

## FCTM - crabs - 20

①

$$E = kT^2 \left( \frac{\partial \ln Q}{\partial T} \right)_{N,V} \quad Q = \frac{1}{N!} \left( \frac{2\pi m k T}{h^2} \right)^{\frac{3N}{2}} Z_N$$

$$\begin{aligned} a). E &= kT^2 \frac{\partial}{\partial T} \left( \ln \frac{1}{N!} + \frac{3N}{2} \ln \left( \frac{2\pi m k T}{h^2} \right) + \ln Z_N \right)_{N,V} = \\ &= kT^2 \left( \frac{3N}{2} \cdot \frac{h^2}{2\pi m k T} \cdot \frac{2\pi m k}{h^2} + \left( \frac{\partial \ln Z_N}{\partial T} \right)_{N,V} \right) = \\ &= \frac{3}{2} N k T + kT^2 \left( \frac{\partial \ln Z_N}{\partial T} \right)_{N,V}. \end{aligned}$$

b). i).  $E = E_{kin} + \langle U \rangle$  (= sum of kinetic + potential energy)

$E_{kin} = \frac{3}{2} N k T \rightarrow$  thermal kinetic energy

$\langle U \rangle \rightarrow$  potential energy  $\rightarrow$  contains all interactions via  
 $Z_N = \int \dots \int e^{-\beta U(\dots)} d\tau$

$$\begin{aligned} ii) \langle U \rangle &= kT^2 \left( \frac{\partial \ln Z_N}{\partial T} \right)_{N,V} = kT^2 \frac{1}{Z_N} \frac{\partial}{\partial T} (Z_N)_{N,V} = \\ &= \frac{kT^2}{Z_N} \frac{\partial}{\partial T} \left( \int \dots \int e^{-\beta U(\dots)} d\tau \right)_{N,V} \rightarrow \text{change} \\ &\quad \frac{\partial}{\partial T} \rightarrow \frac{\partial}{\partial \beta} \quad \beta = \frac{1}{kT} \end{aligned}$$

$$\therefore \frac{\partial \beta}{\partial T} = -\frac{1}{kT^2} \rightarrow \frac{1}{\partial T} = -\frac{1}{kT^2} \frac{\partial}{\partial \beta}$$

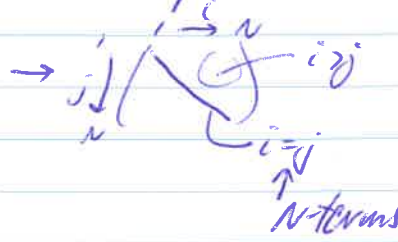
$$\Rightarrow \langle U \rangle = \frac{kT^2}{Z_N} \cdot \frac{1}{kT^2} \frac{\partial}{\partial \beta} \left( \int \dots \int e^{-\beta U(\dots)} d\tau \right)_{N,V} =$$

$$= \frac{-1}{Z_N} \int \dots \int \frac{\partial}{\partial \beta} \left( e^{-\beta U(\dots)} \right)_{N,V} d\tau =$$

$$= \frac{-1}{Z_N} \int \dots \int -U e^{-\beta U(\dots)} d\tau_1 \dots d\tau_N$$

$$\langle U \rangle = \frac{\int \dots \int U e^{-\beta U} d\tau_1 \dots d\tau_N}{Z_N}$$

d).  $U = \sum_{i < j}^N \phi_{ij}$  pair-wise additivity implies that you write the total potential energy as the sum of all the potential energies between the pairs of particles  $\rightarrow$  i.e. the pair potential.

$\sum_{i < j}^N \rightarrow$    $\frac{N^2 - N}{2} = \frac{N(N-1)}{2}$  terms  
prevent double counting.

d).  $g(r) = \frac{1}{V^2} \frac{\int d\vec{r}_3 \dots \int d\vec{r}_N e^{-\beta U}}{Z_N}$  (leave  $\frac{1}{V^2}$   $\rightarrow$   $g(r)$ )

$\langle U \rangle = \frac{\int d\vec{r}_1 \dots \int d\vec{r}_N U e^{-\beta U}}{Z_N} = \frac{\int d\vec{r}_1 \dots \int d\vec{r}_N \sum_{i < j} \phi_{ij} e^{-\beta U}}{Z_N}$

$= \frac{N(N-1)}{2} \frac{\int d\vec{r}_1 \dots \int d\vec{r}_N \phi_{12} e^{-\beta U}}{Z_N} =$

$= \frac{N(N-1)}{2} \int d\vec{r}_1 \int d\vec{r}_2 \phi_{12} \left[ \frac{\int d\vec{r}_3 \dots \int d\vec{r}_N e^{-\beta U}}{Z_N} \right] \rightarrow = \frac{g(r)}{V^2}$

$= \frac{N(N-1)}{2V^2} \int d\vec{r}_1 \int d\vec{r}_2 \phi_{12} g(r)$

particle 1 can be anywhere  $\rightarrow \int d\vec{r}_1 \rightarrow V$   
 $r = \vec{r}_1 - \vec{r}_2$

$= \frac{N(N-1)}{2V^2} \cdot V \int d\vec{r} \phi(r) g(r)$

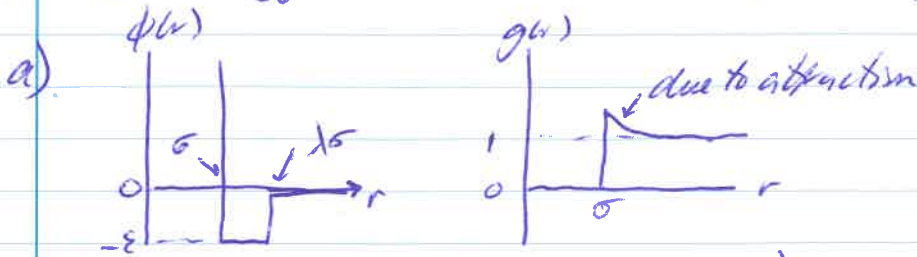
$\downarrow \frac{N-1}{V} = \rho \quad \& \quad d\vec{r} \rightarrow 4\pi r^2 dr$

$= \frac{N}{2} \rho \int_0^\infty 4\pi r^2 \phi(r) g(r) dr$

$\Rightarrow \langle U \rangle = 2\pi N \rho \int_0^\infty r^2 \phi(r) g(r) dr$

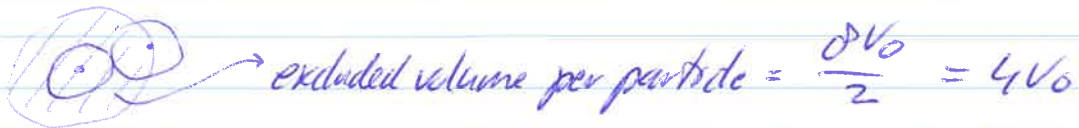


$$(2) \quad B_2 = -\bar{v} \int_0^\infty (e^{-\beta\phi(r)} - 1) r^2 dr \quad \phi(r) = \begin{cases} \infty & r < \sigma \\ -\epsilon & \sigma \leq r \leq \lambda\sigma \\ 0 & r > \lambda\sigma \end{cases}$$



$$\begin{aligned} \text{b). i) } B_2 &= -\bar{v} \int_0^\sigma (e^{-\beta \cdot \infty} - 1) r^2 dr - \bar{v} \int_\sigma^{\lambda\sigma} (e^{\beta\epsilon} - 1) r^2 dr - \bar{v} \int_{\lambda\sigma}^\infty (e^{-\beta \cdot 0} - 1) r^2 dr \\ &\quad \text{HS part} \qquad \qquad \qquad \text{ATT part} \\ &= \bar{v} \int_0^\sigma r^2 dr - \bar{v} (e^{\beta\epsilon} - 1) \int_\sigma^{\lambda\sigma} r^2 dr \\ &\quad \underbrace{\hspace{1.5cm}}_{B_2^{\text{HS}}} \qquad \underbrace{\hspace{1.5cm}}_{B_2^{\text{ATT}}} \end{aligned}$$

$$\text{ii) } B_2^{\text{HS}} = \bar{v} \int_0^\sigma r^2 dr = \frac{2\pi\sigma^3}{3} = 4V_0 \quad \begin{matrix} \text{volume per} \\ \text{particle with} \\ \text{diameter } \sigma \end{matrix}$$



$B_2^{\text{HS}}$  does not depend on  $T$  as Boltzmann factor  $e^{-\beta u}$   $\begin{cases} \rightarrow 0 & \text{overlap} \\ \rightarrow 1 & \text{no overlap} \end{cases}$

So, temperature dependence drops out.

$$\begin{aligned} \text{d) } \langle u \rangle &= \bar{v} \rho N \int_0^\infty r^2 \phi(r) g(r) dr \qquad \qquad \qquad g(r) = e^{-\beta\phi(r)} \\ &= \bar{v} \rho N \int_0^\sigma r^2 \cdot \infty \cdot e^{-\beta \cdot \infty} dr + \bar{v} \rho N \int_\sigma^{\lambda\sigma} r^2 \cdot (-\epsilon) \cdot e^{\beta\epsilon} dr + \bar{v} \rho N \int_{\lambda\sigma}^\infty r^2 \cdot 0 \cdot e^{-\beta \cdot 0} dr \\ &\quad \text{no exponent wins} \qquad \qquad \qquad \underbrace{\hspace{1.5cm}}_{\text{ATT part survives}} \end{aligned}$$

$$\begin{aligned} \langle u \rangle &= -\bar{v} \rho N \epsilon e^{\beta\epsilon} \int_\sigma^{\lambda\sigma} r^2 dr = \rho N \epsilon e^{\beta\epsilon} \cdot \underbrace{-\bar{v} \int_\sigma^{\lambda\sigma} r^2 dr}_B \\ \Rightarrow \langle u \rangle &= \frac{\rho N \epsilon e^{\beta\epsilon}}{(e^{\beta\epsilon} - 1)} B_2^{\text{ATT}} / (e^{\beta\epsilon} - 1) \end{aligned}$$

average potential only depends on ATT part of potential! As repulsive part is hard-sphere potential  $\rightarrow$  no overlap  $\rightarrow u_{\text{HS}} = 0$ .

$$d). 1 + 4\pi\rho \int_0^\infty (g(r)-1) r^2 dr = \rho k_B T k_T$$

$$k_T = \frac{1}{\rho k_B T} \left( 1 + 4\pi\rho \int_0^\sigma (e^{-\beta u} - 1) r^2 dr \right) \quad \left. \vphantom{\int_0^\sigma} \right\} \text{HS part stays}$$

$$+ 4\pi\rho \int_\sigma^\infty (e^{-\beta u} - 1) r^2 dr \quad \left. \vphantom{\int_\sigma^\infty} \right\} \text{ATT part stays too}$$

$$+ 4\pi\rho \int_\sigma^\infty (e^{-\beta \cdot 0} - 1) r^2 dr \quad \left. \vphantom{\int_\sigma^\infty} \right\} \text{zero.}$$

$$k_T = \frac{1}{\rho k_B T} \left( 1 + 4\pi\rho \left[ - \int_0^\sigma r^2 dr + 4\pi\rho (e^{-\beta u} - 1) \int_\sigma^\infty r^2 dr \right] \right) =$$

$$= \frac{1}{\rho k_B T} \left( 1 - 2\rho \cdot \underbrace{\left[ 2\pi \int_0^\sigma r^2 dr \right]}_{B_2^{\text{HS}}} - 2\rho \cdot \underbrace{\left[ -2\pi (e^{-\beta u} - 1) \int_\sigma^\infty r^2 dr \right]}_{B_2^{\text{ATT}}} \right)$$

$$= \frac{1}{\rho k_B T} \left( 1 - 2\rho B_2^{\text{HS}} - 2\rho B_2^{\text{ATT}} \right) =$$

$$k_T = \frac{1}{\rho k_B T} \left( 1 - 2\rho (B_2^{\text{HS}} + B_2^{\text{ATT}}) \right) = \frac{1}{\rho k_B T} (1 - 2\rho B_2)$$

16 mins  $\rightarrow$  so compressibility depends on both HS & ATT parts of potential.

$$(3) a). I(k) \sim P(k) S(k) \quad \& \quad S(k) = 1 + \rho \int (g(r)-1) e^{i\vec{k}\cdot\vec{r}} d\vec{r}$$

at low  $\rho$ :  $S(k) = 1$  and  $I(k) = P(k)$  then  
at high  $\rho$   $I(k)/P(k) = S(k) \rightarrow$  that's how to measure  $S(k)$ .

$$b). S(k \rightarrow 0) = 1 + \rho \int (g(r)-1) e^{i\vec{0}\cdot\vec{r}} d\vec{r} = 1 + \rho \int (g(r)-1) d\vec{r}$$

$$= 1 + \rho \cdot \int_0^\infty (g(r)-1) 4\pi r^2 dr$$

$$= 1 + 4\pi\rho \int_0^\infty (g(r)-1) \cdot r^2 dr = \quad (\text{use compressibility relation q. 2d.})$$

$$= \rho k_B T k_T$$

3 min.

$\Sigma = 34$  mins.

**Exam Fundamentals of Condensed Matter, 28 October 2024. Solids Part 1. De Gelder. Q4.**

- a) At 5 °C, iron (Fe) is found to show a bcc structure with a lattice parameter of 0.2866 nm. When heating iron above 912 °C, its crystal structure changes to a face-centered cubic (fcc) crystal structure with a lattice parameter of 0.3571 nm. Calculate the atomic radius of iron in both the bcc and fcc structures. (2 points)

**Answer:**

In a bcc structure the body diagonal is  $a\sqrt{3}$ ,  $a$  being the lattice parameter. The body diagonal is also equal to  $4r$ ,  $r$  being the radius of the atom.  $r = 1/4\sqrt{3}a = 0.1241$  nm.

In an fcc structure the face diagonal is  $a\sqrt{2}$ ,  $a$  being the lattice parameter. The face diagonal is also equal to  $4r$ ,  $r$  being the radius of the atom.  $r = 1/4\sqrt{2}a = 0.1263$  nm.

- b) Obtain the density of iron in the fcc structure as described in a). The atomic weight (molar mass) per 1 mole of Fe is 55.845 g. Avogadro's number is  $6.02214076 \cdot 10^{23} \text{ mol}^{-1}$ . (3 points)

**Answer:**

In an fcc structure there are 4 atoms in the unit cell. The volume of the unit cell is  $a^3$ ,  $a$  being the lattice parameter. The volume of 1 mole of Fe atoms is  $N_A \cdot a^3/4$ ,  $N_A$  being Avogadro's number. The density of the fcc structure of Fe is  $55.845/(N_A \cdot a^3/4) = 8.146 \cdot 10^6 \text{ g m}^{-3}$ .

- c) Calculate the length of the unit cell edges and the unit cell volume when you describe the fcc structure of iron, as described in a), with a rhombohedral unit cell. (2 points)

**Answer:**

The length of the rhombohedral unit cell edge is half the face diagonal of the fcc unit cell:  $a' = 1/2\sqrt{2}a = 0.2525$  nm. The volume of the rhombohedral unit cell is a quarter of the volume of the fcc unit cell =  $a^3/4 = 0.01138 \text{ nm}^3$  (the rhombohedral unit cell contains only 1 atom). Alternatively, take the expression of problem f):  $V = a'^3(1 - 1/4 - 1/4 - 1/4 + 1/4)^{1/2} = 0.01138 \text{ nm}^3$ .

- d) The symmetry matrix  $M$  for a rotation  $\theta$  around the z-axis is:

$$M = \begin{vmatrix} \cos(\theta) & -\sin(\theta) & 0 \\ \sin(\theta) & \cos(\theta) & 0 \\ 0 & 0 & 1 \end{vmatrix}$$

Prove with matrices that point group 3/m (not used) is equivalent to point group -6 (which is being used) and show that point group 3/m (or -6) does not contain an inversion center. Hint: choose in both cases the rotation axes along the z-axis. (6 points)

**Answer:**

Point group 3/m means: a 3-fold rotation axis perpendicular to a mirror plane. Point group -6 means: a 6-fold roto-inversion axis which includes a rotation around 60 degrees immediately followed by inversion.

Repeated 3-fold rotation along z can be described by the following matrices:

$$M_3 = \begin{vmatrix} -1/2 & -1/2\sqrt{3} & 0 \\ 1/2\sqrt{3} & -1/2 & 0 \\ 0 & 0 & 1 \end{vmatrix}$$

$$\mathbf{M}_3 \cdot \mathbf{M}_3 = \begin{vmatrix} -\frac{1}{2} & \frac{1}{2}\sqrt{3} & 0 \\ -\frac{1}{2}\sqrt{3} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{vmatrix}$$

$$\mathbf{M}_3 \cdot \mathbf{M}_3 \cdot \mathbf{M}_3 = \begin{vmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{vmatrix}$$

A mirror operation perpendicular to the z-axis can be described by the following matrix:

$$\mathbf{M}_m = \begin{vmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{vmatrix}$$

Combining 3-fold rotation with the mirror operation gives:

$$\mathbf{M}_3 \cdot \mathbf{M}_m = \begin{vmatrix} -\frac{1}{2} & \frac{1}{2}\sqrt{3} & 0 \\ -\frac{1}{2}\sqrt{3} & -\frac{1}{2} & 0 \\ 0 & 0 & -1 \end{vmatrix}$$

Combining two times 3-fold rotation with the mirror operation gives:

$$\mathbf{M}_3 \cdot \mathbf{M}_3 \cdot \mathbf{M}_m = \begin{vmatrix} -\frac{1}{2} & \frac{1}{2}\sqrt{3} & 0 \\ -\frac{1}{2}\sqrt{3} & -\frac{1}{2} & 0 \\ 0 & 0 & -1 \end{vmatrix}$$

Any other combination of matrices will not lead to a new one. This means that point group 3/m can be described with 6 symmetry matrices.

6-fold roto-inversion can be described with the following matrix:

$$\mathbf{M}_{-6} = \begin{vmatrix} -\frac{1}{2} & \frac{1}{2}\sqrt{3} & 0 \\ -\frac{1}{2}\sqrt{3} & -\frac{1}{2} & 0 \\ 0 & 0 & -1 \end{vmatrix} = \mathbf{M}_3 \cdot \mathbf{M}_3 \cdot \mathbf{M}_m$$

Repeating this 6-fold roto-inversion operation leads to the same set of matrices as for point group 3/m:

$$\mathbf{M}_{-6} \cdot \mathbf{M}_{-6} = \mathbf{M}_3$$

$$\mathbf{M}_{-6} \cdot \mathbf{M}_{-6} \cdot \mathbf{M}_{-6} = \mathbf{M}_m$$

$$\mathbf{M}_{-6} \cdot \mathbf{M}_{-6} \cdot \mathbf{M}_{-6} \cdot \mathbf{M}_{-6} = \mathbf{M}_3 \cdot \mathbf{M}_3$$

$$\mathbf{M}_{-6} \cdot \mathbf{M}_{-6} \cdot \mathbf{M}_{-6} \cdot \mathbf{M}_{-6} \cdot \mathbf{M}_{-6} = \mathbf{M}_3 \cdot \mathbf{M}_m$$

$$\mathbf{M}_{-6} \cdot \mathbf{M}_{-6} \cdot \mathbf{M}_{-6} \cdot \mathbf{M}_{-6} \cdot \mathbf{M}_{-6} \cdot \mathbf{M}_{-6} = \mathbf{M}_3 \cdot \mathbf{M}_3 \cdot \mathbf{M}_3$$

Both 3/m and -6 do not contain an inversion center as the matrix for this symmetry element would be:

$$\mathbf{M}_i = \begin{vmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{vmatrix}$$

- e) For a perfect crystal the structure factor  $F(hkl)$  determines the amplitude and phase of the diffracted beams:

$$F(hkl) = \sum_j f_j(\theta) \cdot \exp[2\pi i(hx_j + ky_j + lz_j)] = |F(hkl)| \cdot \exp[i\varphi(hkl)]$$

where the sum is over all atoms in the unit cell,  $x_j$ ,  $y_j$  and  $z_j$  are the positional coordinates of the atoms and  $f_j(\theta)$  is the scattering factor of the  $j$ -th atom.  $hkl$  are the indices of the lattice planes.

Show that for a fcc structure, like Fe at high temperature, the structure factor has values different from zero only for  $h, k, l =$  all even or  $h, k, l =$  all odd. (6 points)

**Answer:**

For an fcc structure we have atoms at positions  $(0,0,0)$ ,  $(\frac{1}{2}, \frac{1}{2}, 0)$ ,  $(0, \frac{1}{2}, \frac{1}{2})$  and  $(\frac{1}{2}, 0, \frac{1}{2})$ . The scattering factor is the same for the two atoms and can be written as  $f(\theta)$ .

$$\begin{aligned} F(hkl) &= \sum_j f_j(\theta) \cdot \exp[2\pi i(hx_j + ky_j + lz_j)] \\ &= f(\theta)(1 + \exp[\pi i]^{h+k} + \exp[\pi i]^{k+l} + \exp[\pi i]^{h+l}) \\ &= f(\theta)(1 + [-1]^{h+k} + [-1]^{k+l} + [-1]^{h+l}) \end{aligned}$$

$F(hkl) = 4f(\theta)$  for  $h, k, l =$  all even or all odd,  $F(hkl) = 0$  for  $h, k, l$  with mixed parity.

- f) The  $d$ -spacing in a triclinic crystal is given by:

$$\frac{1}{d^2} = \frac{1}{V^2} \left( \begin{aligned} &h^2 b^2 c^2 \sin^2 \alpha + k^2 a^2 c^2 \sin^2 \beta + l^2 a^2 b^2 \sin^2 \gamma \\ &+ 2hkabc^2 (\cos \alpha \cos \beta - \cos \gamma) \\ &+ 2kla^2 bc (\cos \beta \cos \gamma - \cos \alpha) \\ &+ 2hlab^2 c (\cos \alpha \cos \gamma - \cos \beta) \end{aligned} \right)$$

$$V = abc(1 - \cos^2 \alpha - \cos^2 \beta - \cos^2 \gamma + 2 \cos \alpha \cos \beta \cos \gamma)^{1/2}$$

Consider a crystal with a hexagonal unit cell with  $a = 10 \text{ \AA}$  and  $c = 20 \text{ \AA}$ . Using the Bragg equation,  $2d \sin \theta = n\lambda$ , calculate the Bragg angle  $\theta$  for the first and second order reflections from the lattice planes  $(100)$ ,  $(200)$ ,  $(002)$  and  $(111)$ , using an X-ray wavelength  $\lambda = 1.54 \text{ \AA}$ , for this crystal.

(6 points)

**Answer:**

For the hexagonal unit cell  $a = b$  and  $\gamma = 120^\circ$  ( $\alpha$  and  $\beta$  are  $90^\circ$ ). For the spacing of lattice planes the expression for the triclinic system can be simplified to:

$$1/(d_{hkl})^2 = 4/3(h^2 + hk + k^2)/a^2 + l^2/c^2.$$

The  $d$ -spacings and corresponding Bragg angles  $\theta$  for the first and second order reflections from the lattice planes  $(100)$ ,  $(200)$ ,  $(020)$  and  $(111)$  are:

(100): $1/(d_{100})^2 = 4/3(1 + 0 + 0)/10^2 + 0/20^2$	$d = 8.66 \text{ \AA}$
(200): $1/(d_{200})^2 = 4/3(4 + 0 + 0)/10^2 + 0/20^2$	$d = 4.33 \text{ \AA}$ [The same would be true for (020)]
(002): $1/(d_{002})^2 = 4/3(0 + 0 + 0)/10^2 + 4/20^2$	$d = 10.0 \text{ \AA}$
(111): $1/(d_{111})^2 = 4/3(1 + 1 + 1)/10^2 + 1/20^2$	$d = 4.85 \text{ \AA}$

Bragg equation:  $n\lambda = 2d\sin\theta$ , so  $\sin\theta = n\lambda/2d$

(100): $\sin\theta = (n \cdot 1.54)/(2 \times 8.66) = n \cdot 0.089$	$n = 1, \theta = 5.10^\circ$	$n = 2, \theta = 10.24^\circ$
(200): $\sin\theta = (n \cdot 1.54)/(2 \times 4.33) = n \cdot 0.178$	$n = 1, \theta = 10.24^\circ$	$n = 2, \theta = 20.83^\circ$
(002): $\sin\theta = (n \cdot 1.54)/(2 \times 10.0) = n \cdot 0.077$	$n = 1, \theta = 4.42^\circ$	$n = 2, \theta = 8.86^\circ$
(111): $\sin\theta = (n \cdot 1.54)/(2 \times 4.85) = n \cdot 0.159$	$n = 1, \theta = 9.14^\circ$	$n = 2, \theta = 18.51^\circ$



Answers exam questions 5 and 6, Solids Part 2

5a) For intrinsic semiconductors the free electron and hole density is equal ( $n$ ) also their charge is equal (but opposite,  $q$ ) so their contribution to the conductivity is only given by ratio of their mobility.

Given:  $\sigma_i = 4 \times 10^{-4} \Omega^{-1}m^{-1}$   
 $\mu_e = 0.14 \text{ m}^2/(V.s)$   
 $\mu_h = 0.05 \text{ m}^2/(V.s)$

$$\sigma_i = \sigma_{i,h} + \sigma_{i,e} = n \cdot q (\mu_h + \mu_e) \text{ and } \sigma_{i,h} = n \cdot q \cdot \mu_h \rightarrow \sigma_{i,h} = \sigma_i \cdot \mu_h / (\mu_h + \mu_e) = 1.053 \times 10^{-4} \Omega^{-1}m^{-1}$$

b) First use the known room temperature conductivity to determine  $\sigma_{i0}$

Given:  $E_g = 1.11 \text{ eV}$   
 $T = 298 \text{ K}$   
 $k = 8.62 \times 10^{-5} \text{ eV/K}$

$$\sigma_i = \sigma_{i0} \exp(-E_g/2kT) \rightarrow \sigma_{i0} = \sigma_i \exp(E_g/2kT) = 9.67 \times 10^5 \Omega^{-1}m^{-1}$$

Next use this value to calculate  $\sigma_i$  at  $150^\circ\text{C}$

Given:  $T = 423 \text{ K}$

$$\sigma_i(423K) = \sigma_{i0} \exp(-E_g/2kT) = 0.272 \Omega^{-1}m^{-1}$$

c) The electron and hole mobilities of intrinsic and extrinsic semiconductors are the same. In the doped semiconductor the conductivity will be fully carried by free electrons from the donor atoms  $n = N_D \gg p$  so  $\sigma_e = n \cdot q \cdot \mu_e$

Given:  $\sigma_e = 150 \Omega^{-1}m^{-1}$   
 $\mu_e = 0.14 \text{ m}^2/(V.s)$   
 $q = 1.6 \cdot 10^{-19} \text{ C}$

$$N_D = n = \sigma_e / (q \cdot \mu_e) = 6.696 \times 10^{21} \text{ m}^{-3}$$

d) The donor has 5 electrons in its outer shell. Four are required for the covalent bondings with the lattice so the 5th is donated as a free electron without a missing electron (hole) in the valence band.

e)

$$N_{Si} = N_{Av} \cdot \rho_{Si} / M_{Si} = 4.93 \times 10^{28} \text{ m}^{-3} \quad (\text{from given constants})$$

$$N_D = n = \sigma_e / (q \cdot \mu_e) = 6.696 \times 10^{21} \text{ m}^{-3} \quad (\text{calculated in c})$$

$$\sigma_i = 4 \times 10^{-4} \Omega^{-1}m^{-1} \quad (\text{given})$$

$$\sigma_e = 150 \Omega^{-1}m^{-1} \quad (\text{given under c})$$

A small change in material composition of  $N_D/N_{Si} = 1.36 \times 10^{-7} = 136 \text{ ppb}$  results in an enormous increase in conductivity ( $\sigma_e/\sigma_i = 3.75 \times 10^5$  times). This is a structure sensitive property.

N.B. It is not necessary to calculate  $N_{Si}$ . It is also fine to just state as a known fact that typical doping concentrations in semiconductor materials are maximally around  $1 \text{ ppm}$  ( $10^{-6}$ ).

6a) No the lattice constants of the n and p type doped materials is the same so no misfit dislocations required to cope with a potential lattice mismatch.

b) Maximum light induced current is obtained if there are no loss mechanisms (like reflection of light at the semiconductor surface or internal recombination of produced electrons). In that case each incident photon to the sensitive area (A) of the photodiode having sufficient energy (i.e.  $E_p > E_g$ ) will be absorbed to produce one electron (with charge q) for the external current.

So  $I_{L,max} = q \cdot A \cdot \text{incident photon flux}$ .

Given:  $h = 6.63 \times 10^{-34} \text{ J}\cdot\text{s}$   
 $c = 3 \times 10^8 \text{ m/s}$   
 $\lambda = 400 \text{ nm}$   
 $q = 1.6 \cdot 10^{-19} \text{ C}$   
 $P = 300 \text{ W/m}^2$  (intensity or power flux)  
 $A = 10^{-4} \text{ m}^2$  (sensitive or irradiated area)

Photon energy  $E_p = h \cdot c / \lambda = 4.96 \times 10^{-19} \text{ J}$  (= 3.1 eV)

Photon flux  $F = P / E_p = 6.05 \times 10^{20} \text{ s}^{-1} \cdot \text{m}^{-2}$

$E_p > E_g \rightarrow$  For Si photodiode  $I_{L,max} = q \cdot A \cdot F = 0.0387 \text{ C/s} = 9.68 \text{ mA}$ .

c) Evaporation and sputter deposition techniques.

d) Ag reflects well over the entire visible range of light while Cu has a reddish appearance indicating that i) light from the blue part of the spectrum is reflected less or ii) light from the blue part is reflected at a longer (red-shifted) wavelength compared to the incident 400 nm. In case of i) the current with a Cu mirror will be less as the cell is sensitive for the blue part of the spectrum. In case of ii) the current with the Cu mirror might be the same as with the Ag mirror because Si will absorb all photons in the visible range and each of them will contribute equally to the current but longer wavelength photons require a thicker semiconductor slab to be absorbed so they may escape again at the front side of the diode. Overall Ag would be the safest choice.

N.B. With the notion for which part of the spectrum the cell is sensitive, either argument i) or ii) is already enough to get the full score (2pt).

e) Si is an in-direct semiconductor in which the misalignment of the minima and maxima in the conduction and valence band result in a low absorption of light compared to a direct semiconductor which typically have 100 times larger absorption coefficients. So using a direct semiconductor like GaAs would solve the transmission loss.

N.B. Just stating the use of a direct semiconductor because it has a much higher absorption coefficient than an indirect semiconductor like Si is already sufficient to get the full score (2pt).