MASSACHUSETTS INSTITUTE OF TECHNOLOGY

Physics of Solids II —6.732

Quiz #1 October 4, 1996

1. 30 points

$KMoO_3$ crystallizes in a cubic perovskite structure, where the atomic electronic configurations are K: $4s$, Mo: $4d^5 5s$, and O: $2s^2 2p^4$. The calculated electronic band structure is shown. Note 1 Rydberg is 13.6 eV.

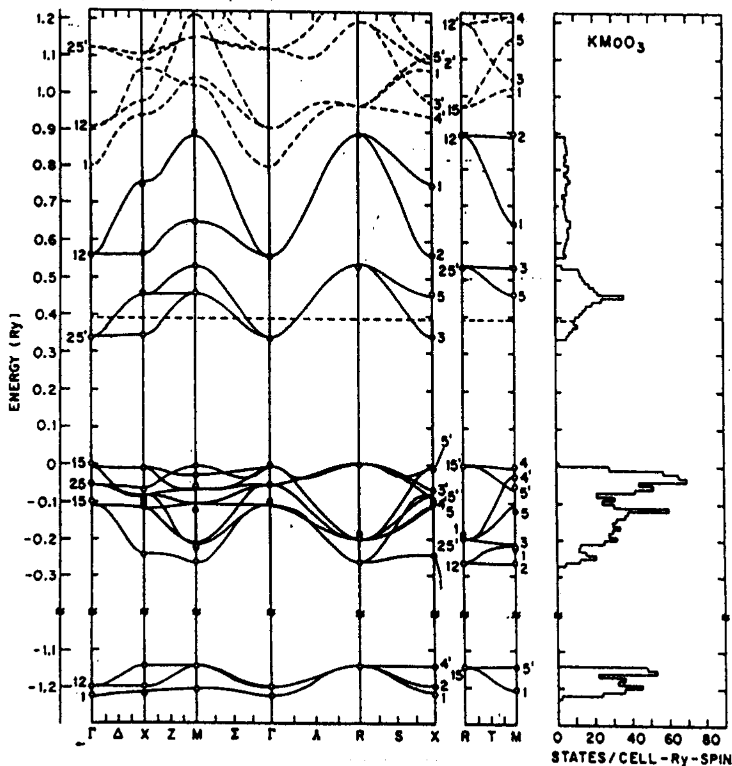
(a) Based on the one electron band diagram, is the material a metal, semiconductor or insulator?

(b) Which energy bands at $k = 0$ (the Γ-point) are derived from oxygen atomic levels?

(c) Which energy bands at $k = 0$ are derived from K atomic levels? and which from Mo atomic levels? Which are hybridized?

(d) What is the shape of the Fermi surface (or surfaces) around $k = 0$? Are the carriers at the Fermi level electrons or holes?

(e) Suppose that we could prepare $KNbO_3$ and $KZrO_3$ in the same cubic crystal structure (Nb: $4d^4 5s$ and Zr: $4d^2 5s^2$). What would you expect the shape of the Fermi surfaces to be in these cases? What is the nature of the electronic transport for each of the 3 cases (Mo, Nb, & Zr)?



1(a) metal because E_F goes through $\Gamma_{25'}$ bands. Further discussion in part (e)

(b) The Γ_{15}, Γ_{25} and Γ_{15} bands below $E=0$ (valence bands) are oxygen 2p-bands for 3 oxygen atoms / unit cell (perovskite structure), thereby accomodating $3\times 6 = 18$ electrons

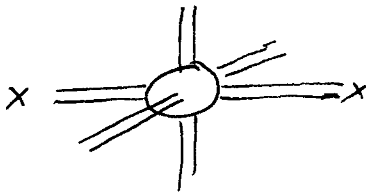
The Γ_1 and Γ_{12} bands are the three 2s bands for the three oxygen atoms. The linear combinations are

$$\Gamma_1 = \psi_1 + \psi_2 + \psi_3$$

$$\Gamma_{12} = \left\{ \begin{array}{l} \psi_1 + e^{2\pi i/3}\psi_2 + e^{-2\pi i/3}\psi_3 \\ \text{and } \psi_1 + e^{-2\pi i/3}\psi_2 + e^{2\pi i/3}\psi_3 \end{array} \right.$$

(c) $\Gamma_{25'}$ and Γ_{12} are hybridized 3d bands for K and 4d bands for Mo. The Γ_1 band relates to a hybridized 4s band for K and 5s band for Mo

(d) Electron Fermi surface is spherical around Γ point with cylindrical tubes stretching in the six (100) directions all the way out to the Brillouin zone boundary



(e) Number of electrons available from $KMoO_3$ is $K\to 1$, $Mo\to 6$, $O\to 3\times 6$ = total of 25 electrons

occupied $2s^2 \times 3 = 6$ electrons, $2p^6 \times 3 = 18$ electrons } → 24 electrons, so one is left for conduction band in $KMoO_3$

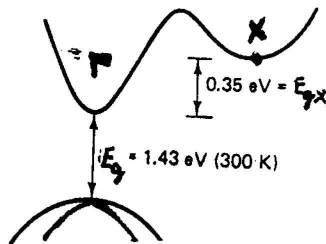
For $KNbO_3$ available number of electrons = 24, so $KNbO_3$ is a semiconductor with no Fermi surface

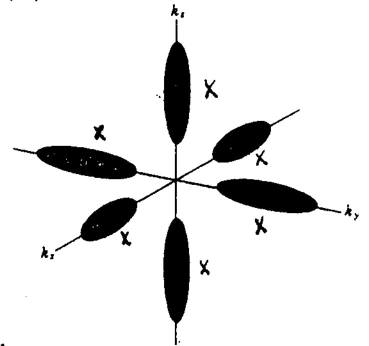
For $KZrO_3$ available number of electrons is 23, so $KZrO_3$ is a metal with a Fermi surface containing 1 hole/unit cell. Fermi surface stretches out to zone edge in many directions and E_F lies a little below $E=0$.

2.

40 points

The direct band gap semiconductor GaAs has a band gap of 1.43 eV at 300 K, and a second higher-lying conduction band extremum at the X-point in the Brillouin zone which is 0.35 eV above the Γ point conduction band minimum. Assume effective masses $m_e(\Gamma) = 0.065m_0$ for the Γ-point electrons, $m_l(X) = 1.2m_0$ and $m_t(X) = 0.3m_0$ for the X-point electrons, and $m_{hh}(\Gamma) = 0.5m_0$ and $m_{lh}(\Gamma) = 0.12m_0$ for the Γ-point heavy and light holes. Assume all bands are parabolic.





(a) With intrinsic material and only thermal excitation, at what carrier concentration will the number of Γ point electrons equal the number of X-point electrons?

(b) For n-type material at $T = 0$K, what is the carrier concentration just before the X-point electrons start to fill?

(c) Where does the Fermi level lie for cases (a) and (b)?

(d) Physically, what happens to the temperature dependence of the Fermi level as the X-point electrons start to fill. Indicate the conditions that must be satisfied when both Γ-point and X-point electrons are present?

(e) Compare the electrical conductivity of case (a) and case (b). Include contributions from all carriers in both cases.

(f) Write an expression for the Hall coefficient corresponding to (a) and including contributions from the holes.

(a) First I give a solution to the $T=0$ problem, and consider state filling

For Γ-point electrons, $\quad n_e(\Gamma) = \frac{1}{3\pi^2}\left(\frac{2m_e(\Gamma)E_F}{\hbar^2}\right)^{3/2}$

X-point electrons $\quad n_e(X) = \frac{3}{3\pi^2}\left(\frac{2[E_F - E_{gX}]}{\hbar^2}\right)^{3/2}(m_\ell m_t^2)^{1/2}$

When $n_e(X) = n_e(\Gamma)$ $\quad [m_e(\Gamma)E_F]^{3/2} = 3\,[E_F - E_{gX}]^{3/2}(m_\ell m_t^2)^{1/2}$

Substitution for values of masses, E_{gX} yields

$$\frac{E_F}{E_F - E_{gX}} = 22.75 \qquad \text{or } E_F = 0.366\text{ eV}$$

Then substitution in $n_e(\Gamma)$ relation yields

$$n_e(\Gamma) = \frac{1}{3\pi^2}\left[\frac{2\times 9.1\times10^{-28}\times 0.065\,(.366)\times 1.6\times10^{-12}}{(1.054\times10^{-27})^3}\right]^{3/2}$$

$$n_e(\Gamma) = 1.66\times10^{19}/\text{cm}^3 = n_e(X)$$

$$n_e[\text{total}] = 3.32\times10^{19}/\text{cm}^3$$

(b) When all electrons fill states up to $E_F = 0.35\,eV$ at $T=0$

$$n_e(\Gamma) = \frac{1}{3\pi^2}\left(\frac{2\,m_e(\Gamma)\,E_F}{\hbar^2}\right)^{3/2} \qquad E_F = 0.35\,eV$$

making use of arithmetic done above

we can write $n_e(\Gamma) = 1.66\times10^{19}/cm^3 \left[\frac{.35}{.366}\right]^{3/2} = 1.55\times10^{19}/cm^3$

This shows that there is not much change in the Γ point electron carrier density for the two cases.
Of course, the hole concentration in (a) is $3.32\times10^{19}/cm^3$ while in case (b) it is $1.55\times10^{19}/cm^3$.

(a,b) Now we will consider the thermal excitation problem
We then write expressions for each of the carrier types:
For the electrons:

$$n_e(\Gamma) = 2\left(\frac{k_B T}{2\pi\hbar^2}\right)^{3/2}\left[m_e(\Gamma)\right]^{3/2} e^{-E_F^e/k_B T}$$

while for the X-point electrons

$$n_e(X) = 2\cdot3\left(\frac{k_B T}{2\pi\hbar^2}\right)^{3/2}\left(m_\ell m_t^2\right)^{1/2} e^{-(E_F^e + E_{gx})/k_B T}$$

For the holes

$$n_h = n_e = n_e(\Gamma) + n_e(X) = 2\left(\frac{k_B T}{2\pi\hbar^2}\right)^{3/2}\left[m_{hh}^{3/2} + m_{\ell h}^{3/2}\right] e^{-E_F^h/k_B T}$$

subject to the condition $E_F^e + E_F^h = E_g$

To solve for the condition $n_e(X) = n_e(\Gamma)$ require knowledge of E_F^e which is temperature dependent. The temperature dependence of E_F^e is quite weak so we can do some iterative solutions to find n_e when $n_e(\Gamma) = n_e(X)$.
We give the numerical solution in connection with (c) which determines E_F^e.

(c) We now consider the temperature dependence of E_F^e to find E_F^e when $n_e(\Gamma) = n_e(X)$.

The condition $n_e = n_h$ is used to find E_F^e, so that

$$[m_e(\Gamma)]^{3/2} e^{-E_F^e/k_BT} + 3(m_e m_t^2)^{1/2} e^{-(E_F^e + E_{gX})/k_BT} = [m_{hh}^{3/2} + m_{lh}^{3/2}] e^{-\frac{(E_g - E_F^e)}{k_BT}}$$

Solution for E_F^e yields a general expression for $E_F^e(T)$

so that $$E_F^e = \frac{E_g}{2} - \frac{k_BT}{2} \ln F(m^*, T)$$

where $$F(m^*, T) = \frac{[m_{hh}^{3/2} + m_{lh}^{3/2}]}{\left[\{m_e(\Gamma)\}^{3/2} + 3(m_e m_t^2)^{1/2} e^{-E_{gX}/k_BT}\right]}$$

When the number of Γ point electrons = number of X point electrons

$$[m_e(\Gamma)]^{3/2} e^{-E_F^e/k_BT} = 3(m_e m_t^2)^{1/2} e^{-E_F^e/k_BT} e^{-E_{gX}/k_BT}$$

so that $$e^{-E_{gX}/k_BT} = \frac{[m_e(\Gamma)]^{3/2}}{3(m_e m_t^2)^{1/2}}$$

or $$k_BT = \frac{E_g}{\ln\left[\frac{3(m_e m_t^2)^{1/2}}{(m_e(\Gamma))^{3/2}}\right]} = \frac{0.35 \text{ eV}}{\ln(59.5)} = \frac{0.35}{4.086} \text{ eV} = .086 \text{ eV}$$

$T = 1028$ K below melting point of GaAs ($T_m = 1510$ K)

at this temperature

$$E_F^e = \frac{1.43}{2} - \frac{.086}{2} \ln F(m^*, T) = .715 - .043 (\ln 11.9) = .609 \text{ eV}$$

In the event that there is only occupation of the Γ pt electron pocket

$$E_F = \frac{E_g}{2} - k_BT\,(1.58) \qquad \text{or for } T = 1028\text{ K} \qquad E_F = .579 \text{ eV}$$

the carrier density for the Γ point electrons is

$$n_e = 2\left[\frac{m_e(\Gamma)}{2\pi\hbar^2}\right]^{3/2} (k_BT)^{3/2} e^{-E_F^e/k_BT} = 1.41 \times 10^{16}/\text{cm}^3$$

(d) Physically when the X point electrons start to fill, they fill very rapidly, so that E_F drops in order for the holes to remain equal to the total number of electrons. At low T the conduction band is governed by a low density of states while at high T the conduction density of states is large.

(e) In general the conductivity will be given by

$$\sigma = \frac{n_e(\Gamma) e^2\tau}{m_e(\Gamma)} + \frac{n_e(X) e^2\tau}{m_e(X)} + \frac{n_{hh} e^2\tau}{m_{hh}} + \frac{n_{lh} e^2\tau}{m_{lh}}$$

assuminging that τ is the same for all carriers. (this is the simplest assumption).

$n_e = n_e(\Gamma) + n_e(X)$

$n_h = n_{hh} + n_{lh}$

$n_e = n_h$ so that $\quad \frac{n_{hh}}{n_{lh}} = \left(\frac{m_{hh}}{m_{lh}}\right)^{3/2} = 8.503$

$n_{lh} = n_e\,(.105)$

$n_{hh} = n_e\,(.895)$

case (b) $\quad n_e(X) = 0$ and $n_e = n_e(\Gamma) = 1.55\times10^{19}/cm^3$

case (a) $\quad n_e(X) = n_e(\Gamma) = 1.41\times10^{16}/cm^3$

$m_e(X)$ is the effective drift mass for X-point conduction

where $\frac{1}{m_e(X)} = \frac{1}{3}\left(\frac{1}{m_l} + \frac{2}{m_t}\right) = \frac{1}{3}\left(\frac{1}{1.2} + \frac{2}{0.3}\right) = 2.5$

$m_e(X) = 0.40\, m_0$

Numerically, comparison of case (a) and case (b) hinges on $\sum_i \frac{n_i}{m_i}$

case (a) : $1.44\left[\underset{\Gamma\text{ pt electrons}}{15.4} + \underset{X\text{ pt electrons}}{2.5}\right] + 2(1.44)\left[\underset{hh}{\frac{.895}{1.2}} + \underset{lh}{\frac{.105}{0.3}}\right] = 28.4\times10^{16}$

case (b) : $1.55\left[\underset{\Gamma\text{ electrons}}{15.4}\right] + 1.55\left[\underset{hh}{\frac{.895}{1.2}} + \underset{lh}{\frac{.105}{0.3}}\right] = 25.6\times10^{19}$

Here we can see contributions for each of the carrier types in the two cases.

(f) Hall Effect

Condition $j_y = 0 = \sigma_{yy} E_y - \sigma_{xy} E_x$

$$E_y = E_x \frac{\sigma_{xy}}{\sigma_{yy}}$$

$\sigma_{yy} = \sigma_{xx}$ as before in (e)

$$= e^2\tau \left[\frac{n_e(\Gamma)}{m_e(\Gamma)} + \frac{n_e(X)}{m_e(X)} + \frac{n_{hh}}{m_{hh}} + \frac{n_{\ell h}}{m_{\ell h}} \right] = e^2\tau \; Den$$

$$\sigma_{xy} = e^2\tau \left(\frac{eB\tau}{c}\right) \left[\frac{n_e(\Gamma)}{m_e^2(\Gamma)} + \frac{n_e(X)}{3m_\ell} \frac{1}{\sqrt{m_\ell m_t}} + \frac{n_e(X)}{3m_t} \frac{1}{\sqrt{m_\ell m_t}} + \frac{n_e(X)}{3m_t} \frac{1}{m_t} + \frac{n_{hh}}{m_{hh}^2} + \frac{n_{\ell h}}{m_{\ell h}^2} \right]$$

$$= e^2\tau \left(\frac{eB\tau}{c}\right) Num$$

$$E_y = E_x \frac{e^2\tau (eB\tau)\, Num}{e^2\tau\,(c)\, Den} = \frac{E_x\, eB\tau}{c} \frac{Num}{Den}$$

$$R_{Hall} = \frac{E_y}{j_x B} = \frac{E_x\, eB\tau\, Num}{e^2\tau\, e\, Den^2\, B\, E_x} = \frac{Num}{[Den]^2\, ec}$$

Num = Numerator where terms are of the form $\left(\frac{n_i}{m_i^2}\right)$

and Den = Denominator where terms are of the form $\left(\frac{n_i}{m_i}\right)$
so that R_{Hall} is dominated by the high mobility Γ point electrons.

For case (e)

$$Num = \frac{n_e}{2} \left[-236.7 - 0.46 - 1.85 - 3.70 + \frac{2\,(.895)}{.25} + \frac{2\,(.105)}{.0144} \right]$$

$$Num = \frac{n_e}{2} \quad [-220.97]$$

$$Den = \frac{n_e}{2} \left[20.1 \right]$$

$$\boxed{R_{Hall} = \frac{-1.09}{n_e\, ec}}$$

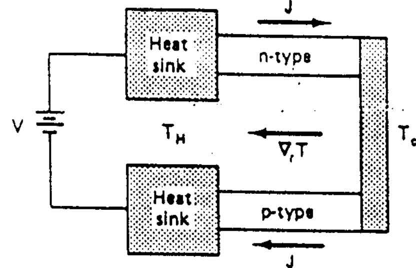
3.

30 points

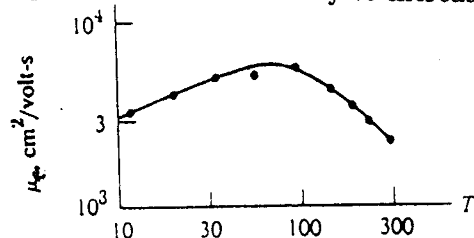
(a) Suppose that you measure the thermal conductivity of a sample at 100°C. How would you estimate the fraction of the heat that is carried by electron (or hole) carriers?

(b) Suppose that Si is doped with an isoelectronic impurity in column IV of the periodic table (such as Ge or Sn), will the effect be greater on the electrical conductivity or on the thermal conductivity, and why?

(c) Could this thermoelectric cooler (see figure) be modified to become a thermoelectric heater? If so, explain how it can be done.



(d) The mobility of a semiconductor sample has the following temperature dependence (see figure below). Explain how it is possible for the mobility to increase with increasing temperature.



(a) $\kappa_{total} = \kappa_e + \kappa_L$

At 100°C the Wiedemann-Franz law is normally valid so by measurement of σ, we can obtain a good estimate for κ_e, thereby from knowledge of κ_{total}, we can predict κ_L.

(b) Isoelectronic impurities (such as Ge in Si) will not give rise to strong electron scattering, so that σ will be largely unaffected. However, the mass of Ge is quite different from Si, so the force constants in the solid will be quite different, leading to strong phonon scattering.

(c) Since the heat/power balance equation

$$\text{Power} = \vec{j} \cdot \overleftrightarrow{\sigma}^{-1} \cdot \vec{j} - \vec{j} \cdot \overleftrightarrow{\tau}_b \cdot \vec{\nabla} T$$

we see that for the same ∇T temperature gradient a reversal of the sign of the current flow (keeping the temperature gradient) will change the sign of the thermoelectric term, changing cooling to heating. Likewise if the n-type and p-type legs are interchanged, keeping the same directions of $\vec{\nabla} T$ and $\vec{j}$, then also cooling is changed to heating.

(d) At low T we see the mobility is increasing as T increases. As the temperature increases so with the carrier velocity. As the carrier spends less time in passing the charged impurity, the interaction strength decreases. Also as T increases, more carriers are excited. An increase in carrier density will increase the screening and therefore also reduce the interaction strength. At yet higher temperatures when electron-phonon scattering becomes important μ will decrease as T increases, as shown above ~ 50K in figure.