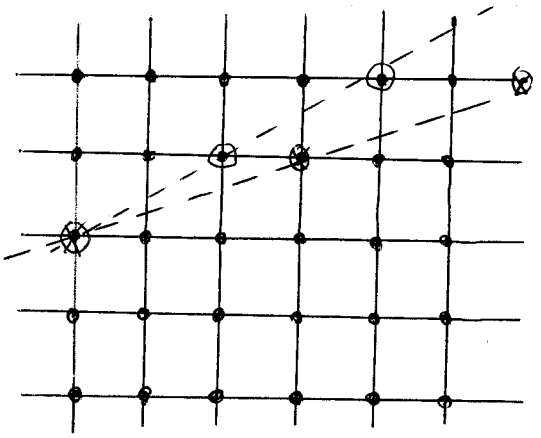
Worked example

* square lattice in 2D
  → described by lattice vectors $\vec{a}_1 = a\hat{e}_x$, $\vec{a}_2 = a\hat{e}_y$
  → trivial basis
  → lattice consists of all points $\vec{R} \in \mathbb{Z}\vec{a}_1 + \mathbb{Z}\vec{a}_2$ (infinite set)



→ lines connecting nearest neighbor sites are just guides to the eye (not part of the lattice per se)

→ actually an infinite number of planes (through an infinite subset of lattice points) we could draw with slope

$$\frac{1}{\infty}, \ldots \frac{1}{3}, \frac{1}{2}, \frac{1}{1}, 1, 2, 3, \ldots, \infty$$

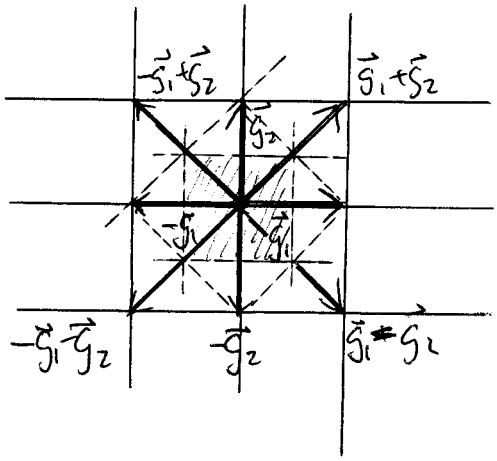
→ in 2D we can include a dummy vector $\vec{a}_3 = \hat{e}_z$ so that all the 3D formulas hold: e.g. vol. unit cell $\Omega_0 = (\vec{a}_1 \times \vec{a}_2)\cdot\vec{a}_3 = a^2$

→ reciprocal lattice vectors

$$\vec{g}_1 = \frac{2\pi}{\Omega_0}\vec{a}_2 \times \vec{a}_3 = \frac{2\pi}{a^2} a\hat{e}_y \times \hat{e}_z = \frac{2\pi}{a}\hat{e}_x$$

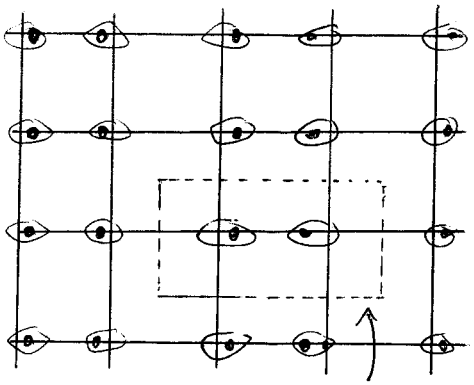
$$\vec{g}_2 = \frac{2\pi}{\Omega_0}\vec{a}_3 \times \vec{a}_1 = \frac{2\pi}{a^2}\hat{e}_z \times a\hat{e}_x = \frac{2\pi}{a}\hat{e}_y$$

→ in this special case, the reciprocal lattice $\mathbb{Z}\vec{G}_1 + \mathbb{Z}\vec{G}_2$ is just a rescaled version of the real-space lattice



→ Wigner-Seitz construction ⇒ $BZ = \left[-\frac{\pi}{a}, \frac{\pi}{a}\right) \times \left[-\frac{\pi}{a}, \frac{\pi}{a}\right)$

* Consider a deformed lattice where atoms have been shifted alternately left and right

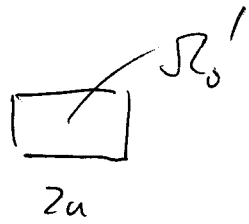


doubled unit cell with a nontrivial 2-site basis

→ new lattice with doubled repeat unit in the $\hat{e}_x$ direction

$\vec{a}_1 = 2a\hat{e}_x$

$\vec{a}_2 = a\hat{e}_y$



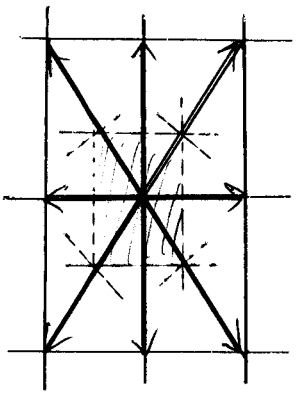
$\Omega_0' = 2a^2$

$\frac{\Omega_0'}{\text{dim(basis)}} = \Omega_0 = a^2$

→ corresponding reciprocal lattice vectors

$\vec{G}_1 = \frac{2\pi}{2a^2} a\hat{e}_y \times \hat{e}_z = \frac{\pi}{a}\hat{e}_x$

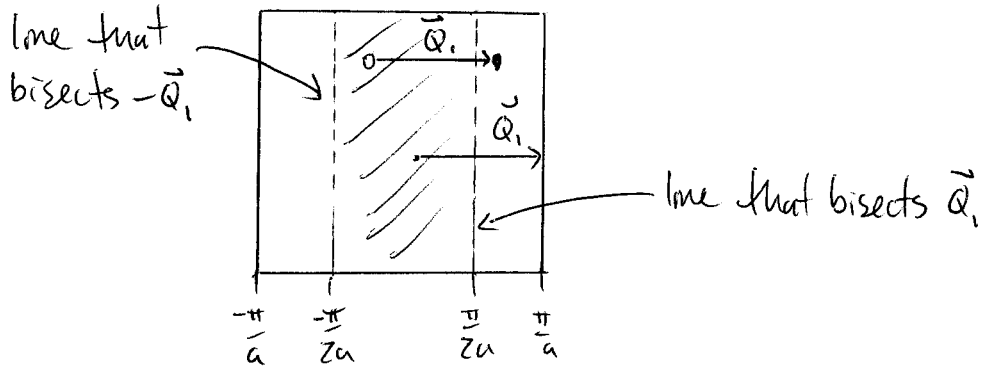
$\vec{G}_2 = \frac{2\pi}{2a^2} \hat{e}_z \times (2a\hat{e}_x) = \frac{2\pi}{a}\hat{e}_y$



→ new BZ' = $\left[\frac{-\pi}{2a}, \frac{\pi}{2a}\right) \times \left[\frac{-\pi}{a}, \frac{\pi}{a}\right)$

<u>Compressed</u> by a factor of two in the $\hat{e}_x$ direction

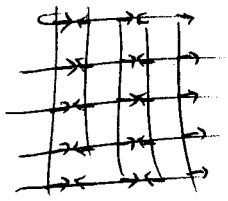
→ note that the old BZ can be "folded" into the reduced BZ by a vector $\vec{Q}_1 = \frac{\pi}{a}\hat{e}_x = \frac{\pi}{a}(1,0)$



→ $\vec{Q}_1$ is related to the ordering vector of the atomic displacement:

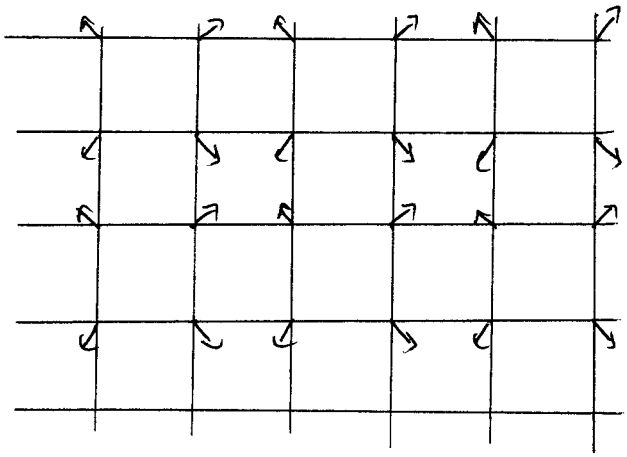
$$\vec{d} = \alpha_1 e^{i\vec{Q}_1 \cdot \vec{R}} \hat{e}_x = \alpha_1 (-1)^{R_x} \hat{e}_x$$

i.e. each atom $\vec{R}$ in the original lattice was moved to $\vec{R} + \vec{d}$



* Consider a more complicated distortion $\vec{d} = \alpha_1 \hat{e}_x e^{i\vec{Q}_1 \cdot \vec{R}} + \alpha_2 \hat{e}_y e^{i\vec{Q}_2 \cdot \vec{R}}$

with $\vec{Q}_1 = \frac{\pi}{a}(1,0)$ and $\vec{Q}_2 = \frac{\pi}{a}(0,1)$



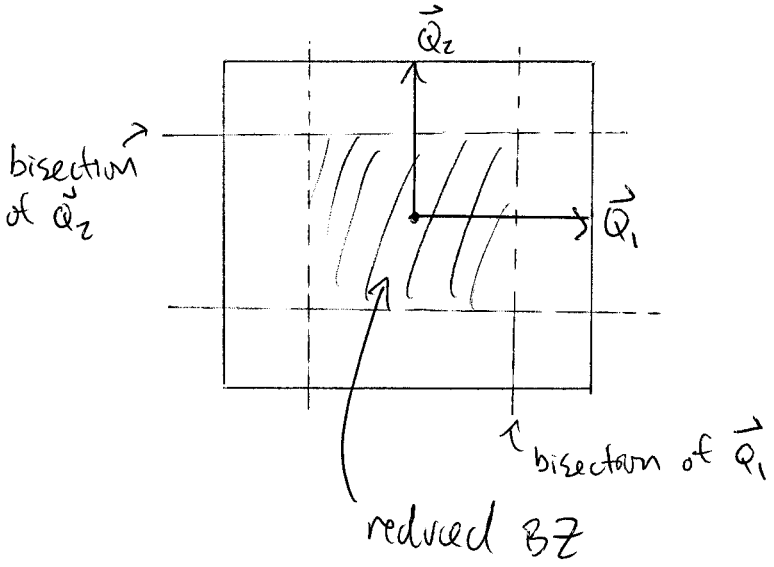
→ real-space $\hat{e}_x$ and $\hat{e}_y$ atomic distortions alternating by row and column

→ $\alpha_1 \neq 0$, $\alpha_2 \neq 0$ leads to unit cell doubling in both directions:

$\vec{a}_1 = 2a\hat{e}_x$

$\vec{a}_2 = 2a\hat{e}_y$

$\Omega_0 = 4a^2$ and a 4-atom basis



→ pattern is invariant (modulo translations and 90° rotations) under $\alpha_1 \to -\alpha_1$, $\alpha_2 \to -\alpha_2$ and the swap $\alpha_1 \leftrightarrow \alpha_2$

→ implies that the most general Ginzburg-Landau functional $F[\alpha_1, \alpha_2]$ is a mixed powerseries in α_1^2 and α_2^2:

$$F[\alpha_1, \alpha_2] = r(\alpha_1^2 + \alpha_2^2) + s\alpha_1^2\alpha_2^2 + u(\alpha_1^4 + \alpha_2^4) + \dots$$

Alternatively, we could parameterize $\alpha_1 = \alpha\cos\theta$

$\alpha_2 = \alpha\sin\theta$

$$F[\alpha,\theta] = r\alpha^2 + s\alpha^4\cos^2\theta\sin^2\theta + u\left(\alpha^4\cos^4\theta + \alpha^4\sin^4\theta\right)$$

$$= r\alpha^2 + \left[\, s\left(\tfrac{1}{4}\sin^2 2\theta\right) + u\left(1 - \tfrac{1}{2}\sin^2 2\theta\right)\right]\alpha^4$$

$u>0$ is required for stability; at the special point $s = 2u$, the free energy is degenerate in θ; other values of s tend to favour or penalize solutions along the lines $\alpha_2 = \pm\alpha_1$.

→ find the stationary points:

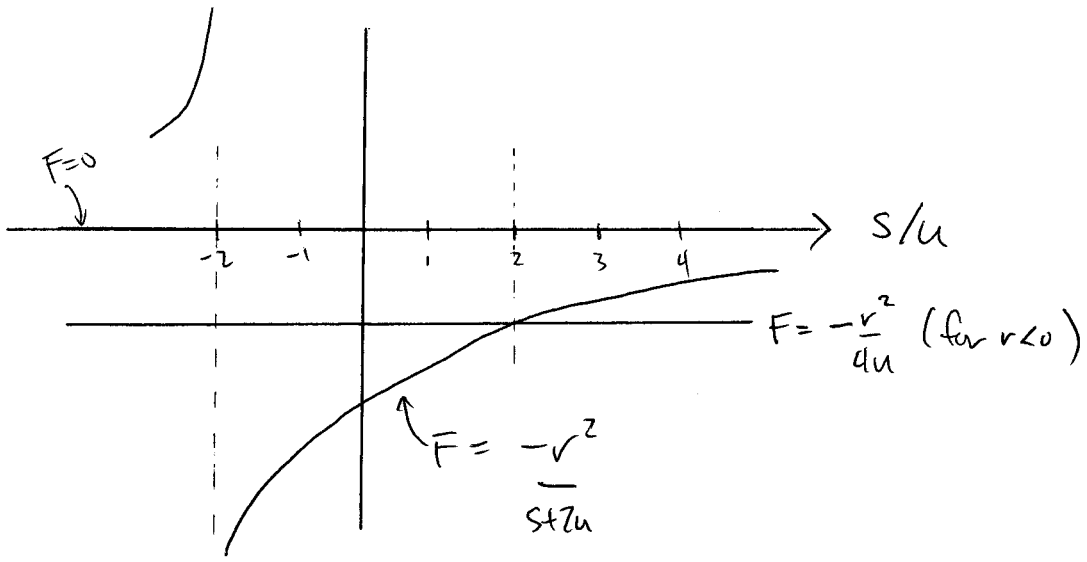
$$\frac{\partial F}{\partial \alpha_1} = 2r\alpha_1 + 2s\alpha_1\alpha_2^2 + 4u\alpha_1^3 = 2\alpha_1\left(r + s\alpha_2^2 + 2u\alpha_1^2\right) = 0$$

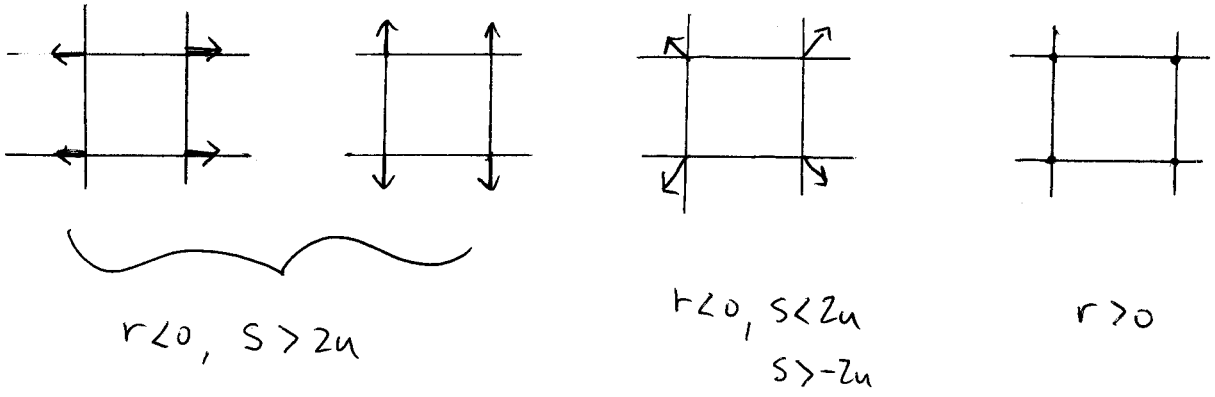
$$\frac{\partial F}{\partial \alpha_2} = 2r\alpha_2 + 2s\alpha_1^2\alpha_2 + 4u\alpha_2^3 = 2\alpha_2\left(r + s\alpha_1^2 + 2u\alpha_2^2\right) = 0$$

→ Solutions $\alpha_1 = \alpha_2 = 0$ with $F = 0$

$$\left.\begin{aligned} &\alpha_1 = 0,\ \alpha_2 = \pm\sqrt{\frac{-r}{2u}} \\ &\alpha_2 = 0,\ \alpha_1 = \pm\sqrt{\frac{-r}{2u}} \end{aligned}\right\} \text{ with } F = -\frac{r^2}{4u} \quad (r<0 \text{ only})$$

$$\alpha_1 = \alpha_2 = \pm\sqrt{\frac{-r}{s+2u}} \text{ with } F = -\frac{r^2}{s+2u}$$





r<0, S>2u

r<0, S<2u
S>-2u

r>0

QUESTIONS:

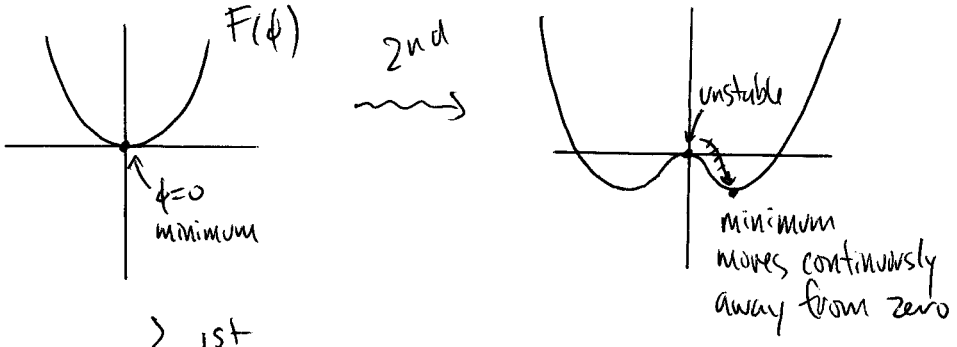
① Consider the transition from r>0 to r<0 where the crystal initially distorts. Is this first- or second-order?

② Consider the transition of the distorted lattice (r<0) from one kind of distortion to another (i.e. S-2u changes sign). Is this first- or second-order?

Crystal Growth

* the transition from liquid to solid is first order

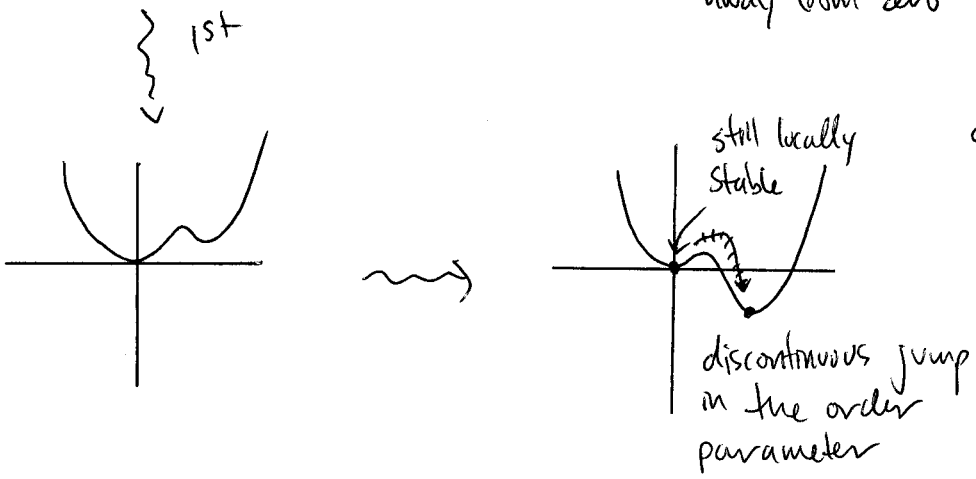
→ recall our classifications



infinitesimal change in φ

$d(\text{Push}) = d(\text{Amplitude}) \times$ Sample

across the whole system



$d(\text{Push}) = \text{Amplitude} \times d(\text{Sample})$

finite change in φ

in a microscopic region

* crystals grow from a nucleation point

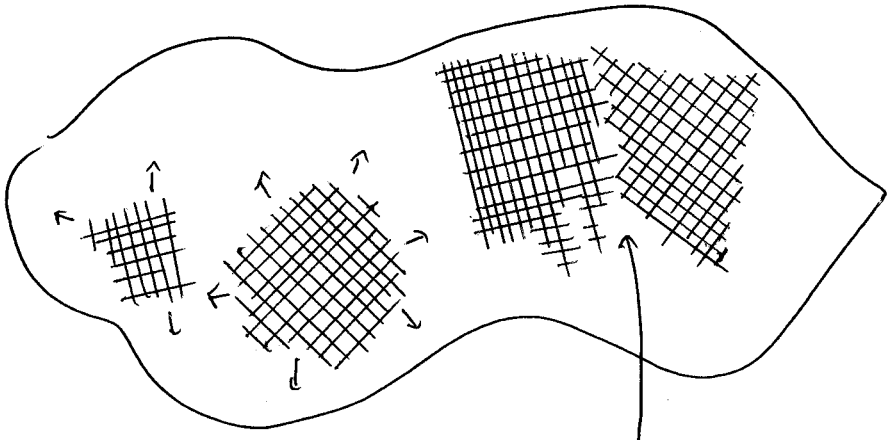
→ jump in the free energy ⇒ latent heat of formation

→ liquid can be supercooled below its solidification temp.

→ may have to wait a very long time for local fluctuations to initiate the crystallization process

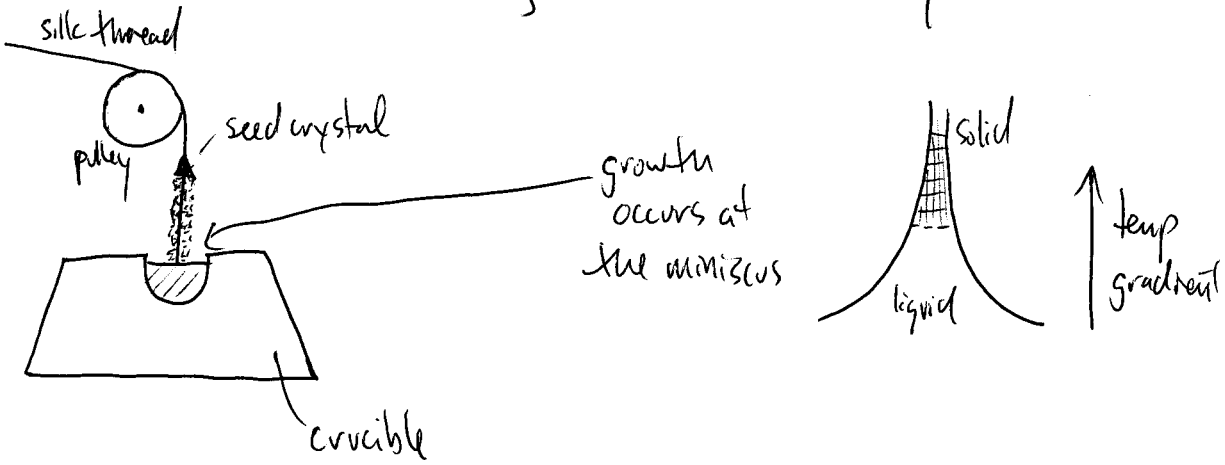
→ crystals are most often <u>seeded</u> by a nucleation centre

* it can be difficult to grow large, single-crystal samples
  → lattice arrangements arising from two separated nucleation centres may be incompatible

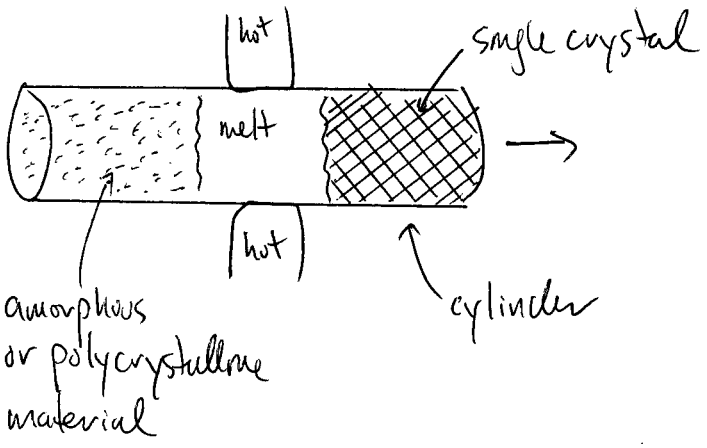


* growth methods

① Pull crystals from a melt using a small seed crystal



(2) draw packed powder through a hot zone



→ multiple passes help to eliminate defects, impurities, and mismatched grains (zone refinement)

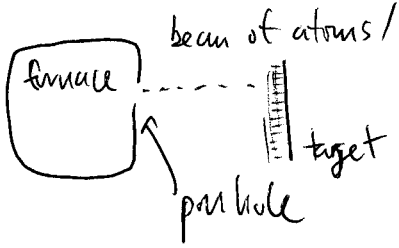
(3) nucleated in supersaturated solution (like sugar in syrup)

(4) grown in vapour (only good for small single crystals)

Modern techniques lay down material on a surface layer by layer

(5) Molecular beam epitaxy

(6) Chemical vapour deposition



X-ray diffraction

1895 Roentgen discovers x-rays

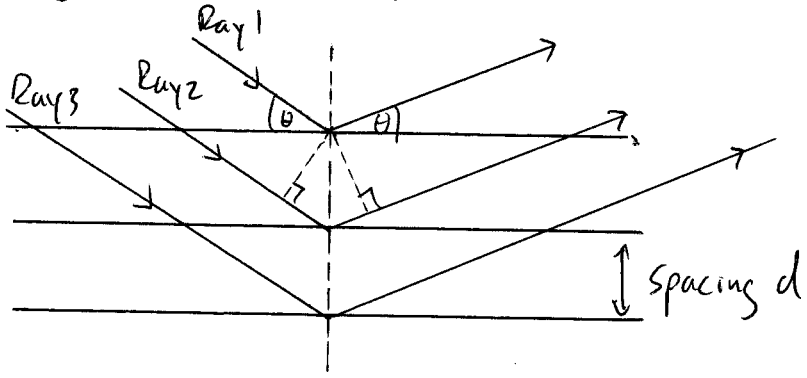
→ unknown emission later understood to be high-energy EM radiation (photons)

→ recall that $hc = 12400\ eV\cdot\text{Å}$, hence $E = \frac{hc}{\lambda} \sim 8keV$ corresponds to $\lambda \sim 1.5\text{Å}$ (atomic seperation in a solid)

1912 von Laue proposes using x-rays for diffraction in a crystal

→ lattice planes act as a diffraction grating

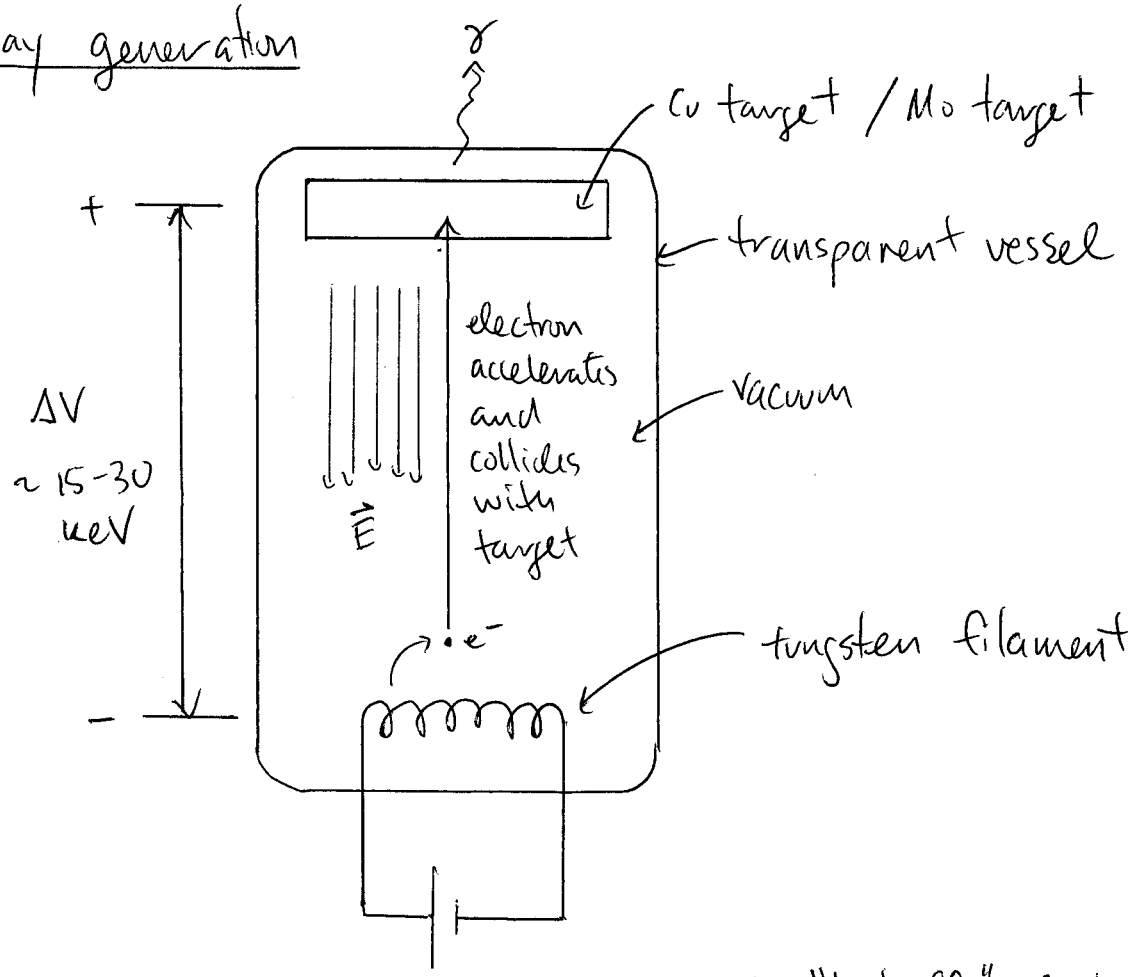
1913 Bragg picture imagines monochromatic light specularly reflecting off atomic planes



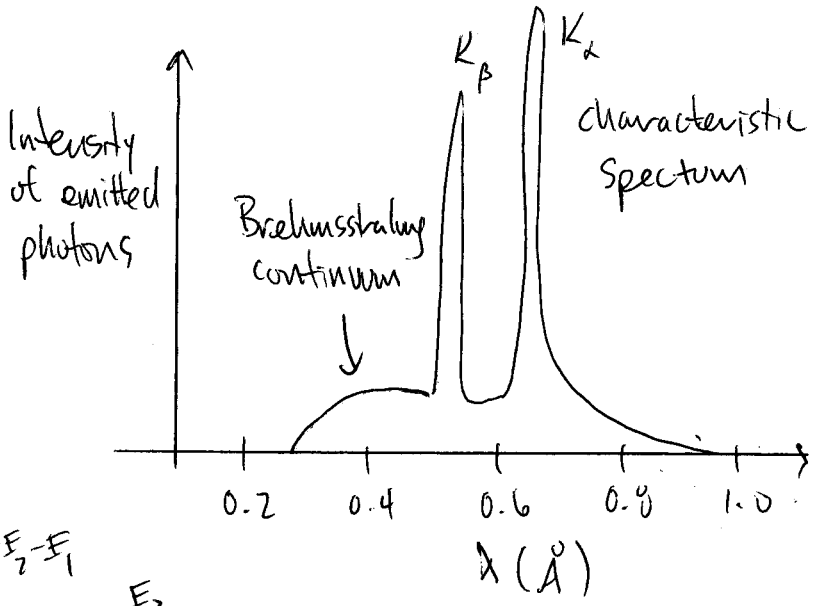
- successive path differences of $2d\sin\theta$
- if all the phase shifts associated with reflection are constant then there is constructive interference whenever

$$2d\sin\theta = \text{integer} \times \lambda$$

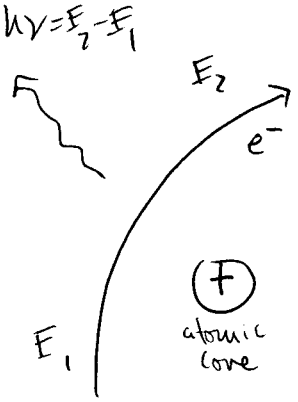
Xray generation



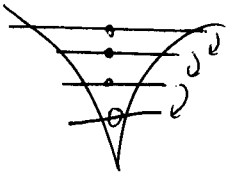
10-15 mA is enough to "boil off" electrons



The sharp emission lines are discrete and correspond to the cascade of level changes when an electron is kicked out of a core



Brehmsstralung gives a continuous spectrum of photon energies from deflection



Scattering

Recall: Any function $f(\vec{r})$ can be expanded in a Fourier series. And if it shares the periodicity of the lattice, i.e. $f(\vec{r}+\vec{R}) = f(\vec{r})$ for any lattice vector $\vec{R}$, then its only nonzero Fourier components are at reciprocal lattice vectors:

$$f(\vec{r}) = \sum_{\vec{G}} f_{\vec{G}}\, e^{i\vec{G}\cdot\vec{r}}$$

$$f_{\vec{G}} = \int_{\Omega_0} \frac{d^3r}{\Omega_0}\, f(\vec{r})\, e^{-i\vec{G}\cdot\vec{r}}$$

* minimal coupling of EM field to electrons

$$H = \frac{1}{2m}\sum_i \left[p_i - eA(r_i)\right]^2$$

$$= H_0 + \vec{J}\cdot\vec{A} + V$$

where $V = \frac{e^2}{2m}\sum_i |A(r_i)|^2 = \frac{e^2}{2m}\int d^3r\, n(\vec{r})\, |A(\vec{r})|^2$

$n(\vec{r}) = \sum_j \delta(\vec{r} - r_j)$ is the electron density

nonlinear interaction of EM field with electron density

* simple scattering event for photon

$$\vec{A}(\vec{r}) = \vec{A}_{in}\, e^{i\vec{k}\cdot\vec{r}} + \vec{A}_{out}\, e^{i\vec{k}'\cdot\vec{r}}$$

$$|\vec{A}(\vec{r})|^2 = |\vec{A}_{in}|^2 + |\vec{A}_{out}|^2 + 2\vec{A}_{in}\cdot\vec{A}_{out}\, e^{i(\vec{k}-\vec{k}')\cdot\vec{r}}$$

$$\Rightarrow \frac{e^2}{2m}\int d^3r\, n(\vec{r})\,|\vec{A}(r)|^2 = \frac{e^2}{2m}\int d^3r\, n(\vec{r})\,\Big[(\text{trivial constant}) + 2\vec{A}_{in}\cdot\vec{A}_{out}\, e^{i(\vec{k}-\vec{k}')\cdot\vec{r}}\Big]$$

$$= \text{const} + \frac{e^2}{m}\vec{A}_{in}\cdot\vec{A}_{out}\int d^3r \sum_{\vec{G}} n_{\vec{G}}\, e^{i\vec{G}\cdot\vec{r}}\, e^{i(\vec{k}-\vec{k}')\cdot\vec{r}}$$

$$= \text{const} + \frac{e^2}{m}\vec{A}_{in}\cdot\vec{A}_{out}\sum_{\vec{G}} n_{\vec{G}}\int d^3r\, e^{i\vec{r}\cdot(\vec{k}+\vec{G}-\vec{k}')}$$

$$\int d^3r\, e^{i\vec{r}\cdot(\vec{k}+\vec{G}-\vec{k}')} = \delta_{\vec{k}+\vec{G},\,\vec{k}'}$$

→ elastic scattering can only change the photon wavevector by a reciprocal lattice vector

→ scattering x-section $\propto \frac{e^2}{m_e}$, which is what we expect of classical Rayleigh scattering from a charged particle

→ x-rays only sensitive to the electronic configuration since $m_p = 2000 \times m_e$

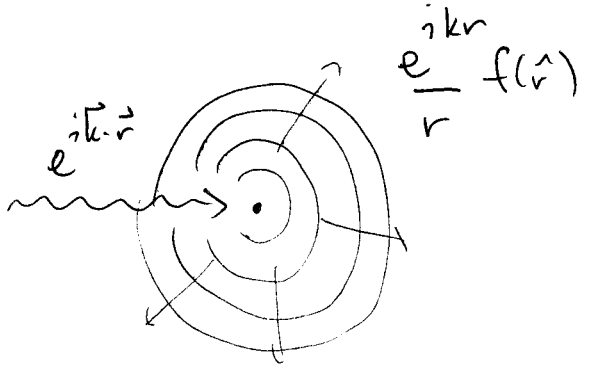
Array of point scatterers

* Bragg picture is highly oversimplified (there is not actually specular reflection off planes)

* We need to consider a lattice of points that absorb and re-emit photons in a circular wavefront

$$\psi \simeq A e^{-i\omega t}\left[e^{i\vec{k}\cdot\vec{r}} + \frac{e^{ikr}}{r} f(\hat{r})\right]$$

↑ radial wave with $k = |\vec{k}|$, $r = |\vec{r}|$, scattered from a point at the origin



$|\psi_{outgoing}|^2 \sim \frac{1}{r^2}$ is required by normalization over spherical shells:

$$\int d^3r\, |\psi|^2 = \int dr\, 2\pi r^2 |\psi|^2 \sim 1$$

* Scatter instead from a lattice site at $\vec{R}$

$$\psi \sim A e^{-i\omega t}\left[e^{i\vec{k}\cdot\vec{r}} + e^{i\vec{k}\cdot\vec{R}} f(\hat{r-R})\, \frac{e^{ik|\vec{r}-\vec{R}|}}{|\vec{r}-\vec{R}|} \right]$$

→ at distant points $r \gg R$,

$$\hat{r-R} \simeq \hat{r} \quad \text{(rays become parallel)}$$

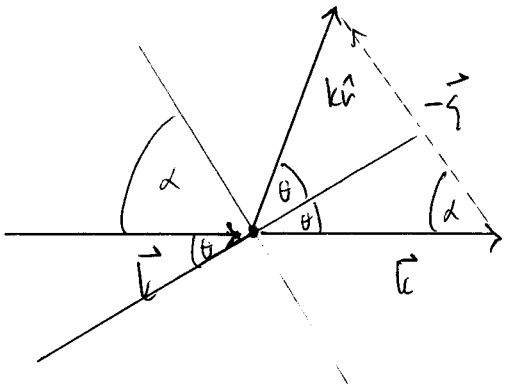
and $$k|\vec{r}-\vec{R}| = k\sqrt{r^2 - 2\vec{r}\cdot\vec{R} + R^2}$$

$$= kr\sqrt{1 - \underbrace{2\hat{r}\cdot\frac{\vec{R}}{r}}_{} + \underbrace{\frac{R^2}{r^2}}_{}}$$

$$\simeq kr - k\hat{r}\cdot\vec{R}$$

→ net phase in the outgoing wave is

$$k|\vec{r}-\vec{R}| + \vec{k}\cdot\vec{R} \simeq kr - \underbrace{(\vec{k} - k\hat{r})}_{\text{def}^n\ \vec{q}}\cdot\vec{R}$$



with $\alpha = \frac{\pi}{2} - \theta$

→ combine ① $\vec{k}\cdot\vec{q} = kq\cos\alpha$
$= kq\sin\theta$

② $\vec{k}\cdot(k\hat{r}) = k^2\cos 2\theta$

$= \vec{k}\cdot(\vec{k}-\vec{q})$

$= k^2 - \vec{k}\cdot\vec{q}$

$\Rightarrow \vec{k}\cdot\vec{q} = k^2(1-\cos 2\theta)$
$= 2k^2\sin^2\theta$

to get $q = 2k\sin\theta$

* Sum over contributions from all lattice points

$$\psi \sim A e^{-i\omega t}\left[e^{i\vec{k}\cdot\vec{r}} + \sum_{\vec{R}} f_{\vec{R}}(\hat{r})\, \frac{e^{ikr + i\vec{\varsigma}\cdot\vec{R}}}{r} \right]$$

→ outgoing intensity is

$$I \propto \frac{1}{r^2} \left| \sum_{\vec{R}} f_{\vec{R}}(\hat{r})\, e^{i\vec{\varsigma}\cdot\vec{R}} \right|^2$$

→ for identical scatterers

$$I = I_{atom} \left| \sum_{\vec{R}} e^{i\vec{\varsigma}\cdot\vec{R}} \right|^2$$

↑ strong scattering only when $\vec{\varsigma}\cdot\vec{R} = 2\pi \times \text{integer}$, otherwise, perfect cancellation

i.e. we only see intensity peaks for $\vec{\varsigma} = \vec{G}$ for some $\vec{G}$ in the reciprocal lattice

Scattering with a basis

$$I \propto \left| \sum_{\vec{R}} \sum_{\vec{t}} f_{\vec{R}+\vec{t}}(\hat{r})\, e^{i\vec{\varsigma}\cdot(\vec{R}+\vec{t})} \right|^2$$

↑ sum over lattice

↑ sum over basis in each unit cell

$\dagger$ by translational invariance, $f_{\vec{R}+\vec{\tau}} = f_{\vec{\tau}}$

$$I \propto \left| \sum_{\vec{\tau}} e^{2\pi i \vec{\zeta}\cdot\vec{\tau}} f_{\vec{\tau}}(\hat{r}) \cdot \sum_{\vec{R}} e^{2\pi i \vec{\zeta}\cdot\vec{R}} \right|^2$$

$$= \left| \sum_{\vec{\tau}} e^{2\pi i \vec{\zeta}\cdot\vec{\tau}} f_{\vec{\tau}}(\hat{r}) \right|^2 \cdot \left| \sum_{\vec{R}} e^{2\pi i \vec{\zeta}\cdot\vec{R}} \right|^2$$

"atomic form factors" have arbitrary amplitude and phase (complex numbers)

selects $\vec{\zeta} = \vec{G}$

→ intensity now premultiplied by a "structure factor"

→ possible to have valid $\vec{\zeta} = \vec{G}$ scattering events with zero amplitude (extinction)