Thermoelectric power Masatsugu Sei Suzuki Department of Physics, SUNY at Binghamton (Date: April 13, 2018)

When I was a graduate student, I was doing an experiment on the temperature dependence of niobium (Nb) at low temperatures as my first experiment. I got a result which is almost the same as that shown below. The conduction electrons as well as phonons shift from the high temperature side $(T + \Delta T)$ to the low temperature side (T) under the presence of temperature difference ΔT . There are two components of thermoelectric power; (a) the diffusion of electrons which is negative (usually) and very small in magnitude, and (b) phonon drag which is very large at low temperatures. Due to the interaction between electrons and phonons, when phonons shift from the high temperature side to the low temperature side, electrons are swept by phonons. During my research, my teacher suggested me to read a book. I was very impressed with the book of D.K.C. MacDonald, Thermoelectricity; An Introduction to the Principles. I guessed that the positive phonon drag observed in Nb (superconductor)) may be related to the possible hole-like Fermi surface (small size). Unfortunately, I could not explain quantitatively the overall behavior of thermoelectric power of Nb.

For many metals a qualitative understanding of the thermoelectric properties has now emerged, taking into account the details of the Fermi surface and of the electron-phonon interaction. In Phys.472-572, I have an opportunity to teach topics on the thermoelectric power. Here we discuss the physics of the thermoelectric power, based on the Boltzmann transport theory.

There are important relations

$$E = -\nabla_r V = S \nabla_r T \quad \text{(Seebeck effect)}$$

$$\Pi = TS , \quad \text{(Peltier co-efficient)} \quad \text{Thomson relation}$$

$$\mu_T = T \frac{dS}{dT} \quad \text{(Thomson co-efficient)} \quad \text{Thomson relation}$$

$$S(T) = \int_0^T \frac{\mu_T}{T} dT$$

The Peltier effect:

 $J_o = \pi J_e$

1. Seebeck, Peltier, and Thomson effect

Three thermoelectric effects occur when an electric field and a temperature gradient exist simultaneously in metals; Seebeck effect, Peltier effect, and Thomson effect.



Fig.1 (a) Seebeck effect. (b) Peltier effect. (c) Thomson effect.



Fig.2 Unsymmetrical thermoelectric circuits constructed from different metals A, B, and C. In both cases the Seebeck emf. $V_{AB} = E_{AB}$, determined solely by the metals A and B, is measured.

(a) Seebeck effect

The phenomenon of thermoelectricity was first observed in 1826 by Seebeck, who found that a current will flow in a closed circuit made of two dissimilar metals when the two junctions are maintained at different temperatures. Today, when we speak of the Seebeck effect, we generally envisage an open circuit, such as that shown in where E .2. The voltage $\Delta V = V_A - V_B$ is the thermoelectric voltage developed by this couple, and the thermoelectric power of the couple is defined by

$$S_{AB} = \lim_{\Delta T \to 0} \frac{\Delta V_{AB}}{\Delta T}$$

We consider a temperature gradient in a specimen that is on open circuit. Putting J = 0, we have the electric field E which is given by

$$\boldsymbol{E} = S \nabla T$$

We note that

$$E = -\nabla V$$
, $\nabla V = -S\nabla T$ $dV = -SdT$

where E is the electric field and V is the electric potential. We consider a closed circuit of two metals A and B, with junctions at different temperatures T_1 and T_2 , and with a voltmeter interposed at some intermediate point, temperature T_0 . The emf round the circuit is defined by the integral of E along the length of the wire, is given by



Fig. Seebeck effect.

$$V_{a} - V_{d} = (V_{a} - V_{b}) + (V_{b} - V_{c}) + (V_{c} - V_{d})$$

$$= \int_{b}^{a} dV + \int_{c}^{b} dV + \int_{d}^{c} dV$$

$$= -\int_{b}^{a} S_{B} dT - \int_{c}^{b} S_{A} dT - \int_{d}^{c} S_{B} dT$$

$$= -\int_{b}^{a} S_{B} dT - \int_{c}^{b} S_{A} dT - \int_{a}^{c} S_{B} dT$$

$$= -\int_{b}^{c} S_{B} dT - \int_{c}^{b} S_{A} dT$$

$$= -\int_{c}^{c} S_{B} dT - \int_{c}^{b} S_{A} dT$$

since $\Delta V = -SdT$. The voltage generated in the circuit looks like a function of the difference in temperature of the two junctions, and of the difference in the absolute thermoelectric power, A, of the two metals. This is the well-known Seebeck effect. We note that the thermoelectric power of superconductors is absolutely zero.

(b) Peltier effect

Two metals A and B are connected on the junction. No temperature gradient exists. These two metals are at the same temperature. Suppose that a steady electric current flows from A to B. This electric current creates an interesting situation at the junction. The electric current flow at the junction is

$$J_A = n_A e v_A, \quad J_B = n_B e v_B$$

with $J_A = J_B = J$. The heat flow at the junction is given by

$$(J_Q)_A = n_A h_A v_A, \qquad (J_Q)_B = n_B h_B v_B$$

where v_A and v_B are the electron velocity inside the metal A and metal B, respectively. $h_A (= \varepsilon_A - \mu_A)$ and $h_B (= \varepsilon_B - \mu_B)$ are the energy of electrons in the metal A and metal B from each chemical potential. The net rate of release or absorption of the heat energy is

$$\Delta J_Q = n_A h_A v_A - n_B h_B v_B$$
$$= \frac{J_e}{e} (h_A - h_B)$$

If $h_A \neq h_B$, an absorption or release of heat will take place at the junction via the interaction of electrons with the lattice. This reversible heat absorption process is known as the Peltier effect. The Peltier coefficient is defined by

$$\Pi_{AB} = \frac{\Delta J_u}{J_e} = \frac{1}{e}(h_A - h_B) = \Pi_A - \Pi_B$$

 $\Delta J_u = \prod_{AB} J_e$

We now drive a current J round the circuit by means of a battery. In the branch A, there will be a heat current $\pi_A J$. In the branch B there will be a different heat current $\pi_B J$. At the junction, the balance heat must be restored; the heat flux $(\pi_A - \pi_B)J$ will be emitted at one junction and absorbed at the other. One junction will become warmer, the other colder. This is the Peltier effect. The Peltier coefficient is related to the absolute thermoelectric power;

$$\Pi_{AB} = S_{AB}T$$

((Note))

$$S_{AB} = \frac{\Delta V_{AB}}{\Delta T} = \frac{e\Delta V_{AB}}{e\Delta T} = \frac{h_A - h_B}{e\Delta T} = \frac{\Pi_{AB}}{\Delta T} \quad \text{or} \quad \Pi_{AB} = S_{AB}\Delta T$$



(c) Thomson effect

We consider a single metal A, where a current density is flowing and a temperature gradient exists.

$$J = n_A e v_A = n_A' e v_A',$$

$$(J_u)_A = n_A h_A v_A, \qquad (J_u')_A = n_A' h_A' v_A' = n_A' (h_A + \frac{\partial h_A}{\partial T} \Delta T) v_A$$

Thus we get

$$\left(\Delta J_u\right)_A = n_A h_A v_A - n_A' (h_A + \frac{\partial h_A}{\partial T} \Delta T) v_A'$$

= $-\frac{J_e}{e} \frac{\partial h_A}{\partial T} \Delta T$

or

$$\frac{\left(\Delta J_{u}\right)_{A}}{\Delta x} = -\frac{J_{e}}{e}\frac{\partial h_{A}}{\partial T}\frac{\Delta T}{\Delta x} = -\mu_{T}J_{e}\frac{\Delta T}{\Delta x}$$

The heat is released or absorbed in a conductor in which a fixed temperature gradient and an electric field exist. This effect is called the Thomson effect. The Thomson coefficient μ_T is defined as

$$\mu_T = \frac{1}{e} \frac{\partial h_A}{\partial T}$$

If $\varepsilon_A = h_A = \frac{3}{2}k_BT$ (Maxwell-Boltzmann statistics)

$$\mu_T = \frac{3k_B}{2e} = 129.26 \ \mu \text{V/K}$$

 μ_T can be rewritten as

$$\mu_T = \frac{1}{e} \tilde{c}_{el}$$

where \tilde{c}_{el} is the heat capacity per electron. It was because of this connection that Thomson suggested that the Thomson heat be regarded as the specific heat of electricity.

We note that

$$\frac{dQ}{dt} = J_e E = \rho J_e^2 - \mu_T J_e \nabla_r T$$
$$\mu_T = T \frac{dS}{dT}$$

The thermoelectric power of a substance is obtained from the Thomson coefficient by integration,

3. Derivation of thermoelectric power (D.K.C. MacDonald)

We start with two equations for current density and heat current density

$$J_{e} = \sigma (E + \frac{1}{e} \frac{\partial \mu}{\partial x}) - \sigma S \frac{\partial T}{\partial x}$$
$$J_{Q} = -\kappa \frac{\partial T}{\partial x} - \sigma ST (E + \frac{1}{e} \frac{\partial \mu}{\partial x})$$

((Thermoelectric power))

When $J_e = 0$ (in open circuit)

$$S = \frac{E_x}{\left(\frac{\partial T}{\partial x}\right)} + \frac{1}{e} \frac{\frac{\partial \mu}{\partial x}}{\frac{\partial T}{\partial x}} = \frac{E_x}{\left(\frac{\partial T}{\partial x}\right)} + \frac{1}{e} \frac{\partial \mu}{\partial T}$$

Using the Boltzmann equation, we calculate the current density as

$$J_{x} = \frac{1}{V} \sum_{k} (-e) v_{k} \delta f_{k} = \frac{1}{V} \frac{2V}{(2\pi)^{3}} \int (-e) v_{k} \delta f_{k} dk$$

or

$$J_{x} = -\frac{e}{4\pi^{3}} \int v_{x} \delta f_{k} dk$$
$$= -\frac{e}{4\pi^{3}} \int dk (\frac{e\tau}{\hbar} v_{x} E_{x} \frac{\partial f_{0}}{\partial k_{x}} - \tau v_{x}^{2} \frac{\partial T}{\partial x} \frac{\partial f_{0}}{\partial T})$$

with

$$\delta f_{k} = \frac{e\tau}{\hbar} E_{x} \frac{\partial f}{\partial k_{x}} - \tau v_{x} \frac{\partial f}{\partial x} = \frac{e\tau}{m} E_{x} \frac{\partial f}{\partial v_{x}} - \tau v_{x} \frac{\partial T}{\partial x} \frac{\partial f}{\partial T}$$

The condition of $J_x = 0$ (open circuit) leads to

$$E_x \int d\mathbf{k} \, \frac{e\tau}{m} v_x \frac{\partial f_0}{\partial v_x} = \frac{\partial T}{\partial x} \int d\mathbf{k} \, \tau v_x^2 \frac{\partial f_0}{\partial T}$$

For convenience, we use $dv = dv_x dv_y dv_z$ instead $dk = dk_x dk_y dk_z$,

$$\frac{E_x}{\frac{\partial T}{\partial x}} = \frac{m}{e} \frac{\int d\mathbf{k} v_x^2 \frac{\partial f_0}{\partial T}}{\int d\mathbf{k} v_x \frac{\partial f_0}{\partial v_x}} = \frac{m}{e} \frac{\int d\mathbf{v} v_x^2 \frac{\partial f_0}{\partial T}}{\int d\mathbf{v} v_x \frac{\partial f_0}{\partial v_x}}$$

or

$$\frac{E_x}{\frac{\partial T}{\partial x}} = -\frac{m}{e} \frac{\int d\mathbf{v} v_x^2 \frac{\partial f_0}{\partial T}}{\int d\mathbf{v} f_0}$$

We use $v_x^2 \rightarrow \frac{1}{3}v^2$. Then we get

$$\frac{E_x}{\frac{\partial T}{\partial x}} = -\frac{m}{3e} \frac{\frac{\partial}{\partial T} \int dv v^2 f_0}{\int dv f_0} = -\frac{2}{3e} \frac{\frac{\partial}{\partial T} \int dv \frac{m}{2} v^2 f_0}{\int dv f_0} = -\frac{2}{3e} \frac{1}{N} \frac{\partial U}{\partial T}$$

or

$$\frac{\frac{E_x}{\partial T}}{\frac{\partial x}{\partial x}} = -\frac{2}{3e}c_{el}$$

where U is the internal energy of the system and the specific heat capacity per electron is

$$c_{el} = \frac{C_{el}}{N} = \frac{1}{N} \frac{dU}{dT} = \frac{\pi^2 k_B^2 T}{2\varepsilon_F}$$

To obtain the Seebeck potential or absolute thermoelectric power we have primarily to determine the electric field produced in the conductor when a temperature gradient and no current is permitted to flow in the circuit (i.e. open conditions). One can then show rather generally that the absolute thermoelectric power of a conductor is given by:

$$S = -\frac{2c_{el}}{3e} + \frac{1}{e}\frac{d\mu}{dT}$$

We use the chemical potential of free electron derived from the Sommerfeld's formula

$$\mu \approx \varepsilon_F - \frac{\pi^2 k_B^2 T^2}{12\varepsilon_F}$$

where ε_F is the Fermi energy at T = 0 K. Then we have

$$S = -\frac{\pi^{2}k_{B}^{2}T}{3e\varepsilon_{F}} - \frac{\pi^{2}k_{B}^{2}T}{6e\varepsilon_{F}} = -\frac{\pi^{2}k_{B}^{2}T}{2e\varepsilon_{F}} = -\frac{c_{el}}{e}$$

4. Definition of current density and heat current density

In order to get the general form of thermoelectric power, we use the following current density along the x direction as

$$J_{x} = \frac{e^{2}E_{x}}{4\pi^{3}\hbar} \int \tau(\varepsilon) \frac{v_{x}^{2}}{v} dS(-\frac{\partial f_{0}}{\partial \varepsilon_{k}}) d\varepsilon.$$

We define the conductivity as

$$\sigma_x(\varepsilon) = \frac{e^2}{4\pi^3\hbar} \int \frac{\tau v_x^2}{v} dS \,.$$

Thus the current density can be rewritten as

$$J_{x} = E_{x} \int \sigma(\varepsilon) (-\frac{\partial f_{0}}{\partial \varepsilon_{k}}) d\varepsilon ,$$

which is in effect the conductivity of the conduction electrons that have energy ε .



The charge ΔQ passing through the area ΔA per unit time Δt

$$\Delta Q = qn\Delta V = qn(v\Delta t)\Delta A$$

or



The energy passing through the area ΔA per unit time Δt

$$\Delta U = hn\Delta V = hn(v\Delta t)\Delta A$$

or

$$\frac{\Delta U}{\Delta t} = hnv\Delta A$$

where h is the energy of electron

$$h = \varepsilon - \mu$$

and μ is the chemical potential. The Fermi energy ε_F is the chemical potential at T = 0 K. The Peltier heat is defined by

$$\Pi = \frac{\sum_{i} h_i v_i}{\sum_{i} q_i v_i}$$

The thermoelectric power S is related to the Peltier heat as

$$\Pi = TS.$$

The thermoelectric power S is obtained as

$$S = -\frac{1}{eT} \frac{\sum_{i} (\varepsilon_i - \mu) v_i}{\sum_{i} v_i}.$$

This can be rewritten as

$$S = -\frac{1}{eT} \frac{\int_{0}^{\infty} d\varepsilon \sigma_{x}(\varepsilon)(\varepsilon - \mu)(-\frac{df_{0}}{d\varepsilon})}{\int_{0}^{\infty} d\varepsilon \sigma_{x}(\varepsilon)(-\frac{df_{0}}{d\varepsilon})}$$

5. The expression of thermoelectric power

$$I = \int_{0}^{\infty} \sigma(\varepsilon)(\varepsilon - \mu) \frac{\partial f_0}{\partial \varepsilon} d\varepsilon = -\int_{0}^{\infty} g'(\varepsilon) f_0 d\varepsilon$$

where

$$g(\varepsilon) = \sigma(\varepsilon)(\varepsilon - \mu)$$

Using the Sommerfeld formula, we get

$$I = -\int_{0}^{\infty} g'(\varepsilon) f_{0} d\varepsilon$$

= $-\int_{0}^{\mu} g'(\varepsilon) d\varepsilon - \frac{\pi^{2} k_{B}^{2} T^{2}}{6} g''(\mu)$
= $-[g(\varepsilon)]_{0}^{\mu} - \frac{\pi^{2} k_{B}^{2} T^{2}}{6} g''(\mu)$
= $-\frac{\pi^{2} k_{B}^{2} T^{2}}{6} g''(\mu)$

Noting that

$$g'(\mu) = \frac{\partial \sigma(\varepsilon)}{\partial \varepsilon} (\varepsilon - \mu) + \sigma(\varepsilon)$$
$$g''(\mu) \approx g''(\varepsilon_F) = 2 \frac{\partial \sigma(\varepsilon)}{\partial \varepsilon} |_{\varepsilon = \varepsilon_F}$$

we have

$$I = -\frac{\pi^2 k_B^2 T^2}{3} \frac{\partial \sigma(\varepsilon)}{\partial \varepsilon} \Big|_{\varepsilon = \varepsilon_F}$$

The thermopower can be expressed as

$$S = -\frac{\pi^2}{3} \frac{k_B^2 T^2}{eT} \frac{1}{\sigma(\varepsilon)} \frac{\partial \sigma(\varepsilon)}{\partial \varepsilon} \Big|_{\varepsilon = \varepsilon_F}$$
$$= -\frac{\pi^2}{3} \frac{k_B}{e} k_B T \frac{\partial \ln \sigma(\varepsilon)}{\partial \varepsilon} \Big|_{\varepsilon = \varepsilon_F}$$

Using

$$\frac{\partial \ln \sigma(\varepsilon)}{\partial \varepsilon} = \frac{\partial \ln \varepsilon}{\partial \varepsilon} \frac{\partial \ln \sigma(\varepsilon)}{\partial \ln \varepsilon} = \frac{1}{\varepsilon} \frac{\partial \ln \sigma(\varepsilon)}{\partial \ln \varepsilon}$$

S can be rewritten as

$$S = -\frac{\pi^2 k_B^2 T}{3e\varepsilon_F} \frac{\partial \ln \sigma(\varepsilon)}{\partial \ln \varepsilon} \Big|_{\varepsilon = \varepsilon_F}$$

This expression for S provides the most valuable way of interpreting the thermoelectric power of metal.

6. Phonon drag

Phonon flow frags electrons with it and extra ele4ctrons tend to pile up at the cold end over and above those electrons which are there as a result of the diffusive process. We assume a gas of phonons in which electrons are travelling. The average pressure on the electrons due to the phonon gas is

$$P = \frac{1}{3}U(T)$$

where U is the energy per unit volume of this gas. When the temperature is homogeneous, this pressure is isotropic and has no effect on any preferential orientation for electron travel. But a temperature gradient would generate a pressure gradient; in other words, a net force on electrons along the temperature gradient. The density of this force would be

$$f = -\nabla P = -\frac{1}{3} \frac{\partial U}{\partial T} \nabla T = -\frac{1}{3} C_L \nabla T$$

This force is to be counterbalanced to keep the net flow zero. This can be done by an electric field acting on the charge of carriers, with a density of

$$f = neE$$

Here n is the carrier density, and -e is the charge of electron. Now the temperature derivative of the phonon's energy density U(T), is basically the phon specific heat C_L . So, all this will add up to

$$neE = -\frac{1}{3}C_L \nabla T$$

In other words, the additional Seebeck signal caused by phonon drag is

$$S_g = -\frac{E}{\nabla T} = \frac{1}{3} \frac{C_L}{ne}$$

The phonon drag is proportional to the phonon specific heat. The larger the capacity of the lattice to stock energy, the more efficient are phonons to damp the impulsion of the travelling electrons. Phonon drag also inversely proportional to the carrier density: the lower concentration, the higher the ability of phonons to pull them.



Fig. Sketch of idealized absolute thermoelectric power of a simple quasi-free electron metal. A: electron diffusion component of thermoelectric power approximately proportional to T. B: Phonon drag component with magnitude increasing as T^3 at very low temperatures $(T \ll \Theta)$, and decaying as 1/T at high temperatures $(T > \Theta)$ [D.K.C. MacDonald, 1962].

7. Puzzles ((Behnia))

For more than thirty years the absolute thermoelectric power of pure samples of monovalent metals has remained a nagging embarrassment to the theory of the ordinary electronic transport properties of solids. All familiar simple theory has promised us that in these materials the sign of the electron-diffusion contribution to the thermopower should be that of the charge carriers as determined by the Hall effect, i.e. negative; but instead it turns out to be positive for Cu, Ag, Au and—even more perversely—for Li. At least two generations of experimentalists have remained completely unshaken in testifying to these results as obstinate facts of life. These are the opening sentences of a 1967 paper by John E. Robinson, who presented a simple solution to this puzzle [Robinson 1967]. Mysteriously, decades later, both the puzzle and the solution he proposed are widely forgotten. The focus of contemporary condensed-matter physics is elsewhere. The puzzle of thermoelectricity in noble metals becomes more striking when one considers that the intricate details of the Fermi surface of these materials are well established and this knowledge is a testimony to the oft celebrated glory of the band theory of metals. The electronic specific heat of noble metals has also been measured with great precision [Martin 1973]. Intriguingly, q, the

dimensionless ratio of thermopower to the electronic specific heat, is close to unity for all these three metals. This confirms that we are indeed facing diffusive thermoelectricity of the right magnitude but with the wrong sign and looking like what one would expect for a free gas of holes! But this cannot be.



Fig. Thermoelectric power of Au (gold), Cu (copper) and Ag (silver) [D.K.C. MacDonald, Thermoelectricity: An Introduction to the Principles (Dover, 2006)



Fig. Thermopower of Li (MacDonald, 1962)

8. Explanation for the positive thermopower in Cu (Ziman, Huebener)





Fig. (a) Electron-like Fermi surface. (b) Hole-like Fermi surface.

The thermopower due to the phonon drag in Cu can be explained in terms of the local differential geometry of the Fermi surface. We have two cases as shown in Fig. If the phonon wave vector, \boldsymbol{q} , in joining the two electron states \boldsymbol{k} and \boldsymbol{k}' , passes through a region in \boldsymbol{k} space, which is occupied with electrons, \boldsymbol{k} and \boldsymbol{k}' are on an electron-like Fermi surface. The group velocity $\boldsymbol{v}_k = \frac{1}{\hbar} \nabla_k \varepsilon_k$ is normal to the Fermi surface. The main component of the difference $\boldsymbol{v}_k' - \boldsymbol{v}_k$ is oriented in the direction of \boldsymbol{q} . Because of the negative electronic charge, we then have a negative phonon drag thermopower. On the other hand, if \boldsymbol{q} passes a region in the \boldsymbol{k} -space which is

unoccupied by electrons, k and k' are on a hole-like Fermi surface. The main component of the difference $v_k' - v_k$ is then oriented opposite to q, and we have a positive phonon drag thermopower.

The curvature of the Fermi surface (the dog's bone) in Cu is such that we are dealing with hole carriers which contribute a positive thermopower. Actually the dog's bone is a hole-like Fermi surface. Note that a negative sign of the Hall effect in Cu may arise from the electron-like Fermi surface (the belly).



Fig. Fermi surface of Cu (M. Suzuki and I.S. Suzuki)

https://www.researchgate.net/publication/322027719_Understanding_of_open_orbits_in_copper _Fermi_surface_with_the_use_of_Mathematica

REFERENCES

J.S. Dugdale, The Electrical Properties of Metals and Alloys (Dover, 2016).
D.K.C. MacDonald, Thermoelectricity: An Introduction to the Principles (Dover, 2006)
R.D. Barnard, Thermoelectricity in Metals and Alloys (Taylor & Francis, 1972)
J.L. Olsen, Electron Transport in Metals (Interscience, 1962).
H.J. Goldsmid, Introduction to Thermoelectricity (Springer, 2010).
F.J. Blatt, P.A. Schroeder, C.L. Foiles, and D. Greig (Plenum Press, 1`976).
F.J. Blatt and P.A. Schroeder, Thermoelectricity in Metallic Conductors (Springer, 1977).

K. Behnia, Fundamentals of Thermoelectricity (Oxford, 2015).

J.M. Ziman, The Physics of Metals 1. Electronics, edited by J.M. Ziman (Cambridge, 1969).

APPENDIX I

(a) Heat capacity:

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

(b) Chemical potential:

$$\mu = \varepsilon_F - \frac{\pi^2}{6} k_B^2 T^2 \left[\frac{d \ln D(\varepsilon)}{d\varepsilon}\right]_{\varepsilon = \varepsilon_F}$$
$$= \varepsilon_F - \frac{\pi^2 k_B^2 T^2}{6\varepsilon_F} \left[\frac{d \ln D(\varepsilon)}{d \ln \varepsilon}\right]_{\varepsilon = \varepsilon_F}$$

(c) Free electron Fermi gas model

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

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

$$c_{el} = \frac{C_{el}}{N} = \frac{1}{3}\pi^{2}k_{B}^{2}\frac{D(\varepsilon_{F})}{N}T = \frac{1}{3}\pi^{2}k_{B}^{2}\frac{3}{2\varepsilon_{F}}T = \frac{\pi^{2}k_{B}^{2}T}{2\varepsilon_{F}} = \frac{\pi^{2}k_{B}}{2}\frac{T}{T_{F}}$$
$$\mu = \varepsilon_{F} - \frac{\pi^{2}k_{B}^{2}T^{2}}{12\varepsilon_{F}}$$

APPENDIX II Thermoelectric power of typical metals

(a) V, Nb, and Ta



Fig. Thermoelectric power of V (vanadium), Nb (niobium) and Ta (tantalum) [R.D. Barnard, Thermoelectricity in Metals and Alloys (Taylor & Francis, 1972)

(b) Mg



Fig. Thermopower of Mg (from Rowe and Schroeder).

(c) Zn



Fig. Thermopower of Zn (from Rowe and Schroeder 1970). Parallel and perpendicular to the hexagonal axis.





Fig. Thermopower of Cd (from Rowe and Schroeder 1970). Parallel and perpendicular to the hexagonal axis.

(e) Rh, Ir



Fig. Thermopower of Rh and Ir (From Carter, Davidson, and Schroeder, 1970).

(f) Pt



Fig. Thermopower of Pt (From Huebener, 1965)

(g) Alkali metals



Fig. Thermopower of alkali metals