F^{5/2} = \frac{4}{15} A E_F^{5/2}$$

$$\textcircled{3} \quad N_{CB}^{el} = \int_{E_F}^{+\infty} g_{CB}(E) f_{CB}(E) dE$$

$$\text{with } f_{CB}(E) = \frac{1}{e^{\beta(E-\mu)} + 1} \ll 1$$

\hookrightarrow Boltzmann distribution

$$f_{CB}(E) \approx e^{-\beta(E-\mu)}$$

Then:

$$N_{CB}^{el} = \int_{E_F}^{+\infty} A \sqrt{E-E_F} e^{-\beta(E-\mu)} dE$$

Again chg. in variables

$$x = \beta(E-E_F)$$

etc...

$$N_{CB}^{el} = \frac{A\sqrt{\pi}}{2} (k_B T)^{3/2} e^{-\beta E_F} e^{\beta\mu}$$

$$\textcircled{4} \quad N_{VB}^h = A \int_{-\infty}^{E_F} \sqrt{E_F-E} e^{\beta(E-\mu)} dE$$

$$N_{VB}^h = A \int_{+\infty}^0 -\sqrt{\frac{x}{\beta}} e^{-x} e^{\beta E_F} e^{-\beta\mu} \frac{dx}{\beta}$$

$$x = \beta(E_F - E)$$

$$dx = -\beta dE$$

$$E = -\frac{x}{\beta} + E_F$$

$$dE = -dx/\beta$$

$$N_{VB}^h = \int_0^{+\infty} \sqrt{x} e^{-x} dx \left(\frac{A}{\beta^{3/2}} e^{\beta E_F} e^{-\beta \mu} \right)$$

$$= \frac{\sqrt{\pi}}{2}$$

9

finally:

$$N_{VB}^h = \frac{A\sqrt{\pi}}{2} (k_B T)^{3/2} e^{\beta E_F} e^{-\beta \mu}$$

⑤ When one electron is promoted to a quantum state in the conduction band, a vacancy or a hole is created in the valence band so that:

$$N_{VB}^h = N_{CB}^{el}$$

⑥ At low T ($k_B T \ll E_F$) and $\mu \approx E_F$

$$\text{So } N_{CB}^{el} = \frac{A\sqrt{\pi}}{2} (k_B T)^{3/2} e^{-\beta E_F} e^{\beta \mu} \approx \frac{A\sqrt{\pi}}{2} \left(\frac{k_B T}{k_B T} \right)^{3/2}$$

$$N_{CB}^{el} \propto T^{3/2}$$

⑦ If $N_{VB}^h = N_{CB}^{el}$ then $e^{\beta E_F} e^{-\beta \mu} = e^{-\beta E_F} e^{\beta \mu}$

$$\Leftrightarrow \beta(E_F - \mu) = \beta(\mu - E_F)$$

$$\Leftrightarrow \mu = E_F$$

So again $N_{CB}^{el} \propto T^{3/2}$ no activation energy.