Homework #6 - Solutions

Problem 1 - Work Functions

The work function of a metal, Φ, represents the energy needed to eject and electron from the Fermi level to the vacuum level. However, this energy depends on the surface of the crystal involved on extracting the electron. Φ depends on the crystal plane from which the electron is ejected. Surface conditions such as a thin oxide layer or contaminants on the surface would obviously modify the observed Φ. Measurements of Φ are therefore done under high vacuum condition on clean crystal surfaces. Table 4.6 lists measured Φ for single crystal and polycrystalline samples of Al, Au and Ag that have a cubic crystal structure (FCC). Φ has been obtained for three different planes in the case of single crystals.

Table 4.6 The work function Φ (in eV) of Al, Au, Ag for single crystal and polycrystalline samples.

	Φ (eV)			
Sample	(100)	(110)	(111)	Polycrystalline
Aluminum (Al)	4.41	4.06	4.24	4.28
Gold (Au)	5.47	5.37	5.31	5.40
Silver (Ag)	4.64	4.52	4.74	4.65

Michaelson (1978) and Uda (1998)

a. What are the average Φ_{av} and mean standard deviation of the work function for the three planes for each crystal?

From the data in the table, we have

In[•]:=
```
Print["The average Φ and standard devations are \nAluminum (Al): \t",
 Mean[{4.41, 4.06, 4.24}], " ± ", StandardDeviation[{4.41, 4.06, 4.24}],
 " eV\n    Gold (Au): \t", Mean[{5.47, 5.37, 5.31}], " ± ",
 StandardDeviation[{5.47, 5.37, 5.31}], " eV\n  Silver (Ag): \t",
 Mean[{4.64, 4.52, 4.74}], " ± ", StandardDeviation[{4.64, 4.52, 4.74}], " eV"]
```

```
The average Φ and standard devations are
Aluminum (Al):      4.23667 ± 0.175024 eV
    Gold (Au):      5.38333 ± 0.080829 eV
  Silver (Ag):      4.63333 ± 0.110151 eV
```

b. What is the percentage difference between the Φ for the polycrystalline sample and Φ_{av}?

The percent difference is

$$\%\,\text{diff} = \left| \frac{\Phi_{poly} - \Phi_{av}}{\text{Mean}\left[\Phi_{poly}, \Phi_{av}\right]} \right| \times 100$$

So, we have

```
In[•]:= Print["The percent differences between Φpoly and Φav are \nAluminum (Al): \t",
 Abs[4.28 - Mean[{4.41, 4.06, 4.24}]] / Mean[{4.41, 4.06, 4.24, 4.28}] 100,
 " %\n    Gold (Au): \t",
 Abs[5.40 - Mean[{5.47, 5.37, 5.31}]] / Mean[{5.47, 5.37, 5.31, 5.40}] 100,
 " %\n  Silver (Ag): \t",
 Abs[4.65 - Mean[{4.64, 4.52, 4.74}]] / Mean[{4.64, 4.52, 4.74, 4.65}] 100, " %"]
```

```
The percent differences between Φpoly and Φav are
          Aluminum (Al):     1.02021 %
             Gold (Au):     0.309358 %
           Silver (Ag):     0.359389 %
```

which are pretty small and indicates that the polycrystalline work functions are very close to a simple average of the single crystal workfunctions for the above plane. However, in some cases, materials have a crystal direction with a much lower surface energy, so a polycrystalline sample may be dominated by certain plane orientations and a simple average would not be accurate.

Problem 2 - Fermi Energy

Eqn. 4.22 in Kasap gives the Fermi energy (at 0 K) as $E_{F0} = \left(\frac{h^2}{8\,m_e}\right)\left(\frac{3n}{\pi}\right)^{2/3}$, where n is the conduction electron concentration. This is equivalent to the equation we derived in class. Kasap Eqn. 4.23 gives the Fermi energy as a function of temperature: $E_F = E_{F0}\left[1 - \frac{\pi^2}{12}\left(\frac{kT}{E_{F0}}\right)^2\right]$.

a. If each copper atom contributes one conduction electron, what is the Fermi energy of copper at 293 K?

Knowing the valence of Cu, its density, and its atomic mass, the electron concentration (in m^{-3}) is

```
In[•]:= nCu = 1 × 6.022 × 10^23 × 8.96 × 10^3 / (63.55 × 10^-3)
```

$$8.4905 \times 10^{28}$$

So at 0 K, the Fermi energy of Cu (in Joules) is

```
In[•]:= EF0KCu = ((6.626 × 10^-34)^2 / (8 × 9.109 × 10^-31)) (3 nCu / π)^(2/3)
```

$$1.12861 \times 10^{-18}$$

At 293 K, the Fermi energy of Cu (in Joules) is

```
In[•]:= EF293KCu = EF0KCu (1 - π^2/12 (1.381 × 10^-23 × 293 / EF0KCu)^2)
```

$$1.1286 \times 10^{-18}$$

In eV, the Fermi energy of Cu at 293 K is

In[•]:= `EF293KCu / (1.602 × 10^-19)`

Out[•]= `7.04495`

Thus, the Fermi energy of Cu at 293 *K* is 7.04 eV.

b. Since this Fermi energy was derived from the Sommerfeld model, the energy is entirely kinetic energy (the energy in the infinite 3D box was zero). Thus, what is the speed v_F for conduction electrons in copper with energies near the Fermi energy calculated in part (a)?

Since the energy is entirely kinetic energy, the electrons at the Fermi energy in a metal have a speed given by

$$KE = \frac{1}{2} m_e v_F^2 = E_F \Rightarrow v_F = \sqrt{\frac{2 E_F}{m_e}}$$

In[•]:= `vF = Sqrt[2 EF293KCu / (9.109 × 10^-31)]`

Out[•]= 1.57416×10^6

Thus, the speed of electrons at Fermi energy of Cu at 293 *K* is 1.57×10^6 *m/s*.

c. If the conduction electrons in copper were treated as an ideal gas following Maxwell-Boltzmann statistics with 1/2kT per degree of freedom and 3 degrees of freedom, what would be their thermal speed v_{th}?

If the conduction electrons in a metal followed Maxwell-Boltzmann statistics, their thermal speed would be

$$\frac{1}{2} m_e v_{th}^2 = 3 \times \left(\frac{1}{2} kT\right) \Rightarrow v_{th} = \sqrt{\frac{3 kT}{m_e}}$$

In[•]:= `vth = Sqrt[3 × (1.381 × 10^-23) × 293 / (9.109 × 10^-31)]`

Out[•]= `115 440.`

The thermal speed of electrons at 293 *K* following Maxwell – Boltzmann statistics is 1.15×10^5 *m/s*.

d. Comment on the difference (or ratio) of v_F to v_{th} by comparing your results from parts (b) and (c). What fundamental quantum mechanical phenomena leads to this difference?

From the above results, we have

In[•]:= `speedratio = vF / vth`

Out[•]= `13.6362`

The velocity of electrons at the Fermi energy in Cu at 293 K is nearly 14 times higher than it would be if they followed Maxwell – Boltzmann statistics. However, at the Fermi energy in a metal, we know that the electrons are described by Fermi – Dirac statistics since they must obey the Pauli exclusion principle and the number of electrons is on the order of the number of available states. To follow the exclusion principle, they must occupy states with higher energy and thus have a higher velocity.

e. The electron drift mobility in copper, from Hall effect measurements, is 33 $cm^2\ V^{-1}\ s^{-1}$. This mobility can be used to calculate the mean free time (or mean scattering time) τ. Calculate the mean free path l_F for electrons with speed v_F.

The drift mobility is related to the mean scattering time τ by $\tau = \frac{\mu m_e}{e}$. With this mean free time, we can calculate the mean free path for electrons with speed v_F: $l_F = v_F \tau$

```
In[•]:= lF = vF 33 × 10^-4 × 9.109 × 10^-31 / 1.602 × 10^-19
Out[•]= 2.95374 × 10^-8
```

The mean free path for electrons in Cu at 293 K is ~29.5 nm.

Problem 3 - Sommerfeld to Drude

In terms of the density of states $g(E_F)$, the general expression for the conductivity of metals at E_F given by

$$\sigma = \frac{1}{3} e^2 v_F^2 \tau g(E_F)$$

Using expressions for v_F and E_F, show that within the free electron theory (Sommerfeld model), this reduces to $\sigma = e^2 n\tau / m_e$, the Drude expression.

As we found above, at the Fermi energy

$$v_F^2 = \frac{2 E_F}{m_e}$$

The density of states is

$$g(E_F) = 8\pi \left(\frac{m_e}{h^2}\right)^{3/2} (2 E_F)^{1/2}$$

and the Fermi energy is

$$E_F = \frac{h^2}{8 m_e} \left(\frac{3 n}{\pi}\right)^{2/3}$$

Putting these in the above equation for conductivity, we have

$$\sigma = \frac{1}{3} e^2 \left(\frac{2 E_F}{m_e}\right) \tau\, 8\pi \left(\frac{m_e}{h^2}\right)^{3/2} (2 E_F)^{1/2}$$

$$\sigma = \frac{1}{3} e^2 \left(\frac{2\sqrt{2}}{m_e}\right) \tau\, 8\pi \left(\frac{m_e}{h^2}\right)^{3/2} (E_F)^{3/2}$$

$$\sigma = \frac{1}{3} e^2 \left(\frac{2\sqrt{2}}{m_e}\right) \tau\, 8\pi \left(\frac{m_e}{h^2}\right)^{3/2} \left(\frac{h^2}{8 m_e} \left(\frac{3 n}{\pi}\right)^{2/3}\right)^{3/2}$$

$$\sigma = \frac{1}{3} e^2 \left(\frac{2\sqrt{2}}{m_e}\right) \tau\, 8\pi \left(\frac{m_e}{h^2}\right)^{3/2} \left(\frac{h^2}{8 m_e}\right)^{3/2} \left(\frac{3 n}{\pi}\right)$$

$$\boxed{\sigma = e^2 \left(\frac{\tau n}{m_e}\right)}, \text{ which is the Drude model result.}$$