Chapter 6.

Free electron Fermi gas

free electron(6장)-electron과 lattice ion과의 interaction(7장)

Sodium의 valence electron은 3s state

3s conduction band

2s 2p는 거의 ion인 상태나 metal 상태나 같다.

ion core는 Sodium crystal의 15% volume fraction 차지

Quantum Mechanics가 나오기 전에 벌써 free electron model이 나오다.

매우 성공적 :	Ohm's law
	electric, thermal conductivity
실패 :	heat capacity, magnetic susceptibility
	"Maxwell distribution → Fermi-Dirac distribution"
	mean free path가 매우 크다.
	low temp에서는 10^8 interatomic spacing(=1cm)

Conducting electron에 대해 왜 transparent한가?

a) Wave가 periodic structure에서 거의 freely propagate한다.

b) 다른 전자에 의한 scattering이 매우 적다.(Pauli's exclusive principle)

→free electron Fermi gas라 불리운다.

Energy levels in One-dimension

$$H\Psi_n = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\Psi_n = \varepsilon_n \Psi_n$$

ε_n의 전자가 orbit에 있다.

이 orbital model은 interaction이 없을 때 성립

$$\Psi_n = A\sin\frac{2\pi}{\lambda_n}x, \quad \frac{1}{2}n\lambda_n = L$$

$\frac{2\pi}{\lambda} L = n\pi$ $\quad L = n\frac{\lambda}{2}$

이것을 代入

$$\varepsilon_n = \frac{\hbar^2}{2m}\left(\frac{2\pi}{\lambda_n}\right)^2 \qquad \lambda_n = \frac{2L}{n}$$

$$= \frac{\hbar^2}{2m}\left(\frac{2\pi n}{2L}\right)^2$$

$$= \frac{\hbar^2}{2m}\frac{n^2\pi^2}{L^2}$$

Pauli exclusion principle: 하나의 level에 ↑↓ 2개 들어갈 수 있다.

$2n_F = N$이 n_F를 결정한다.

Fermi energy를 결정하자.

$$\varepsilon_F = \frac{\hbar^2}{2m}\left(\frac{n_F \pi}{L}\right)^2$$
$$= \frac{\hbar^2}{2m}\left(\frac{N\pi}{2L}\right)^2$$

Effect of temperature on the Fermi-Dirac Distribution

① Fermi-Dirac distribution

$$f(\varepsilon) = \frac{1}{e^{(\varepsilon - \mu)/k_b T} + 1}$$

at T = 0 : $\mu = \varepsilon_F$

μ : chemical potential

high energy tail of the distribution

$\varepsilon - \mu \gg k_B T$

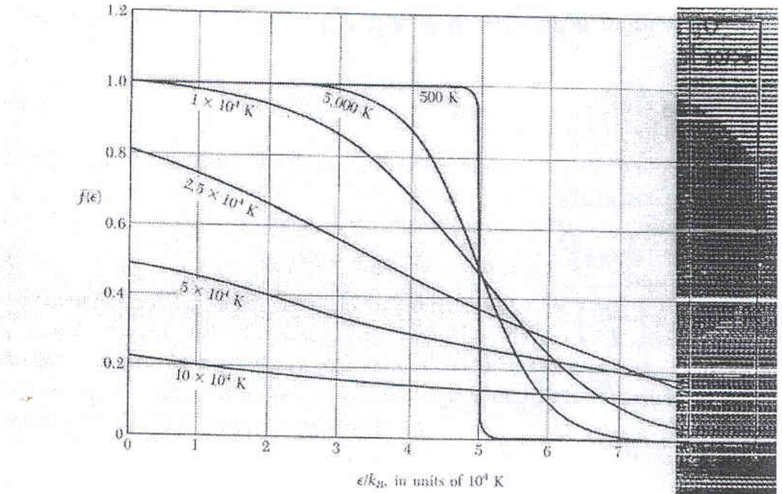

Figure 3 Fermi-Dirac distribution function at various temperatures, for $T_F \equiv \epsilon_F/k_B = 50{,}000$ K. The results apply to a gas in three dimensions. The total number of particles is constant, independent of temperature. The chemical potential at each temperature may be read off the graph as the energy at which $f = 0.5$.

$f(\varepsilon) \cong \exp[(\mu - \varepsilon)/k_b T]$

called ② Boltzman or Maxwell distribution

Free electron gas in 3-D

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)\Psi_n(\vec{r}) = \varepsilon_k \Psi_k(\vec{r})$$

◦ Cube L^3 속에 있다. box normalization

$$\Psi_n(\vec{r}) = A \sin\frac{\pi n_x x}{L} \sin\frac{\pi n_y y}{L} \sin\frac{\pi n_z z}{L}$$

◦ Periodic boundary condition

$$\Psi(x+L, y, z) = \Psi(x, y, z)$$

$k_x L = 2n\pi$

$$\Psi_k(\vec{r}) = \exp(i\vec{k} \cdot \vec{r}) = \exp i(k_x x + k_y y + k_z z)$$

$$\frac{\hbar^2}{2m}(k_x^2 + k_y^2 + k_z^2) = \varepsilon_k \ , \quad k_x = \frac{2n_x\pi}{L}, \ k_y = \frac{2n_y\pi}{L}, \ k_z = \frac{2n_z\pi}{L}$$

$$\therefore \frac{\hbar^2}{2m}\frac{4\pi^2}{L^2}(n_x^2 + n_y^2 + n_z^2)$$

k의 component : $\dfrac{2n\pi}{L}$

n : positive or negative integer

$$\varepsilon = \frac{\hbar^2}{2m}\left(\frac{2\pi}{L}\right)^2 (n_x^2 + n_y^2 + n_z^2), \quad k = \frac{2n\pi}{L}$$

$$P\Psi_k = -i\hbar \nabla \Psi_k(\vec{r}) = \hbar \vec{k}\, \Psi_k(\vec{r})$$

$$\varepsilon_F = \frac{\hbar^2}{2m} k_F^2$$

total # of orbitals

$$N = 2 \cdot \frac{\frac{4}{3}\pi k_F^3}{\left(\frac{2\pi}{L}\right)^3}$$

$$= 2 \cdot \frac{4}{3}\pi k_F^3 \cdot \frac{L^3}{8\pi^3}$$

$$= \frac{V}{3\pi^2} k_F^3$$

$$k_F = \left(\frac{3\pi^2 N}{V}\right)^{1/3}$$

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

Fermi surface에서의 electron의 velocity

$$v_F = \frac{\hbar k_F}{m} = \frac{\hbar}{m}\left(\frac{3\pi^2 N}{V}\right)^{1/3}$$

Density of state

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

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

$$D(\varepsilon) \equiv \frac{dN}{d\varepsilon} = \frac{V}{2\pi^2}\left(\frac{2m\varepsilon}{\hbar^2}\right)^{1/2} \cdot \frac{2m}{\hbar^2}$$

$$= \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} \cdot \varepsilon^{1/2}$$

$$= \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\left(\frac{\hbar^2}{2m}\right)^{1/2}\left(\frac{3\pi^2 N}{V}\right)^{1/3}$$

$$= \frac{Vm}{\pi^2\hbar^2}\left(\frac{3\pi^2 N}{V}\right) \propto m$$

$$\log N = \frac{3}{2}\log\varepsilon + const$$

$$\frac{dN}{N} = \frac{3}{2}\frac{d\varepsilon}{\varepsilon} \qquad \therefore D(\varepsilon) \equiv \frac{dN}{d\varepsilon} = \frac{3}{2}\frac{N}{\varepsilon}$$

Heat capacity of the electron gas

Conduction electron의 heat capacity

Classical statistics : $\frac{3}{2} k_B$

N개의 atom이 하나씩 전자를 내면 : $\frac{3}{2} Nk_B$

electronic contribution : 0.01 정도 밖에 안된다.

왜 잘 움직이는데 heat capacity가 이렇게 작나?

Pauli에 의해 발견이 되다.

$C_V \to 0 \quad as \quad T \to 0$

단지 $\frac{T}{T_F}$ 정도의 전자만이 excite한다.

$$u \sim N \cdot \frac{T}{T_F} k_B T$$

$$C_{el} = \frac{\partial u}{\partial T} \sim Nk_B \left(\frac{T}{T_F} \right)$$

$$T_F \sim 5 \times 10^4 \mathrm{K}$$

$$\Delta u = \int_0^\infty d\varepsilon \, \varepsilon D(\varepsilon) f(\varepsilon) - \int_0^{\varepsilon_F} d\varepsilon \, \varepsilon D(\varepsilon)$$

$$N = \int_0^\infty d\varepsilon \, D(\varepsilon) f(\varepsilon) = \int_0^{\varepsilon_F} d\varepsilon \, D(\varepsilon)$$

여기에 ε_F를 곱하자. 그런데

$$\int_0^{\varepsilon_F} d\varepsilon \cdot \varepsilon_F D(\varepsilon) f(\varepsilon) + \int_{\varepsilon_F}^\infty d\varepsilon \cdot \varepsilon_F D(\varepsilon) f(\varepsilon) = \int_0^{\varepsilon_F} d\varepsilon \cdot D(\varepsilon) \varepsilon_F$$

$$\therefore \int_0^{\varepsilon_F} D(\varepsilon) \cdot \varepsilon_F (f(\varepsilon) - 1) = - \int_{\varepsilon_F}^\infty \varepsilon_F D(\varepsilon) f(\varepsilon) \, d\varepsilon$$

이므로,

$$\Delta U = \int_0^{\varepsilon_F} d\varepsilon \, \varepsilon \cdot D(\varepsilon) (f(\varepsilon) - 1) - \int_0^{\varepsilon_F} d\varepsilon \, \varepsilon_F \cdot D(\varepsilon) (f(\varepsilon) - 1) + \int_{\varepsilon_F}^\infty d\varepsilon \, \varepsilon \cdot D(\varepsilon) f(\varepsilon) - \int_{\varepsilon_F}^\infty d\varepsilon \, \varepsilon_F \cdot D(\varepsilon) f(\varepsilon)$$

$$= \int_0^{\varepsilon_F} d\varepsilon \, (\varepsilon_F - \varepsilon)(1 - f(\varepsilon)) D(\varepsilon) + \int_{\varepsilon_F}^\infty d\varepsilon \, D(\varepsilon) f(\varepsilon) (\varepsilon - \varepsilon_F)$$

$$C_{el} = \frac{du}{dT} = \int_0^\infty d\varepsilon \, (\varepsilon - \varepsilon_F) \frac{df}{dT} D(\varepsilon)$$

metal에서 관심있는 영역은 $\frac{k_B T}{E_F} < 0.01$인 지역이다.

$$\cong D(\varepsilon_F) \int_0^\infty d\varepsilon \, (\varepsilon - \varepsilon_F) \frac{df}{dT}$$

$$f = \frac{1}{e^{(\varepsilon-\varepsilon_F)/kT}+1}$$

$$\frac{df}{dT} = \{\cdots\}^{-2} \cdot \frac{\varepsilon-\varepsilon_F}{k} \cdot \left(\frac{1}{T^2}\right) \cdot e^{(\varepsilon-\varepsilon_F)/kT}$$

$$= \frac{\varepsilon-\varepsilon_F}{kT^2} \frac{e^{(\varepsilon-\varepsilon_F)/kT}}{\{e^{(\varepsilon-\varepsilon_F)/kT}+1\}^2}$$

$$C_{el} = D(\varepsilon_F) \int_0^\infty d\varepsilon \cdot (\varepsilon-\varepsilon_F) \cdot \frac{\varepsilon-\varepsilon_F}{kT^2} \frac{e^{(\varepsilon-\varepsilon_F)/kT}}{\{1+e^{(\varepsilon-\varepsilon_F)/kT}\}^2}$$

$x = \frac{\varepsilon-\varepsilon_F}{kT}$ 로 놓으면

$$= D(\varepsilon_F) \int_0^\infty kT\,dx \cdot x\,kT \cdot \frac{xkT}{kT^2} \frac{e^x}{(1+e^x)^2}$$

$$= D(\varepsilon_F) \int_{-\frac{\varepsilon_F}{kT}}^\infty k^2 T \cdot \frac{e^x x^2}{(1+e^x)^2}\,dx$$

$$= k_B^2 T D(\varepsilon_F) \int_{-\frac{\varepsilon_F}{kT}}^\infty dx\, x^2 \cdot \frac{e^x}{(e^x+1)^2}$$

low temp limit

$$= k_B^2 T D(\varepsilon_F) \int_{-\infty}^\infty x^2 \cdot \frac{e^x}{(e^x+1)^2}\,dx$$

$$= k_B^2 T \cdot D(\varepsilon_F) \cdot \frac{\pi^2}{3}$$

$$= \frac{1}{3} \pi^2 D(\varepsilon_F)\, k_B^2 T$$

$$D(\varepsilon_F) = \frac{3N}{2\varepsilon_F} = \frac{3N}{2k_B T_F}$$

$k_B T_F = \varepsilon_F$이므로

$$= \frac{1}{3} \pi^2 \cdot \frac{3N}{2k_B T_F} \cdot k_B^2 T = \frac{1}{2} \pi^2 N k_B \frac{T}{T_F}$$

Experimental Heat capacity of Metals

$$C = \gamma T + AT^3$$

$$\frac{C}{T} = \gamma + AT^2$$

$$\gamma = \frac{1}{3}\pi^2 D(\varepsilon_F) k_B^2$$

$$= \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} \cdot \varepsilon_F^{1/2} \cdot \frac{1}{3}\pi^2 k_B^2$$

$$= \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} \cdot \left[\frac{\hbar^2}{2m}\left(\frac{3\pi^2 N}{V}\right)^{2/3}\right]^{1/2} \cdot \frac{1}{3}\pi^2 k_B^2$$

$$= \frac{V}{2\pi^2} \cdot \frac{2m}{\hbar^2}\left(\frac{3\pi^2 N}{V}\right)^{1/3} \cdot \frac{1}{3}\pi^2 k_B^2$$

$$\therefore \gamma \propto m$$

실험값과 이론값이 다르다.

$$\frac{m_{th}}{m} = \frac{\gamma(obserbed)}{\gamma(free)}$$

왜 m이 다른가?

1. interaction of the conduction electrons with the periodic potential of the rigid crystal lattice

m_{th} : band effective mass

2. phonon과 interaction

drag ∴mass가 주로 증가한다.

3, electron끼리의 interaction

mass가 증가한다.

Heavy Fermion

two or three order of magnitude higher mass

예) UBe_{12} , $CeAl_3$, $CeCu_2Si_2$

f electron이 1000m ∴f electron이 localized되어있기 때문에

Electrical conductivity and Ohm's law

$$\vec{F} = m\frac{d\vec{v}}{dt} = \hbar\frac{d\vec{k}}{dt} = -e\left(\vec{E} + \frac{1}{c}\vec{v}\times\vec{B}\right)$$

만약 collision이 없으면 Fermi sphere는 uniform rate로 움직인다.

$\vec{B} = 0$ 이면 $k(t) = k(0) - eEt$

$$\delta\vec{k} = -eEt/\hbar$$

만약 collision time이 τ이면

$$v = -eE\tau/m$$

$$j = nqv = ne^2\tau E/m$$

Electrical conductivity σ는 $\vec{j} = \sigma\vec{E}$를 만족하므로

$$\therefore \sigma = \frac{ne^2\tau}{m} = ne\left(\frac{e}{m}\right)\tau$$

개수, *acceleration*, *time*

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

σ : low temp (4K)에서는 room temp보다 10^5정도 더 크다

$l = v_F \cdot \tau$ $\qquad$ v_F : *Fermi surface*의 속도

1.57×10^8cm/sec

mean free path

$l(4K) \approx 0.3\,cm$

$l(300K) \approx 3\times10^{-6}cm$

어떤 metal $l(4K) \sim 10cm$

Experimental Electrical Resistivity of Metals

$$\frac{1}{\tau} = \frac{1}{\tau_L} + \frac{1}{\tau_i}$$

τ_L : collision time for scattering by phonons

τ_i : imperfections

net resistivity

$$\rho = \rho_L + \rho_i$$

ρ_i : resistivity caused by scattering of electron waves by static defect

Matthiessen's rule

ρ_L : defect의 수와는 무관하다.

$\rho_i(0)$: 0K에서 잰다.

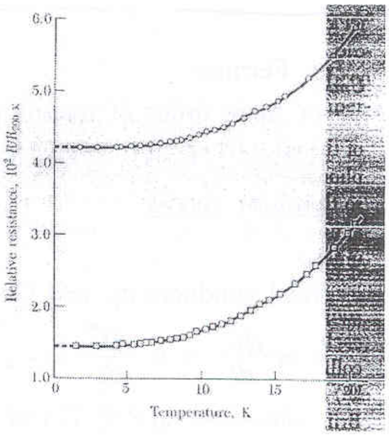

Figure 12 Resistance of potassium below 20 K, as measured on two specimens by D. MacDonald and K. Mendelssohn. The different intercepts at 0 K are attributed to different concentrations of impurities and static imperfections in the two specimens.

$$\therefore \rho_L \rightarrow 0 \quad as \quad T \rightarrow 0$$

$\rho_L(T) = \rho - \rho_i(0)$

대개 ρ_i는 impurity의 atomic percent에 대해 1 $\mu ohm \cdot cm$정도 는다.

Cu : 1.7×10^{-3} $\mu ohm \cdot cm$

impurity concentration이 20ppm

Collision rate with phonon ∝ thermal phonon의 수

$\rho \propto T$ for $T > \theta$

Umklapp Scattering

Umklapp Scattering of electron by phonon

low temp에서 electrical resistivity의 원인

normal electron-phonon scattering보다 Umklapp이 더 크게 기여

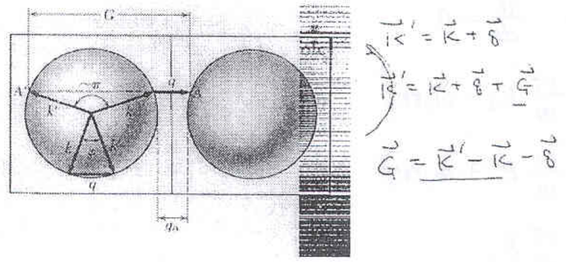

Figure 13 Two Fermi spheres in adjacent zones: a construction to show the role of phonon umklapp processes in electrical resistivity.

Scattering angle이 π 근처이다.

Single collision은 electron을 ground orbital로 보낸다.

Umklapped가 일어날 확률은 $e^{-\theta_u/T}$

θ_u : characteristic temperature calculable from the geometry of the Fermi surface inside the B.Z

Umclapped scattering 일으킬 minimum phonon vector q_0

BCC. sphere일 때 $q_0 = 0.267 k_F$

potasium $\theta = 91\,\mathrm{K}$, $\theta_u = 23\,\mathrm{K}$

낮은 온도에서는 Umklapp process 는 무시할 수 있다.

따라서 scattering은 small angle에서

normal scattering

$\rho_L \propto T^5 / \theta^6$ Bloch의 결과

Motion in magnetic fields

$$\hbar\left(\frac{d}{dt}+\frac{1}{\tau}\right)\delta\vec{k}=\vec{F}$$

$$\vec{F}=-e\left(\vec{E}+\frac{1}{c}\vec{v}\times\vec{B}\right)$$

만약 $m\vec{v}=\hbar\vec{k}$ 이면

eq. of motion $\quad m\left(\frac{d}{dt}+\frac{1}{\tau}\right)\vec{v}=-e\left(\vec{E}+\frac{1}{c}\vec{v}\times\vec{B}\right)$

static magnetic field $\vec{B}=B\hat{z}$ $\qquad \therefore\ m\left(\frac{d\vec{v}}{dt}+\right.$

$$m\left(\frac{d}{dt}+\frac{1}{\tau}\right)v_x=-e(E_x+\frac{B}{c}v_y)\ \text{: 회전 } term$$

$$m\left(\frac{d}{dt}+\frac{1}{\tau}\right)v_y=-e(E_y-\frac{B}{c}v_x)\ \text{: 회전 } term$$

$$m\left(\frac{d}{dt}+\frac{1}{\tau}\right)v_z=-eE_z$$

steady state : $\frac{d}{dt}=0$

$$\therefore\quad v_x=-\frac{e\tau}{m}E_x-\omega_c\tau v_y$$

$$v_y=-\frac{e\tau}{m}E_y+\omega_c\tau v_x$$

$$v_z=-\frac{e\tau}{m}E_z$$

$$\omega_c\equiv\frac{eB}{mc}\qquad (\text{ cyclotron freq}$$

Hall effect

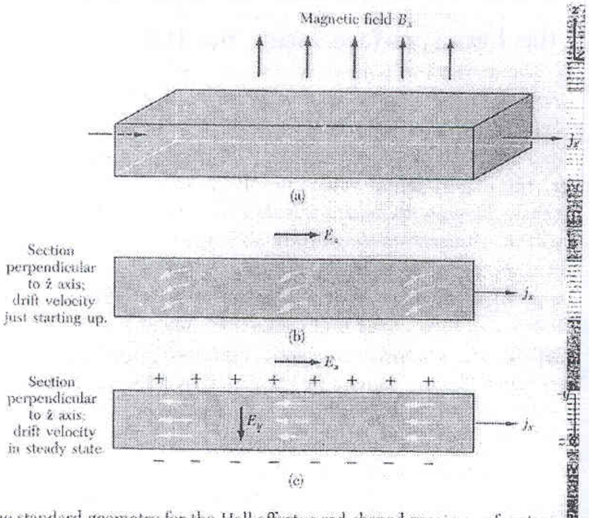

Figure 14 The standard geometry for the Hall effect: a rod-shaped specimen of rectang

y방향의 속도는 zero

$$v_x = -\frac{e\tau}{m} E_x$$

$$0 = -\frac{e\tau}{m} E_y + \omega_c \tau v_x$$

$$\therefore\ E_y = \frac{m\omega_c\tau}{e\tau} v_x = \frac{m\omega_c}{e} v_x$$

$$= \frac{m\omega_c}{e} \cdot \left(-\frac{e\tau}{m}\right) E_x$$

$$= -\omega_c \tau E_x$$

$$= -\frac{\tau e B}{mc} E_x$$

$j_x = nev_x$이고

$$R_H \equiv \frac{E_y}{j_x B} = -\frac{\tau e B}{mc}\frac{E_x}{j_x B} = -\frac{\tau e}{mc} \cdot \frac{m}{ne^2 \tau E_x}$$

$$= -\frac{1}{nec}$$

$R_H = -\frac{1}{nec}$
Hall resistance $\rho_H = BR_H = E_y / j_x$

위에서 모든 relaxation time이 같다고 가정하였다.

만약 relaxation time이 속도의 함수이면 매우 복잡하다.

Conductivity에 hole이 관여하면 더욱 복잡

+, - 두 가지가 다 존재

free electron model로 설명 못함

free electron Fermi gas → Band theory 필요

Thermal conductivity of Metals

Thermal conductivity

$$K = \frac{1}{3} Cvl \qquad C: \text{heat capacity}$$

$$= \frac{1}{3}\left\{\frac{1}{2}\pi^2 Nk_BT \cdot \left(\frac{E_F}{k_B}\right)^{-1} \cdot v_F \cdot l\right\} \qquad C_{el} = \frac{1}{2}\pi^2 Nk_BT/T_F$$

$$= \frac{\pi^2 \cdot Nk_BT \cdot k_B \cdot v_F \cdot l}{6 \cdot \frac{1}{2} mv_F^2} \qquad l = v_F\tau$$

$$= \frac{\pi^2 \cdot Nk_BT \cdot k_B \cdot v_F \cdot v_F\tau}{3mv_F^2}$$

$$= \frac{Nk_B^2\pi^2 T\tau}{3m}$$

impurity가 많이 생겨나면 mean free path가 줄어든다.

phonon에 의한 contribution이 electron에 의한 contribution과 비슷

Ration of thermal to Electric conductivity

$\frac{K}{\sigma}$: metal의 종류에 관계없이 일정

Wiedmann-Frantz law

$$\frac{K}{\sigma} = \frac{\frac{\pi^2 nk_B^2 T\tau}{3m}}{\frac{ne^2\tau}{m}}$$

$$= \frac{\pi^2}{3}\left(\frac{k_B}{e}\right)^2 T$$

$$\text{Lorentz number} \equiv \frac{K}{\sigma T} = \frac{\pi^2}{3}\left(\frac{k_B}{e}\right)^2$$

$$= 2.72 \times 10^{-12} \text{esu/deg}^2$$

n, m, τ가 관여 안함

실험치와 매우 일치 /but [K와 σ가 각각 실험치와 어긋난다.]

Low temp로 내려가면 Lorentz number가 준다.

Cu(15K)에서는 order 하나는 준다.

이유 : thermal과 electric conductivity에 관여하는 collision average의 차이 때문