UNOFFICIAL SOLUTIONS BY TheLongCat

B6. CONDENSED-MATTER PHYSICS

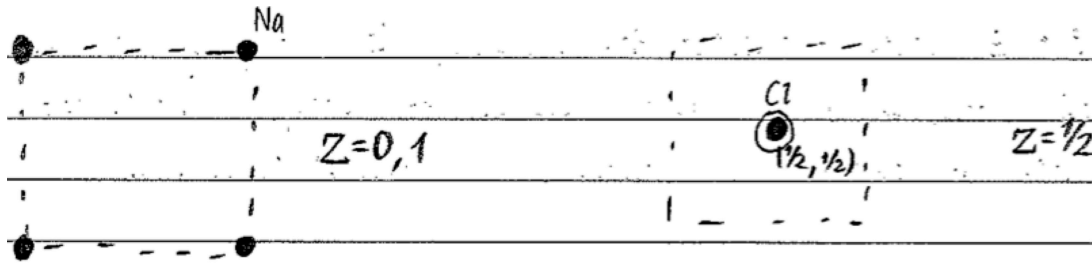### TRINITY TERM 2022

Last updated: 30th May 2025

Disclaimer: due to its unofficial nature, the author does not warrant the accuracy of the presented solutions in any form. However, the author is happy to discuss the typos and errors should one arises.
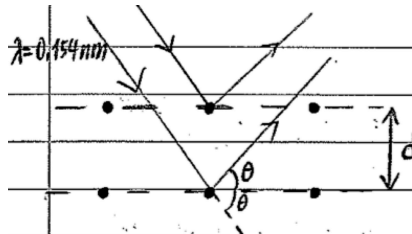
Turn over as you please – we are NOT under exam conditions here.

1. (DRAFT)

(a) i. Within a UC, # of Au atoms: $8 \cdot \frac{1}{8} = 1$;

   # of Cu atoms: $4 \cdot \frac{1}{2} + 2 \cdot \frac{1}{2} = 3$.

   $\Rightarrow \text{Cu}_3\text{Au}$ is consistent with the UC arrangement.

 ii. Structure factor:

$$S_{(hkl)} = \sum_{\substack{\text{atom } j \\ \text{in UC}}} f_j e^{i\mathbf{G}\cdot\mathbf{x}_j} \quad \text{with } \mathbf{G} = h\hat{\mathbf{b}}_1 + k\hat{\mathbf{b}}_2 + l\hat{\mathbf{b}}_3 \text{ the reciprocal lattice vector}$$

$$= f_{\text{Au}}\left[e^{i2\pi(0+0+0)}\right] + f_{\text{Cu}}\left[e^{i2\pi(\frac{h}{2}+0+\frac{l}{2})} + e^{i2\pi(0+\frac{k}{2}+\frac{l}{2})} + e^{i2\pi(\frac{h}{2}+\frac{k}{2}+0)}\right]$$

$$= f_{\text{Au}} + \underbrace{\left[e^{i\pi(h+l)} + e^{i\pi(k+l)} + e^{i\pi(h+k)}\right]}_{\alpha_{hkl}} f_{\text{Cu}}$$

 iii. Bragg's law gives $2d \sin\theta_{hkl} = \lambda$.

   Recall for cubic crystal,

$$\mathbf{G} \cdot \mathbf{d} = 2\pi \quad \text{with reciprocal lattice vector } \mathbf{G}$$

$$\Rightarrow G = \frac{2\pi}{d}$$

   So:

$$\frac{4\pi}{G} \sin\theta_{hkl} = \lambda$$

$$\Rightarrow G = \frac{4\pi \sin\theta_{hkl}}{\lambda}$$

(b)   i. For (110),

$$|\mathbf{G}| = \sqrt{\left(\frac{2\pi}{a}\right)^2 + \left(\frac{2\pi}{a}\right)^2}$$

$$= \sqrt{2}\frac{2\pi}{a}$$

$$\Rightarrow \sin\theta_{hkl} = \frac{\lambda\sqrt{2}2\pi}{4\pi a}$$

$$\theta_{(110)} = \arcsin\left[\frac{0.154\,\text{nm}}{\sqrt{2}(0.375\,\text{nm})}\right]$$

$$= 16.9°$$

$$\Rightarrow 2\theta_{(110)} = 33.8°$$

Similarly for (111),

$$\mathbf{G} = \sqrt{3}\frac{2\pi}{a}$$

$$\Rightarrow \theta_{(111)} = \arcsin\left[\frac{\sqrt{3}0.154\,\text{nm}}{2(0.375\,\text{nm})}\right]$$

$$= 20.9°$$

$$\Rightarrow 2\theta_{(110)} = 41.7°$$

ii. Structure factors:

$$S_{(110)} = f_{\text{Au}} + f_{\text{Cu}}\left[e^{2i\pi} + e^{i\pi} + e^{i\pi}\right]$$
$$= f_{\text{Au}} - f_{\text{Cu}}$$

$$S_{(111)} = f_{\text{Au}} + f_{\text{Cu}}\left[3e^{2i\pi}\right]$$
$$= f_{\text{Au}} + 3f_{\text{Cu}}$$

For (110),

$$f_{\text{Au}} = Z_{\text{Au}}e^{-b_{\text{Au}}(\frac{\sin\theta_{(110)}}{\lambda})^2}$$

$$= 59.4$$

$$\Rightarrow f_{\text{Cu}} = 23.2$$

Similarly (111),

$$f_{\text{Au}} = 51.6$$
$$f_{\text{Cu}} = 20.7$$

Hence:

$$\frac{I_{\{111\}}}{I_{\{110\}}} = \frac{M_{\{111\}}}{M_{\{110\}}} \cdot \left|\frac{S_{\{111\}}}{S_{\{110\}}}\right|^2 \quad \text{with multiplicity } M_{\{hkl\}}$$

$$= \frac{8}{12}\left|\frac{51.6 + 3\cdot(20.7)}{59.4 - 23.2}\right|^2$$

$$= 6.56$$

(c)   i. Replace $f_{\text{Au}} \to \langle f \rangle$, $f_{\text{Cu}} \to \langle f \rangle$, then:

$$S_{(110)} = \langle f \rangle + \langle f \rangle \left[e^{2i\pi} + 2e^{i\pi} \right]$$
$$= 0 \Rightarrow I_{(110)} = 0$$

$$S_{(111)} = \langle f \rangle + \langle f \rangle \left[3e^{2i\pi} \right]$$
$$= 4\langle f \rangle$$
$$= 4\frac{3f_{\text{Cu}} + f_{\text{Au}}}{4}$$
$$= 3f_{\text{Cu}} + f_{\text{Au}} \quad \text{so unchanged!}$$

ii. For the average crystal, we may treat each site as a mixture of $\frac{3}{4}\text{Cu} + \frac{1}{4}\text{Au}$, rendering the UC an FCC structure, thereby abiding the FCC selection rules where h, k, l must all have the same parity.

(d)   i. As the crystal becomes more disordered, each Au would become more Cu-like, so:

$$\langle f_{\text{Au}} \rangle = f_{\text{Au}} + (1 - \rho)\frac{f_{\text{Au}} + 3f_{\text{Cu}}}{4}$$
$$= \frac{1}{4} \left[f_{\text{Au}} \left[3\rho + 1 \right] + 3(1 - \rho)f_{\text{Cu}} \right]$$

Similarly for Cu,

$$\langle f_{\text{Cu}} \rangle = \rho f_{\text{Cu}} + (1 - \rho)\frac{f_{\text{Au}} + 3f_{\text{Cu}}}{4}$$
$$= \frac{1}{4} \left[f_{\text{Cu}} \left[\rho + 3 \right] + (1 - \rho)f_{\text{Au}} \right]$$

ii.

$$S_{(111)} = \langle f_{\text{Au}} \rangle + 3\langle f_{\text{Cu}} \rangle \quad \text{from before}$$
$$= \frac{1}{4} \left[f_{\text{Au}}(3\rho + 1) + 3(1 - \rho)f_{\text{Cu}} + 3(\rho + 3)f_{\text{Cu}} + 3(1 - \rho)f_{\text{Au}} \right]$$
$$= \frac{1}{4} \left[4f_{\text{Au}} + 12f_{\text{Cu}} \right]$$
$$= f_{\text{Au}} + 3f_{\text{Cu}} \not\propto \rho$$

$$S_{(110)} = \langle f_{\text{Au}} \rangle - \langle f_{\text{Cu}} \rangle$$
$$= \frac{1}{4} \left[f_{\text{Au}}(3\rho + 1) + 3(1 - \rho)f_{\text{Cu}} - (\rho + 3)f_{\text{Cu}} - (1 - \rho)f_{\text{Au}} \right]$$
$$= \frac{1}{4} \left[4\rho f_{\text{Au}} - 4\rho f_{\text{Cu}} \right]$$
$$= \rho(f_{\text{Au}} - f_{\text{Cu}})$$
$$\Rightarrow I_{(110)} \propto \left| S_{(110)} \right|^2 \propto \rho^2$$

2. (DRAFT)

(a)   i. At zone boundary, $y = 0$:

$$\Rightarrow E - E_{\text{ZB}}\left[1 \pm \epsilon\right]$$
$$= E_{\text{ZB}} \pm |V_G|$$

E_{ZB} should be the unperturbed eigenvalue for the following Hamiltonian at zone boundary:

$$\hat{H}_0 = \frac{\hbar^2 \hat{k}^2}{2m_{\text{e}}}$$
$$\Rightarrow E_{\text{ZB}} = \frac{\hbar^2}{2m_{\text{e}}} \cdot \left(\frac{\pi}{a}\right)^2$$
$$= \frac{\hbar^2 \pi^2}{2m_{\text{e}} a^2}$$

ii. **(TO EXPAND)** Recall that periodic potential $V(\mathbf{r}) = \dfrac{e^2}{4\pi\epsilon_0 r}$ for each boundary.

$\Rightarrow$ Bloch's theorem then tells us that:

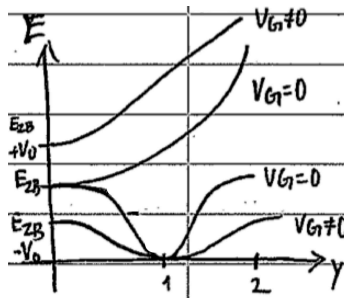$$V_{01} = \int e^{i\mathbf{k}\cdot\mathbf{r}} V(\mathbf{r})\, \mathrm{d}^3\mathbf{r}$$

$\Rightarrow$ Band gap $= 2\,|V_G|$ from above.   Explain how I got this.

Matrix element:

$$\langle k'| V(x) |k\rangle = \int V e^{i(k'-k)x}\, \mathrm{d}x$$

So:

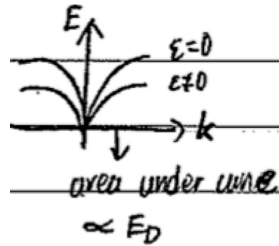$$V_G = \langle k - G| V |k\rangle = \int V e^{iG\cdot x}\, \mathrm{d}x$$

iii.

(b)   i. Density of states within the first Brillouin zone:

$$g_{\text{1D}}(k) = \underset{\substack{\pm \text{ spin}}}{2} \cdot 2 \cdot \frac{L}{2\pi}\, \mathrm{d}k$$

So total energy:

$$E_D = \frac{1}{Na} \int_{-1}^{1} g(y) E \, \mathrm{d}y \quad \text{where } y = 1 - \frac{ka}{\pi} \Rightarrow \mathrm{d}k = -\frac{\pi}{a} \mathrm{d}y$$

$$= \frac{1}{a} \int_{-1}^{1} E \, \mathrm{d}y$$

$$= \frac{E_{\text{ZB}}}{a} \left[\frac{2}{3} + \left(2 - \sqrt{4 + \epsilon^2} \right) + \frac{\epsilon^2}{4} \ln \left(\frac{\sqrt{\epsilon^2 + 4} - 2}{\sqrt{\epsilon^2 + 4} + 2} \right) \right]$$

ii. $-\sqrt{4 + \epsilon^2} < 0$, so $\ln (\ldots)$ always < 0 since denominator $>$ numerator.

iii. Expand $\sqrt{\epsilon^2 + 4} \simeq 2 + \frac{\epsilon^2}{4} + \mathcal{O}(\epsilon^3)$

$$\alpha = 1 \qquad \beta = 2$$

(c) i.

$$G = \frac{2\pi}{a}$$

$$V_G = -2\pi \delta V_0 \quad \text{since FT}\left[\cos(kx)\right] = \delta(k^{\rightarrow} - k)$$

$$= 0 \quad \text{if } \delta = 0$$

ii. $\delta = 0 \Rightarrow V_G = 0 \Rightarrow$ metallic like single e$^-$ chain.

iii. Plug in V_G.

(d) i.

$$V_G = \int e^{i\mathbf{k}\cdot\mathbf{r}} V(\mathbf{r}) \, \mathrm{d}\mathbf{r}$$

$$\Rightarrow V_G = \int_{-\infty}^{\infty} e^{ikx} V_0 \left[\cos\left(\frac{4\pi}{a}x\right) - 2\pi\delta \left(\cos\left(\frac{2\pi}{a}x\right) - \cos\left(\frac{6\pi}{a}x\right) \right) \right] \mathrm{d}x$$

$$= V_0 \left[\delta^{(1)}\left(k - \frac{4\pi}{a}\right) - 2\pi\delta \left(\delta^{(1)}\left(k - \frac{2\pi}{a}\right) - \delta^{(1)}\left(k - \frac{6\pi}{a}\right) \right) \right]$$
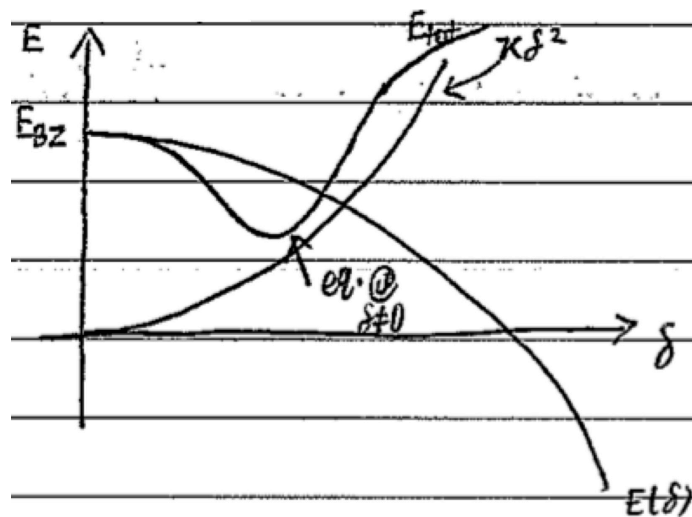
by convolution theorem.

(e) $E_{\text{tot}} = \underbrace{\kappa\delta^2}_{\text{increase}} + \overbrace{E(\delta)}^{\text{decrease}}$

$$\frac{\partial E}{\partial \delta} = 0$$

$$\Rightarrow \text{solution for } \delta > 0$$

Plot w/o calc.

3. (DRAFT)

(a) With $n_{\mathrm{F}}(x) = \dfrac{1}{e^x + 1}$ the Fermi occupation factor, $\beta = \dfrac{1}{k_{\mathrm{B}}T}$ the Boltzmann factor, μ the chemical potential:

$$
\begin{aligned}
f_c(\epsilon) &= n_{\mathrm{F}}\left(\beta(\epsilon - \mu)\right) \\
&= \frac{1}{e^{\beta(\epsilon - \mu)} + 1} \\
&\simeq e^{-\beta(\epsilon - \mu)} \quad \text{for } \mu \text{ well below conduction band}
\end{aligned}
$$

Similarly,

$$
\begin{aligned}
f_v(\epsilon) &= \left[1 - n_{\mathrm{F}}\left(\beta\left(\epsilon - \mu\right)\right)\right] \\
&\simeq e^{\beta(\epsilon - \mu)} \quad \text{for } \mu \text{ well above valence band}
\end{aligned}
$$

Hence:

$$
\begin{aligned}
n(T) &= \int_{\epsilon_c}^{\infty} \frac{(2m_{\mathrm{e}})^{3/2}}{2\pi^2\hbar^3} \sqrt{\epsilon - \epsilon_c} \cdot e^{-\beta(\epsilon - \mu)} \, \mathrm{d}\epsilon \\
&= \int_0^{\infty} \frac{(2m_{\mathrm{e}})^{3/2}}{2\pi^2\hbar^3} \sqrt{x} e^{-\beta x} e^{-\beta\epsilon_c} e^{\beta\mu} \, \mathrm{d}x \\
&= \frac{(2k_{\mathrm{B}}Tm_{\mathrm{e}})^{3/2}}{2\pi^2\hbar^3} \left[\frac{\sqrt{\pi}}{2}\right] e^{-\beta\epsilon_c} e^{\beta\mu}
\end{aligned}
$$

Similarly, with substitution $x = \beta(\epsilon_v - \epsilon) \Rightarrow -\infty \to \infty, \ \epsilon_v \to 0$:

$$
\begin{aligned}
p(T) &= \int_{-\infty}^{\epsilon_v} \frac{(2m_{\mathrm{h}})^{3/2}}{2\pi^2\hbar^3} \sqrt{\epsilon_v - \epsilon} e^{\beta(\epsilon - \mu)} \, \mathrm{d}\epsilon \\
&= \frac{(2m_{\mathrm{h}})^{3/2}}{2\pi^2\hbar^3} e^{\beta\epsilon_v} e^{-\beta\mu} \int_{+\infty}^0 -\sqrt{x} e^{-\beta x} \, \mathrm{d}x \\
&= \frac{(2k_{\mathrm{B}}Tm_{\mathrm{h}})^{3/2}}{2\pi^2\hbar^3} e^{\beta\epsilon_v} e^{-\beta\mu} \cdot \frac{\sqrt{\pi}}{2}
\end{aligned}
$$

Thus:

$$
\begin{aligned}
n(T)p(T) &= \frac{(2k_{\mathrm{B}}Tm_{\mathrm{e}})^{3/2}(2k_{\mathrm{B}}Tm_{\mathrm{h}})^{3/2}}{4\pi^4\hbar^6} \cdot \frac{\pi}{4} e^{-\beta \overbrace{(\epsilon_c - \epsilon_v)}^{E_g}} \\
&= \frac{1}{2}\left[\frac{k_{\mathrm{B}}T}{\pi\hbar^2}\right]^3 (m_{\mathrm{e}}m_{\mathrm{h}})^{3/2} e^{-\beta E_g}
\end{aligned}
$$

(b) i.

$$
\begin{aligned}
n_{\text{occupied}} &= N_D \cdot \text{Probability of occupying energy } \epsilon_D \\
&= N_D \cdot n_{\mathrm{F}}\left[\beta\left(\epsilon_D - \mu\right)\right]
\end{aligned}
$$

$$
n_{\text{empty}} = N_D \cdot \left[1 - n_{\mathrm{F}}\left(\beta\left(\epsilon_D - \mu\right)\right)\right] \quad \text{similar to holes}
$$

Therefore:

$$\frac{n_{\text{occupied}}}{n_{\text{empty}}} = \frac{\frac{1}{e^{\beta(\epsilon_D - \mu)} + 1}}{1 - \frac{1}{e^{\beta(\epsilon_D - \mu)} + 1}}$$

$$= \frac{1}{e^{\beta(\epsilon_D - \mu)} + 1 - 1}$$

$$= e^{\beta(\mu - \epsilon_D)}$$

ii. From a,

$$n = \frac{(2k_{\text{B}}Tm_{\text{e}})^{3/2}}{2\pi^2\hbar^3} \cdot \frac{\sqrt{\pi}}{2} e^{-\beta(\epsilon_c - \mu)}$$

So:

$$\frac{n_{\text{occupied}}}{n_{\text{empty}}} = \frac{N_D - n}{n}$$

$$\Rightarrow \frac{n^2}{N_D - n} = n(T)\frac{n_{\text{empty}}}{n_{\text{occupied}}}$$

$$= 2\left(\frac{m_{\text{e}}}{2\pi\beta\hbar^2}\right)^{3/2} e^{-\beta E_i}$$

In addition, $k_{\text{B}}T \ll E_g \Rightarrow$ all e$^-$ from impurity states so neglect holes.

(c) i. At high temperature, the e$^-$ have enough thermal energy to escape conduction band, forming an intrinsic region where the intrinsic carrier dominates the carrier concentration.

As the sample begins to appouch $T \sim 50\,\text{K}$, the transition between intrinsic and extrinsic regimes begins as the intrinsic e$^-$ start to freeze out from the decreasing thermal energy.
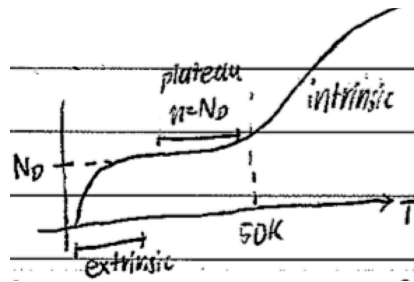
At $T \ll 50\,\text{K}$, the sample enters the extrinsic regime where the donor carrier dominates.

ii. **(TO EXPAND)** For intrinsic e^-,

$$n_i^2 = np = \frac{8 m_{\mathrm{e}}^{3/2} m_{\mathrm{h}}^{3/2}}{\pi^3 \hbar^6} e^{-\beta E_g}$$

$$\Rightarrow n_i = \frac{2\sqrt{2} m_{\mathrm{e}}^{3/4} m_{\mathrm{h}}^{3/4}}{\pi^{3/2} \hbar^3} e^{-\frac{\beta E_g}{2}}$$

$$\Rightarrow \ln\left(n_i\right) \propto -\frac{\beta E_g}{2} = -\frac{E_g}{2 k_{\mathrm{B}} T}$$

$$\Rightarrow \text{gradient} = -\frac{E_g}{2 k_{\mathrm{B}}}$$

$$\Rightarrow \ln\left(10^{21}\right) - \ln\left(10^{19}\right) = -\frac{E_g}{2 k_{\mathrm{B}}} \left(0.01 - 0.02\right) \, \mathrm{K}^{-1}$$

$$\Rightarrow E_g = \frac{6 \ln\left(10\right) k_{\mathrm{B}}}{0.01 \, \mathrm{K}^{-1}}$$

$$= 1.91 \times 10^{-20} \, \mathrm{J} = 0.12 \, \mathrm{eV}$$

which also corresponds to the thermal energy at $\sim 1000 \, \mathrm{K}$.

At low temperature, with $N_D \sim 3 \times 10^{18} \, \mathrm{m}^{-3}$:

$$\frac{n^2}{N_D - n} \simeq \frac{n^2}{n_D} \propto e^{-\beta E_i} \quad \text{since } n \ll N_D$$

$$n = \ldots$$

$$\ln(n) = \ldots$$

$$\Rightarrow \text{gradient} \Rightarrow E_i = \ldots \sim 100 \, \mathrm{K}$$

4. (DRAFT)

(a) Hund's rules:

    1. e^- tend to align their spins;

    2. e^- tend to occupy states that maximises L_z;

    3. Total $J = L + S$ for >half-filled shell, $J = L - S$ for <half-filled.

The alignment of spin has to do with the exchange integral – due to Pauli's exclusion principle, e^- with the same spin cannot come close to each other, increasing the inter-e^- distance, and thus lowering the Coulomb interaction energy.

The tendency to maximise L_z simply has to do with the magnetic Hamitonian:

$$\hat{H} = -\left[-g_s\mu_{\mathrm{B}}\hat{\mathbf{s}} + \mu_{\mathrm{B}}\hat{\mathbf{l}}\right] \cdot \mathbf{B}$$

so maximising $\hat{\mathbf{l}}$ can reduce the overall energy.

(b)   i. Magnetic moment:

$$\boldsymbol{\mu} = -g_s\mu_{\mathrm{B}}\hat{\mathbf{s}} + \mu_{\mathrm{B}}\hat{\mathbf{l}}$$
$$= \tilde{g}\mu_{\mathrm{B}}\hat{\mathbf{J}}$$

where $\tilde{g} = 1 + \dfrac{1}{2}\left[\dfrac{L(L+1)-S(S+1)}{J(J+1)}\right]$.

Susceptibility:

$$\chi_{\mathrm{vol}} = \frac{n\mu_0 m_{\mathrm{eff}}^2 \mu_{\mathrm{B}}^2}{(T-\Theta)3k_{\mathrm{B}}}$$
$$nV_{\mathrm{mol}} = ZN_{\mathrm{A}} \Rightarrow V_{\mathrm{mol}} = \frac{ZN_{\mathrm{A}}}{n} \quad (Z=1)$$
$$\chi_{\mathrm{mol}} = \chi_{\mathrm{vol}} \cdot V_{\mathrm{mol}}$$
$$= \frac{N_{\mathrm{A}}\mu_0\mu_{\mathrm{B}}^2}{3k_{\mathrm{B}}}\frac{m_{\mathrm{eff}}^2}{T-\Theta}$$

  ii. **(TO EXPAND)** $m_{\mathrm{eff}} = \tilde{g}\sqrt{J(J+1)}$

  iii. Θ is transition temperature where paramagnetism no longer applies.

Below Θ, ferromagnetism dominates over paramagnetism and the interaction between neighbouring e^- dictates if the material is ferromagnetic / antiferromagnetic / ferrimagnetic.

$\Theta \propto J$ the Curie temperature. $\Theta > 0$ ferromagnetic, $\Theta < 0$ antiferromagnetic.

$$\hat{H}_{\mathrm{exchange}} = -J\sum_{\langle i,j\rangle} \hat{\mathbf{S}}_i \cdot \hat{\mathbf{S}}_j$$

(c) From b,

$$\chi_{\text{mol}} = \gamma \frac{(m_{\text{eff}})^2}{T - \Theta} \quad \text{where } \gamma = 1.57 \times 10^{-6} \, \text{m}^3 \, \text{K} \, \text{mol}^{-1}$$

$$\Rightarrow \frac{1}{\chi_{\text{mol}}} = \frac{\gamma}{(m_{\text{eff}})^2}(T - \Theta)$$

$$\Rightarrow \text{gradient} = \frac{\gamma}{(m_{\text{eff}}^2)}$$

$$\Rightarrow \frac{18 - 9}{280 - 100} \text{mol} \, \text{m}^{-3} \, \text{K}^{-1} = \frac{\gamma}{(m_{\text{eff}})^2}$$

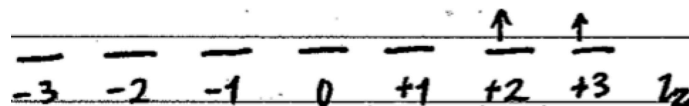$$\Rightarrow (m_{\text{eff}})^2 = ?$$

$$m_{\text{eff}} = 3.57$$

So:

$$\frac{1}{\chi_{\text{mol}}} = 0.05 \left[\text{mol} \, \text{m}^3 \, \text{K}^{-1}\right] (T - \Theta)$$

$$\Rightarrow 14 \, \text{mol} \, \text{m}^{-3} = 0.05(200 - \Theta) \text{mol} \, \text{m}^{-3}$$

$$\Rightarrow \Theta = -80 \, \text{K}$$

Since $\Theta < 0$, Pr^{3+} is antiferromagnetic since $\chi_{\text{mol}} \nrightarrow \infty$ in physical regime.

(d)   i. Pr^{3+}: $[\text{Xe}] \, 4f^2 \Rightarrow 2$ valence e$^-$.

So by Hund's rules,

should be the e$^-$ config.

$\Rightarrow L = 5$, $S = 1 \Rightarrow J = L - S = 4$ as per Hund's rule.

ii.

$$m_{\text{eff}} = \tilde{g}\sqrt{4.5}$$

$$\Rightarrow \tilde{g} = 0.798$$

Theoretically $\tilde{g} = \frac{3}{2} + \frac{2 - 30}{40} = 0.8$, the values match pretty well.