Bragg diffraction and electron-gas heat capacity

GRE undergraduate preparation · local supported objectives

Crystal diffraction and free-electron metals

- Use **Bragg's law 布拉格定律** with the correct angle.
- Find plane spacings in a cubic crystal from its **lattice constant 晶格常数**.
- Use the free-electron model to find the **Fermi energy 费米能**.
- Separate the electron and lattice parts of a metal's heat capacity.

Bragg's law

- θ is the glancing angle measured from the plane, not from the normal. A detector reading 2θ shows the angle between the incident and scattered beams.
- Because $\sin\theta \le 1$, only orders with $n \le 2d/\lambda$ appear.

$$2d\sin\theta = n\lambda$$

Planes in cubic crystals

- (100) planes are a apart; (110) planes are $a/\sqrt{2}$ apart; (111) planes are $a/\sqrt{3}$ apart.
- Some reflections are missing because atoms inside the cell cancel them. Body-centred cubic: $h+k+l$ odd is absent. Face-centred cubic: only all-even or all-odd hkl appear.

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

Free electrons

- For metals E_F is several eV, so the Fermi temperature $T_F = E_F/k_B$ is tens of thousands of kelvin.
- Only electrons within about $k_B T$ of E_F can gain energy, a fraction of roughly T/T_F.

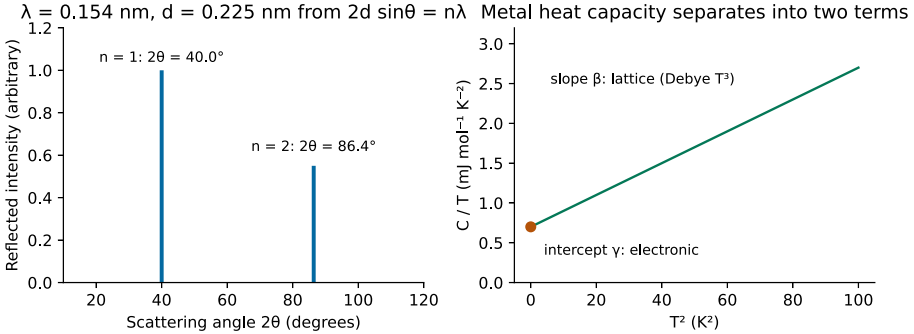
$$k_F = \left(3\pi^2 n\right)^{1/3}, \qquad E_F = \frac{\hbar^2 k_F^2}{2m}$$

Heat capacity of a metal

- Plot C/T against T^2: a straight line with intercept γ and slope β.
- The electron term wins at the lowest temperatures; at room temperature the lattice dominates, near the Dulong–Petit value $3R$.

$$C = \gamma T + \beta T^3$$

Figure: Heat capacity of a metal



- **Bragg's law** 2d sin $\theta = n\lambda$; $C/T = \gamma + \beta T^2$ separates electrons from lattice
- Read the axes and units first.

Worked example: reading a diffraction pattern

- $d = 0.154 / (2 \sin 20.0^\circ) = 0.154 / 0.684 = 0.225$ nm.
- Second order: $\sin\theta = 0.154 / 0.225 = 0.684$, so $\theta = 43.2^\circ$ and $2\theta = 86.4^\circ$. There is no third order, since $3\lambda / 2d > 1$.
- Rock salt ($a = 0.564$ nm) has $d_{200} = 0.282$ nm, giving $\sin\theta = 0.273$ and $\theta = 15.8^\circ$.

Worked example: copper's electrons

- $k_F = (3\pi^2 \times 8.5 \times 10^{28})^{1/3} = 1.36 \times 10^{10}$ m^{-1}.
- $E_F = (1.055 \times 10^{-34})^2 (1.36 \times 10^{10})^2 / (2 \times 9.11 \times 10^{-31}) = 1.13 \times 10^{-18}$ J $= 7.0$ eV, so $T_F = 8.1 \times 10^4$ K.
- If $C/T = 0.7 + 0.05\,T^2$ (mJ mol^{-1} K^{-2}), the two terms are equal where $0.05\,T^2 = 0.7$, at $T = 3.7$ K.

Common errors

- Measuring θ from the normal, or using the detector angle 2θ as θ.
- Allowing orders with $n\lambda > 2d$.
- Forgetting the systematic absences of BCC and FCC lattices.

Common errors (2)

- Expecting every electron to share the thermal energy; only a fraction T/T_F does.
- Fitting C against T instead of C/T against T^2.

Key terms

- **Bragg's law**: The condition $2d\sin\theta = n\lambda$ for strong reflection from crystal planes, with θ measured from the planes.
- **lattice constant**: The side length of a crystal's repeating cubic cell.
- **Fermi energy**: The highest occupied electron energy at absolute zero in the free-electron model.

Check yourself

- A cubic crystal has $a = 0.30$ nm. What is d_{111}?
- Does a body-centred cubic crystal show a (100) reflection?
- A metal's heat capacity is measured at 1 K. Which term usually dominates?