Diffraction

How can we measure the positions of atoms in real materials?

Direct Imaging:

Electron microscopy → SEM, TEM

Field-ion microscopy

Scanning probe microscopy → STM, AFM

→ most applicable for studying surfaces, interfaces or defects
→ generally not sensitive to "Bulk" properties.

Scattering techniques: i.e. diffraction

- X-rays → 1-100 keV
- electrons → 10 eV – 1 keV
- neutrons → 10 meV – 1 eV
- atoms → " "

} probe must have $\lambda <$ lattice i.e. $\lambda \lesssim 1$ Å.

- do to Coulomb interaction, e^-'s & atoms interact very strongly w solids ⇒ limits sample size.
- neutron diff. has some extremely important applications, e.g. study of magnetic materials, of Hydrogen.
  ↳ generation is difficult, not practical for "everyday" use. (need nuclear reactor)
- X-ray diffraction is by far the most useful & widespread technique for studying / solving crystal structures.

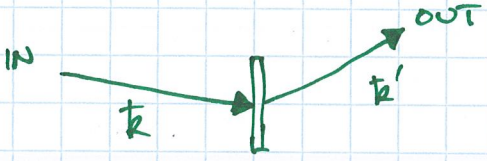
X-ray diffraction & crystallography

- x rays incident on a crystal lattice can scatter off of atomic / $\bar{e}$ planes
- scattered beams interfer constructively @ specific orientations, generating a pattern when detected atside the crystal (spatial)
- analysis of the scattered diffraction pattern lends insight into the positioning / spacing of atoms in the crystal
- crystal reconstruction from x-ray diffraction is very, very complex. We will cover a basic, intuitive understanding.

For atomic resolution $\lambda \approx \text{Å}$

$$\therefore \frac{hc}{\lambda} \approx 12.4 \text{ keV} \Rightarrow \text{x-rays}$$

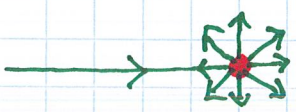
Von Laue formulation of diffraction



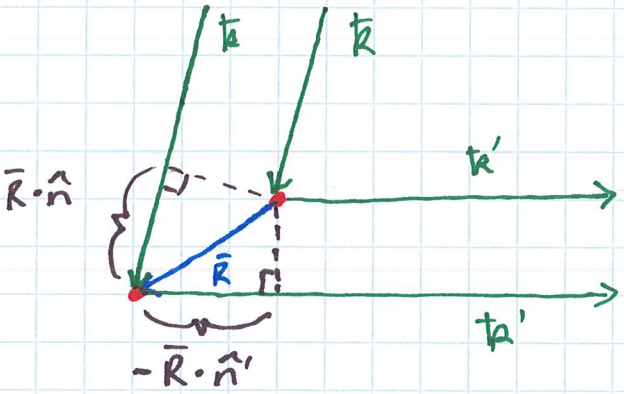
- elastic scattering (no energy loss)

$$|\vec{k}| = |\vec{k}'|$$

- in this model, atoms absorb & re-emit radiation at all angles w/ equal probability: occurs instantaneously



take two atoms, separated by $\bar{R}$:



$$\vec{k} = |\vec{k}|\,\hat{n}$$

$$\vec{k}' = |\vec{k}'|\,\hat{n}'$$

Path difference between two beams is $\bar{R}\cdot\hat{n} - \bar{R}\cdot\hat{n}'$

$$\Delta\ell = \bar{R}\cdot\hat{n} - \bar{R}\cdot\hat{n}' = \bar{R}\cdot(\hat{n}-\hat{n}')$$

$$= \bar{R}\cdot\left(\frac{\vec{k}}{|\vec{k}|} - \frac{\vec{k}'}{|\vec{k}'|}\right) \qquad \text{but } |\vec{k}| = |\vec{k}'|$$

$$\therefore \Delta\ell = \frac{\bar{R}}{|\vec{k}|}\cdot(\vec{k}-\vec{k}')$$

For constructive interference, $\Delta\ell$ must be a multiple of the wavelength of radiation:

Note: $|\vec{k}| = k = \frac{2\pi}{\lambda}$

$$\therefore \Delta\ell = m\lambda \quad , \quad m \text{ integer}$$

$$\therefore \left(\frac{2\pi}{\lambda}\right)^{-1} \bar{R}\cdot(\vec{k}-\vec{k}') = m\lambda$$

$$\therefore \bar{R}\cdot(\vec{k}-\vec{k}') = 2\pi m \quad \text{for } m \text{ integer.}$$

Recall that this condition is precisely that of the reciprocal lattice:

$$\bar{R} \cdot \bar{K} = 2\pi m \quad \text{for } m \text{ integer}$$

$$\therefore \boxed{\bar{k} - \bar{k}' = \bar{K}}$$

This is the condition for constructive interference, i.e. a bright spot on the detector screen.

∴ The diffraction pattern from a crystal is a direct measurement of it's reciprocal lattice!

$$\bar{k} - \bar{k}' = \bar{K} \Rightarrow \bar{k} - \bar{K} = \bar{k}'$$

$$\therefore |\bar{k} - \bar{K}| = |\bar{k}'| = |\bar{k}|$$

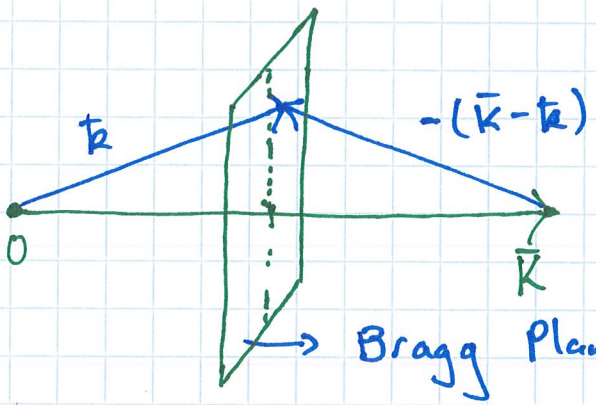
$$\Rightarrow (\bar{k} - \bar{K}) \cdot (\bar{k} - \bar{K}) = k^2$$

$$k^2 - 2\bar{k} \cdot \bar{K} + |\bar{K}|^2 = k^2$$

$$\Rightarrow \frac{\bar{k} \cdot \bar{K}}{|\bar{K}|} = \frac{1}{2}|\bar{K}|$$

→ The projection of $\bar{k}$ onto $\bar{K}$ yeilds $\frac{1}{2}|\bar{K}|$, i.e. $\bar{k}$ falls on the plane which bisects $\bar{K}$.

→ This plane is the defn of the First Brillouin Zone (boundary)!



This condition can be met for each $\bar{K}$, in the reciprocal lattice, though generally not @ the same time

Laue Condition $\quad\Longleftrightarrow\quad$ Bragg Condition

$\bar{K} = \bar{k} - \bar{k}'$ $\quad\Longleftrightarrow\quad$ $2d\sin\theta = m\lambda$

Equiv. through geometric arguments

Structure factor

What about more complicated crystals, such as those w a basis and/or are polyatomic?

- the intensity of the observed Bragg peaks depends on the interference due to the atoms in the primitive cell.

Take two pts in the primitive cell (i.e. basis pt's), given by $\bar{d}_i$ & $\bar{d}_j$.

Th phase difference for the waves scattered by these pts by Bragg plane $\bar{K}$ is

$$\bar{K}\cdot(\bar{d}_i - \bar{d}_j)$$

∴ The amplitude of the two waves differ by a factor of: $e^{i\bar{K}\cdot(\bar{d}_i - \bar{d}_j)}$

If we add up the contribution from all basis pts in the primitive cell we get an amplitude factor of

$$S_K = \sum_{j=1}^{n} f_j(\bar{K})\, e^{i\bar{K}\cdot\bar{d}_j}$$

geometrical structure factor

$\bar{d}_j$ → position of atoms in basis

$f_j(\bar{K})$ – atomic form factor: accounts for specific atomic structure of unit cell

$$f_j(\bar{K}) = \int d^3r\, e^{i\bar{K}\cdot\bar{r}}\, \rho_j(\bar{r})$$

⇒ Fourier transform of the $\bar{e}$ charge distribution of the ion

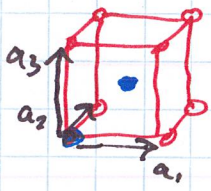
The relative intensity of Bragg peak $\bar{K}$ is given by: $|S_K|^2$

Note: in the simple case of monatomic lattice of pt charges, $f_j(\bar{K})$ reduces to Z (i.e. # of valence $\bar{e}$'s per atom)

Example of structure factor use

BCC can be written as a SC lattice w/ a 2 pt basis:

$$\bar{a}_1 = a\hat{x} \qquad \bar{d}_1 = 0$$
$$\bar{a}_2 = a\hat{y} \qquad \bar{d}_2 = \frac{a}{2}(\hat{x}+\hat{y}+\hat{z})$$
$$\bar{a}_3 = a\hat{z}$$



Find the structure factor & ∴ expected Bragg peak intensity to determine the structure of the reciprocal lattice.

→ assume identical atoms & ions as pt. charges
$\Rightarrow f_j(\bar{K}) = 1$

Structure factor:

$$S_K = \sum_j e^{i\bar{K}\cdot\bar{d}_j}$$
$$= 1 + e^{i(\bar{K}\cdot\bar{d}_2)}$$

For simple cubic lattice, reciprocal lattice vectors take the form:

$$\bar{K} = \frac{2\pi}{a}(n_1\hat{x} + n_2\hat{y} + n_3\hat{z})$$

and $\bar{d}_2 = \frac{a}{2}(\hat{x}+\hat{y}+\hat{z})$

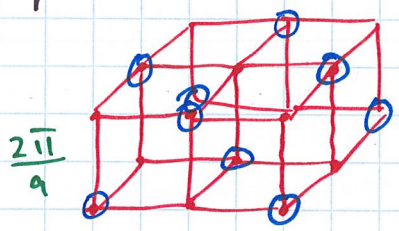
$$\therefore S_K = 1 + e^{i\pi(n_1+n_2+n_3)}$$
$$= 1 + (-1)^{(n_1+n_2+n_3)}$$

We see that if $n_1 + n_2 + n_3 = \text{odd}$, $S_{\vec{K}} = 0$

if $n_1 + n_2 + n_3 = \text{even}$, $S_{\vec{K}} = 2$

$$S_{\vec{K}} = \begin{cases} 2, & n_1+n_2+n_3 \text{ even} \\ 0, & n_1+n_2+n_3 \text{ odd} \end{cases}$$

$\therefore$ if $\sum n_i = \text{odd}$, $S_K = 0$ and the Bragg peak associated w/ that $\vec{K}$ will not appear:



=> Only blue pts appear in reciprocal lattice

=> FCC lattice w/ sides of $\frac{4\pi}{a}$

→ Same result as before!