Diffraction

Fourier series in 1-D, 2-D, or 3-D

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

Reciprocal lattice vectors G
(depend on the Bravais lattice)

Structure factors
(complex numbers)

$$\vec{T}_{hkl} = h\vec{a}_1 + k\vec{a}_2 + l\vec{a}_3$$

$$\vec{a}_i \cdot \vec{b}_j = 2\pi\delta_{ij} \qquad \delta_{ij} = \begin{cases} 1 & \text{for } i = j \\ 0, & \text{for } i \neq j \end{cases}$$

$$\vec{G} = \nu_1\vec{b}_1 + \nu_2\vec{b}_2 + \nu_3\vec{b}_3$$

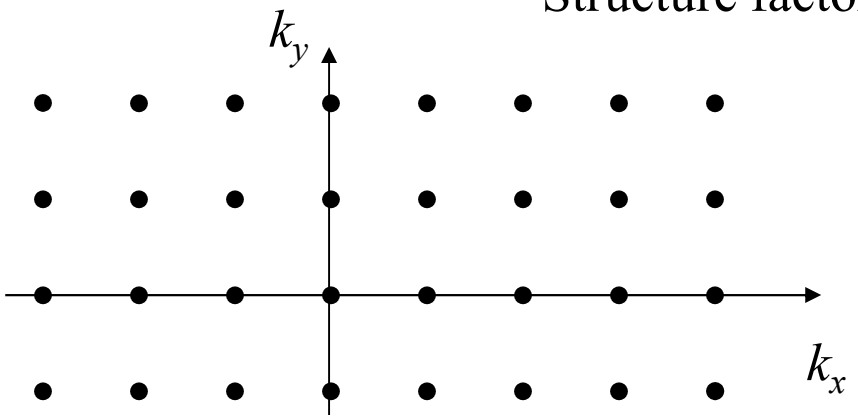
Reciprocal lattice (Reziprokes Gitter)

Any periodic function can be written as a Fourier series

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

Reciprocal lattice vector G

Structure factor



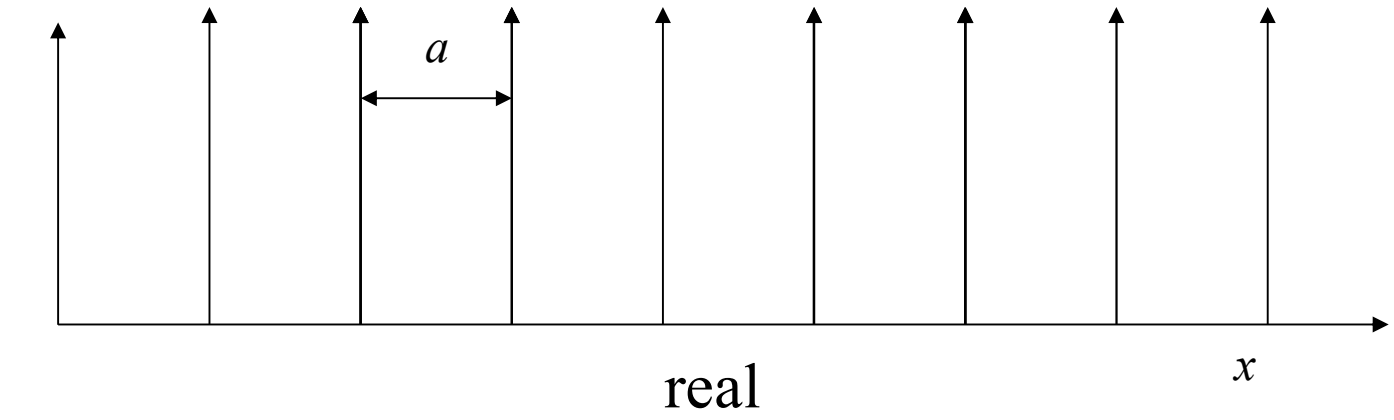
$$\vec{G} = \upsilon_1\vec{b}_1 + \upsilon_2\vec{b}_2 + \upsilon_3\vec{b}_3$$

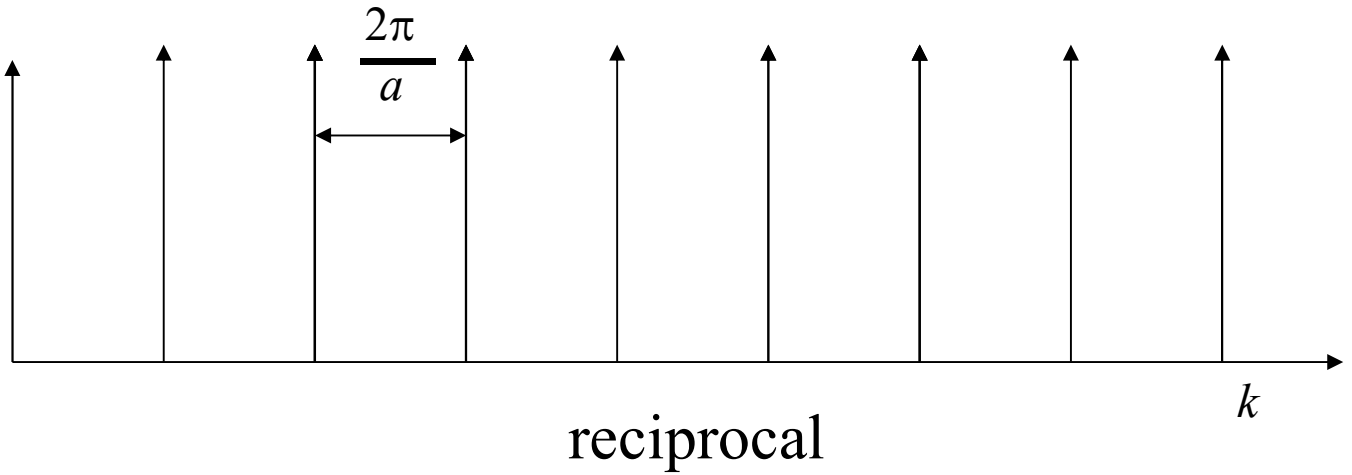
v_i integers

$$\vec{a}_i \cdot \vec{b}_j = 2\pi\delta_{ij}$$

$$\vec{b}_1 = 2\pi\frac{\vec{a}_2\times\vec{a}_3}{\vec{a}_1\cdot(\vec{a}_2\times\vec{a}_3)}, \qquad \vec{b}_2 = 2\pi\frac{\vec{a}_3\times\vec{a}_1}{\vec{a}_1\cdot(\vec{a}_2\times\vec{a}_3)}, \qquad \vec{b}_3 = 2\pi\frac{\vec{a}_1\times\vec{a}_2}{\vec{a}_1\cdot(\vec{a}_2\times\vec{a}_3)}$$

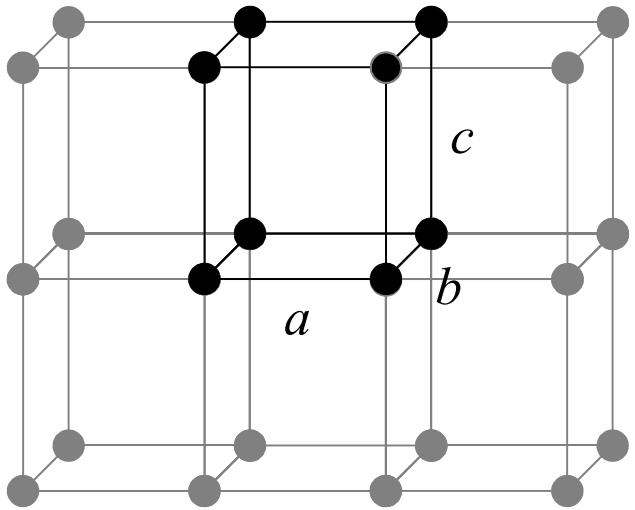
Bravais lattice and reciprocal lattice in 1-D

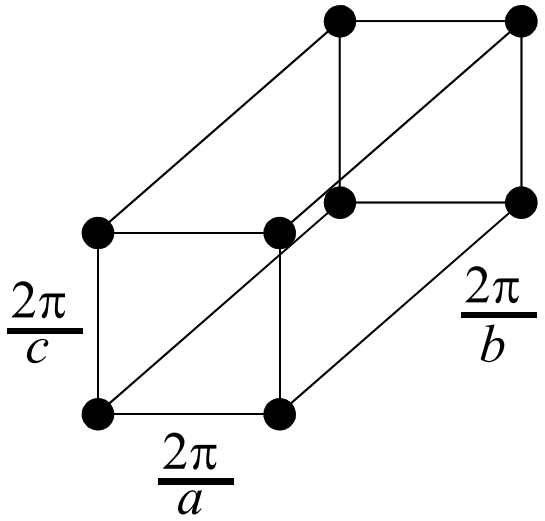




$$\cos\left(\frac{2\pi px}{a}\right) \Rightarrow \cos(Gx) \qquad G = p\frac{2\pi}{a}$$

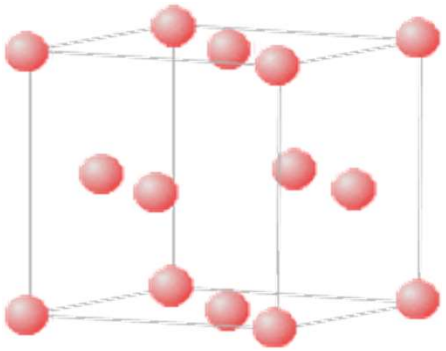
Reciprocal lattice of an orthorhombic lattice is an orthorhombic lattice



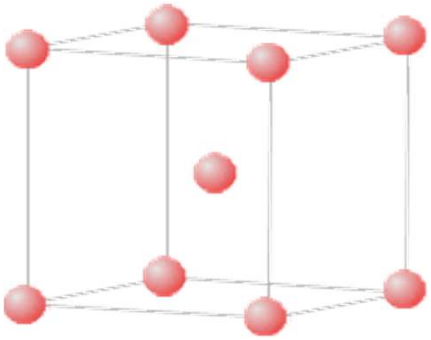


reciprocal lattice

The reciprocal lattice of an fcc lattice is a bcc lattice



a



$\frac{4\pi}{a}$

$$\vec{a}_1 = \frac{a}{2}\hat{x} + \frac{a}{2}\hat{y}$$

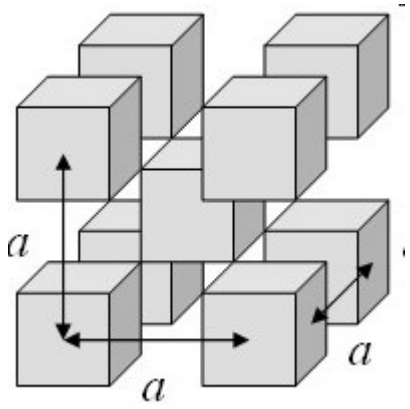
$$\vec{a}_2 = \frac{a}{2}\hat{x} + \frac{a}{2}\hat{z}$$

$$\vec{a}_3 = \frac{a}{2}\hat{y} + \frac{a}{2}\hat{z}$$

$$\vec{b}_3 = 2\pi \frac{\vec{a}_1 \times \vec{a}_2}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)}$$

$$\vec{b}_3 = \frac{2\pi}{a}(\hat{x} - \hat{y} - \hat{z})$$

Cubes on a bcc lattice



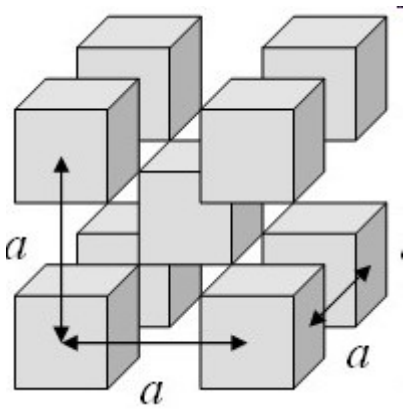
$$f(\vec{r}) = \sum_{\vec{G}} f_{\vec{G}} e^{i\vec{G}\cdot\vec{r}}$$

Multiply by $e^{-i\vec{G}'\cdot\vec{r}}$ and integrate over a primitive unit cell.

$$\int_{\text{unit cell}} f(\vec{r}) e^{-i\vec{G}\cdot\vec{r}} d^3r = f_{\vec{G}} V$$

http://lamp.tu-graz.ac.at/~hadley/ss1/crystaldiffraction/fourier.php

Cubes on a bcc lattice



$$\int_{\text{unit cell}} f(\vec{r}) e^{-i\vec{G}\cdot\vec{r}}\, d^3r = f_{\vec{G}} V$$

V is the volume of the primitive unit cell.

$$f_{\vec{G}} = \frac{1}{V}\int f_{cell}(\vec{r}) \exp\left(-i\vec{G}\cdot\vec{r}\right) d^3r$$

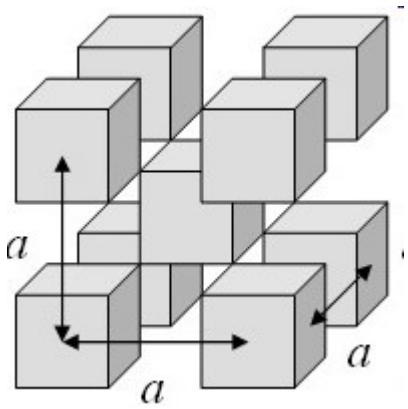
f_G is the Fourier transform of f_{cell} evaluated at G.
f_{cell} is zero outside the primitive unit cell.

$$f_{\vec{G}} = \frac{1}{V}\int f_{cell}(\vec{r}) \exp\left(-i\vec{G}\cdot\vec{r}\right) d^3r = \frac{2C}{a^3} \int_{\frac{-a}{4}}^{\frac{a}{4}} \int_{\frac{-a}{4}}^{\frac{a}{4}} \int_{\frac{-a}{4}}^{\frac{a}{4}} \exp\left(-iG_x x\right) \exp\left(-iG_y y\right) \exp\left(-iG_z z\right) dx\,dy\,dz$$

Volume of conventional u.c. a^3. Two Bravais points per conventional u.c.

Cubes on a bcc lattice

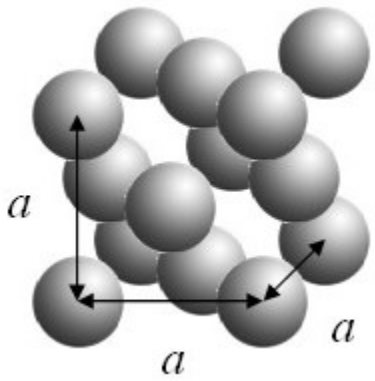
$$\int_{\frac{-a}{4}}^{\frac{a}{4}} \exp\left(-iG_x x\right)dx = \frac{\exp\left(-iG_x x\right)}{-iG_x}\Bigg|_{\frac{-a}{4}}^{\frac{a}{4}} = \frac{\cos\left(-G_x x\right)+i\sin\left(-G_x x\right)}{-iG_x}\Bigg|_{\frac{-a}{4}}^{\frac{a}{4}} = \frac{2\sin\left(\frac{G_x a}{4}\right)}{G_x}$$



$$f_{\vec{G}} = \frac{16C\sin\left(\frac{G_x a}{4}\right)\sin\left(\frac{G_y a}{4}\right)\sin\left(\frac{G_z a}{4}\right)}{a^3 G_x G_y G_z}$$

The Fourier series for any rectangular cuboid with dimensions $L_x \times L_y \times L_z$ repeated on any three-dimensional Bravais lattice is:

$$f(\vec{r}) = \sum_{\vec{G}} \frac{8C\sin\left(\frac{G_x L_x}{2}\right)\sin\left(\frac{G_y L_y}{2}\right)\sin\left(\frac{G_z L_z}{2}\right)}{VG_x G_y G_z}\exp\left(i\vec{G}\cdot\vec{r}\right)$$



Spheres on an fcc lattice

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

Multiply by $e^{-i\vec{G}'\cdot\vec{r}}$ and integrate over a primitive unit cell.

$$f_{\vec{G}} = \frac{1}{V}\int f_{cell}(\vec{r})\exp\left(-i\vec{G}\cdot\vec{r}\right)d^3r = \frac{C}{V}\int_{\text{sphere}} \exp\left(-i\vec{G}\cdot\vec{r}\right)d^3r.$$

The Fourier series for non-overlapping spheres on any three-dimensional Bravais lattice is:

$$f(\vec{r}) = \frac{4\pi C}{V}\sum_{\vec{G}} \frac{\sin\left(|G|R\right) - |G|R\cos\left(|G|R\right)}{|G|^3}\exp\left(i\vec{G}\cdot\vec{r}\right).$$

Molecular orbital potential

$$U(\vec{r}) = \frac{-Ze^2}{4\pi\varepsilon_0} \sum_{r_j} \frac{1}{\left|\vec{r} - \vec{r}_j\right|}$$

position of atom j

The Fourier series for any molecular orbital potential is:

$$U(\vec{r}) = \frac{-Ze^2}{V\varepsilon_0} \sum_{\vec{G}} \frac{\exp\left(i\vec{G}\cdot\vec{r}\right)}{\left|G\right|^2}$$

Volume of the primitive unit cell

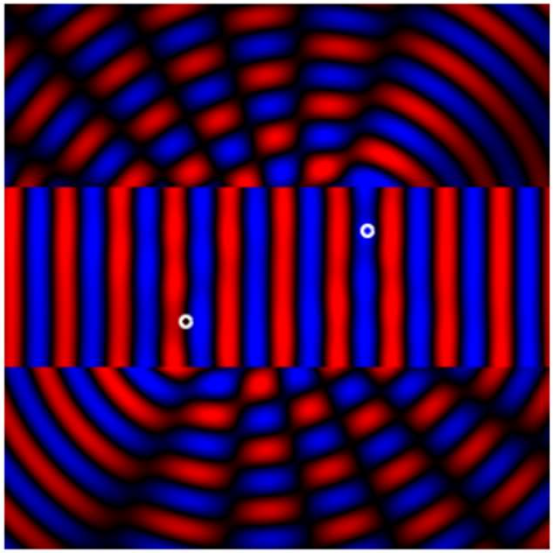
Muffin tin potential

The potential is $U(\vec{r}) = -\frac{Ze^2}{4\pi\epsilon_0}\sum_j \frac{1}{|\vec{r}-\vec{r}_j|}$ around the Bravais lattice points

The potential is constant between the spheres.

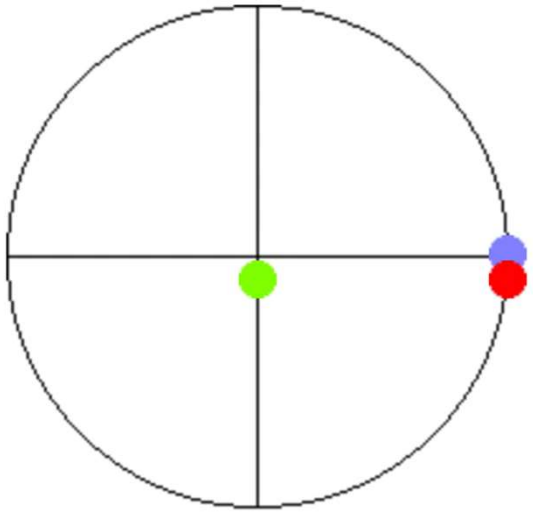
$$U(\vec{r}) = \frac{Ze^2}{V\epsilon_0}\sum_{\vec{G}}\left(\frac{\cos(|G|R)-1}{|G|^2} + \frac{\sin(|G|R)-|G|R\cos(|G|R)}{R|G|^3}\right)\exp\left(i\vec{G}\cdot\vec{r}\right).$$

Intensity of the scattered waves

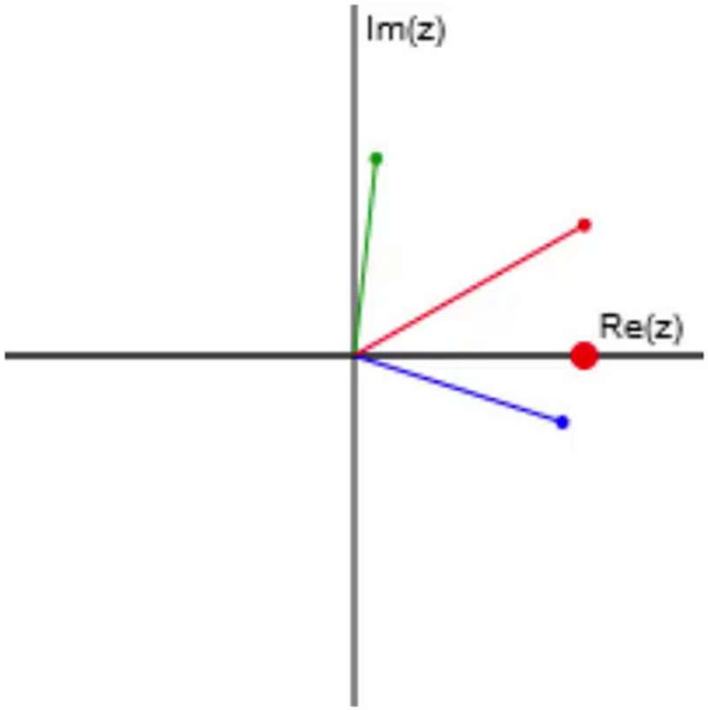


$$F_1 \frac{\cos(k|\vec{r}-\vec{r}_1| - \omega t + kx_1)}{\sqrt{|\vec{r}-\vec{r}_1|}} + F_2 \frac{\cos(k|\vec{r}-\vec{r}_2| - \omega t + kx_2)}{\sqrt{|\vec{r}-\vec{r}_2|}}.$$

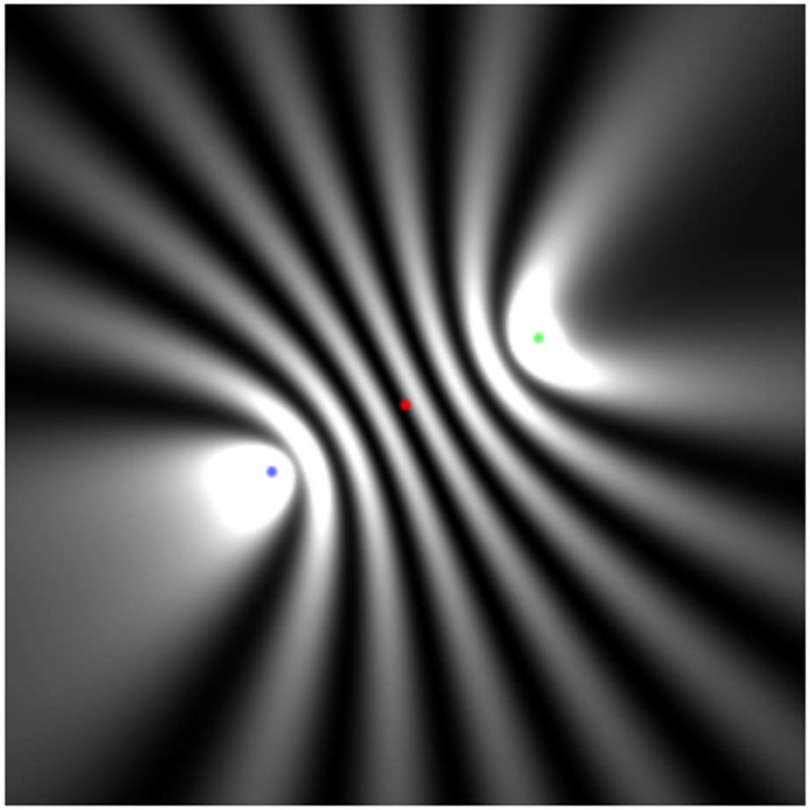
Using complex numbers to describe oscillations



$$e^{i\omega t} = \cos(\omega t) + i\sin(\omega t)$$



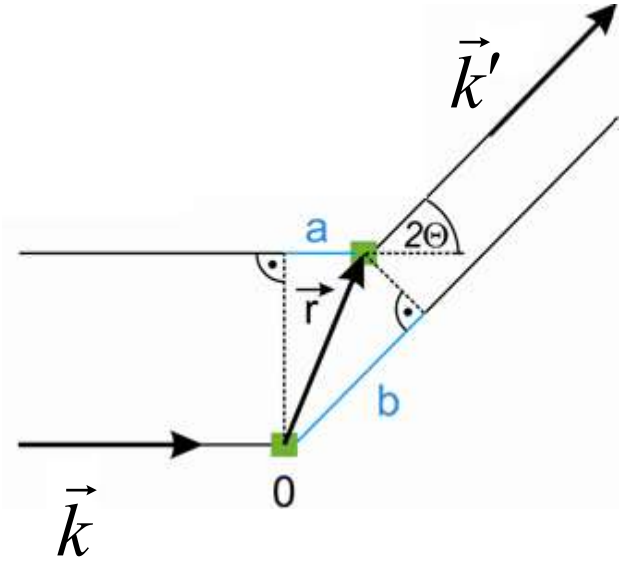
Intensity of the scattered waves



$$F_1 \frac{\cos(k|\vec{r}-\vec{r}_1| - \omega t + kx_1)}{\sqrt{|\vec{r}-\vec{r}_1|}} + F_2 \frac{\cos(k|\vec{r}-\vec{r}_2| - \omega t + kx_2)}{\sqrt{|\vec{r}-\vec{r}_2|}}$$

$$\left(\frac{F_1}{\sqrt{|\vec{r}-\vec{r}_1|}} e^{i(k|\vec{r}-\vec{r}_1|+kx_1)} + \frac{F_2}{\sqrt{|\vec{r}-\vec{r}_2|}} e^{i(k|\vec{r}-\vec{r}_2|+kx_2)} \right) e^{-i\omega t}$$

Interference



$$a = \frac{\vec{r}\cdot\vec{k}}{|k|} \qquad b = \frac{\vec{r}\cdot\vec{k}'}{|k|}$$

elastic scattering

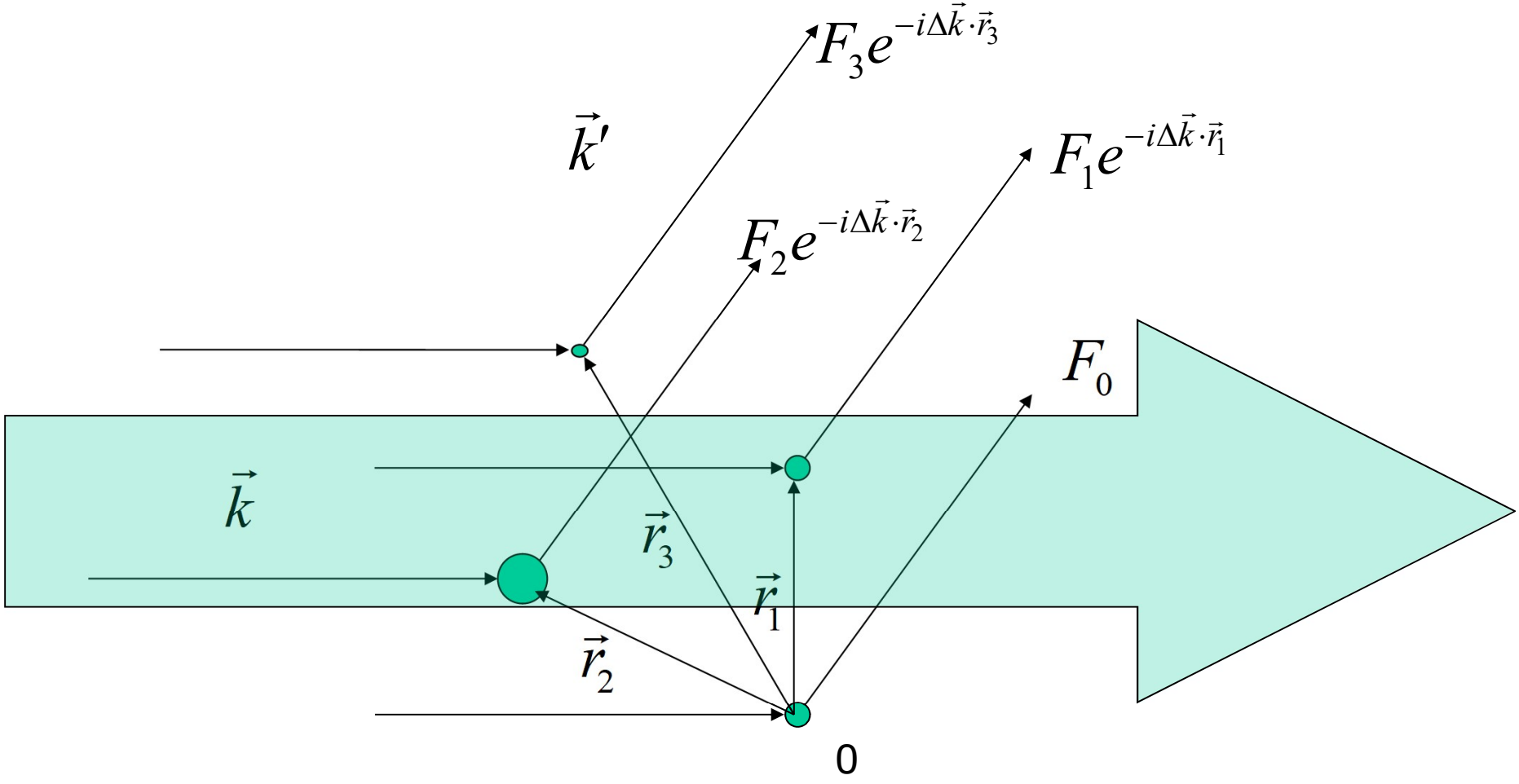
$$|k| = |k'|$$

path difference: $$a - b = \frac{-\vec{r}\cdot\left(\vec{k}' - \vec{k}\right)}{|k|}$$

phase shift: $$\varphi = 2\pi\frac{a-b}{\lambda} = 2\pi\frac{-\vec{r}\cdot\left(\vec{k}' - \vec{k}\right)}{|k|\lambda} = -\vec{r}\cdot\left(\vec{k}' - \vec{k}\right) = -\Delta\vec{k}\cdot\vec{r}$$

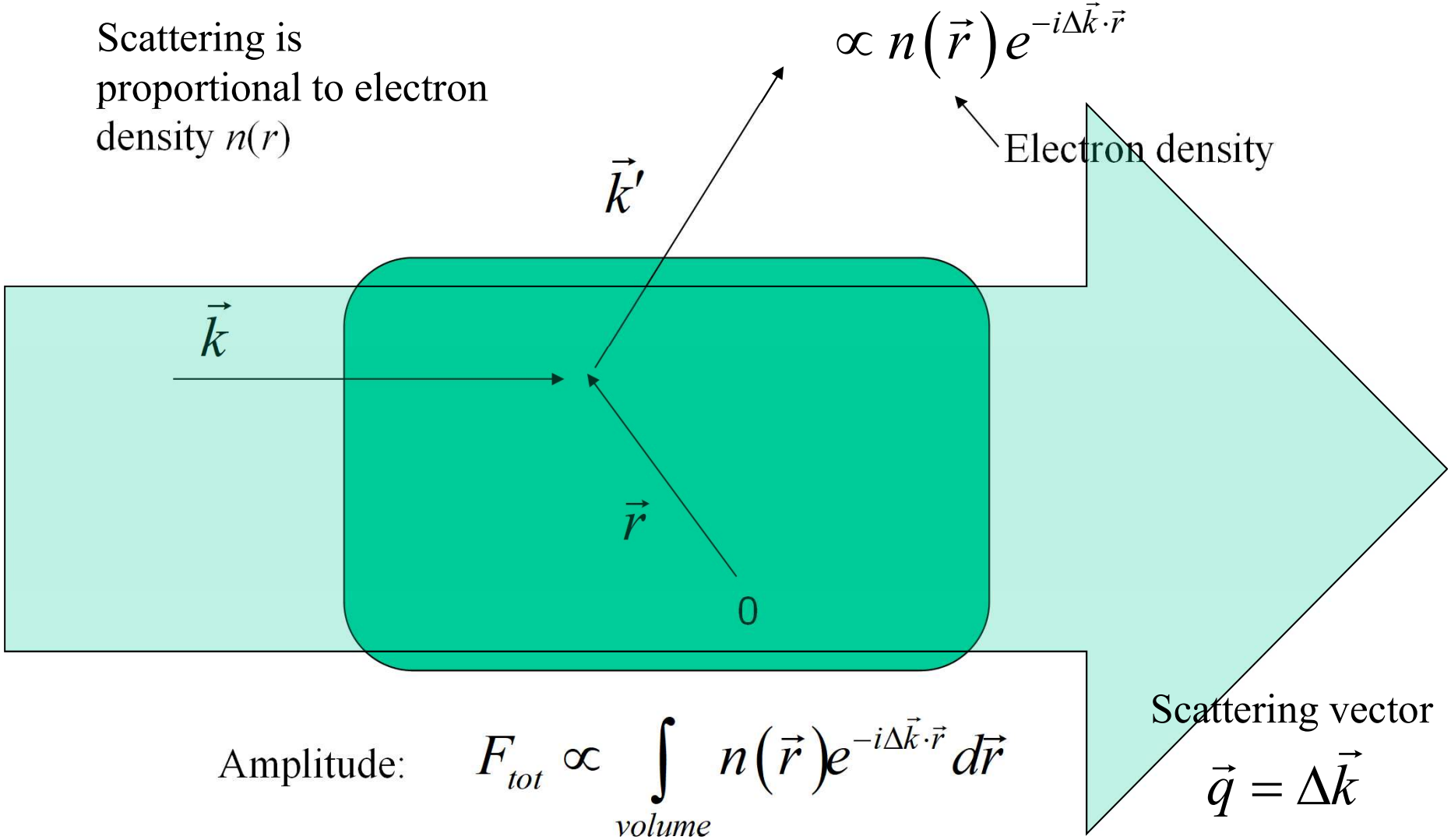
Amplitude: $$F = F_0 + F_0 e^{-i\Delta\vec{k}\cdot\vec{r}}$$

Interference



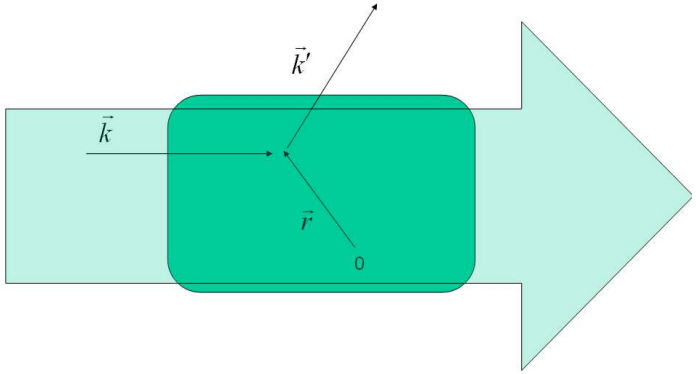
Amplitude: $$F_{tot} = \sum_i F_i e^{-i\Delta\vec{k}\cdot\vec{r}_i}$$

Diffraction



The scattering amplitude is proportional to the Fourier transform of the electron density.

Scattering amplitude



$$F \propto \int n(\vec{r}) \exp(-i\Delta\vec{k} \cdot \vec{r}) dV$$

expand $n(r)$ in a Fourier series $\quad n(\vec{r}) = \sum_{\vec{G}} n_{\vec{G}} \exp(i\vec{G} \cdot \vec{r})$

$$F \propto \sum_{G} \int n_G \exp(i(\vec{G} - \Delta\vec{k}) \cdot \vec{r}) dV$$

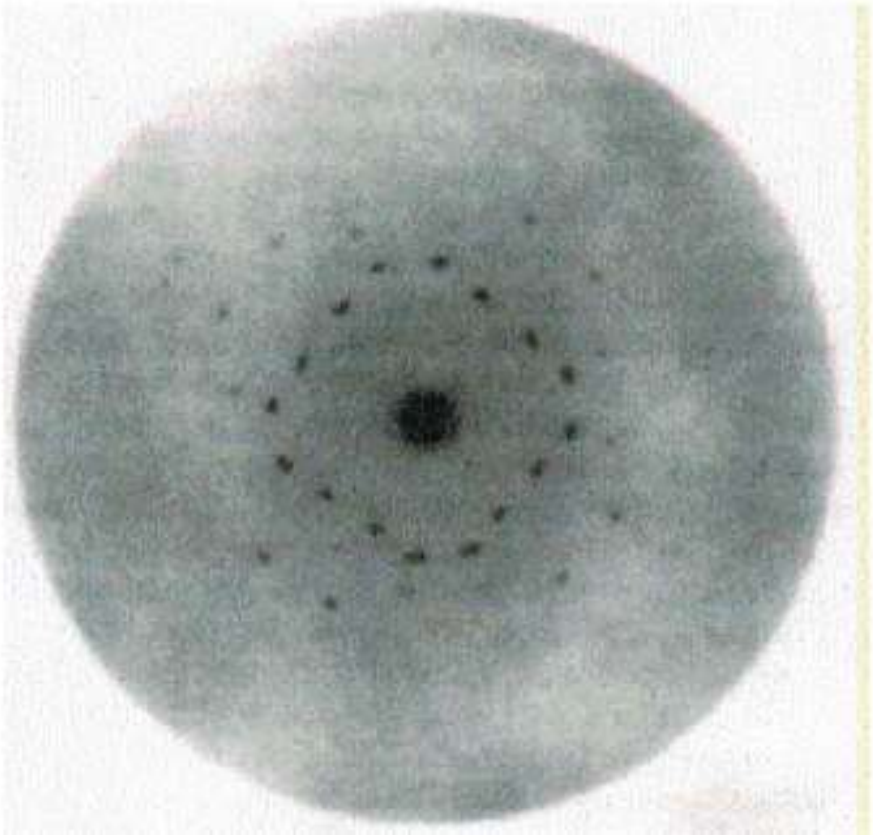
if $\vec{G} = \Delta\vec{k}$, all components add coherently

diffraction condition: $\boxed{\vec{G} = \Delta\vec{k}}$

The intensity of the peak at G is $\propto |n_G|^2$

Nobel Prize 1914

first diffraction experiment of Max von Laue 1912
ZnS single crystal, exposure time 30'
the 5th diffraction pattern

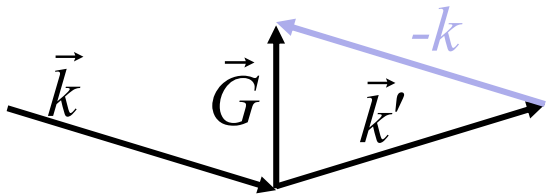


M. von Laue (1879-1960)

$$\vec{G} = \Delta\vec{k}$$

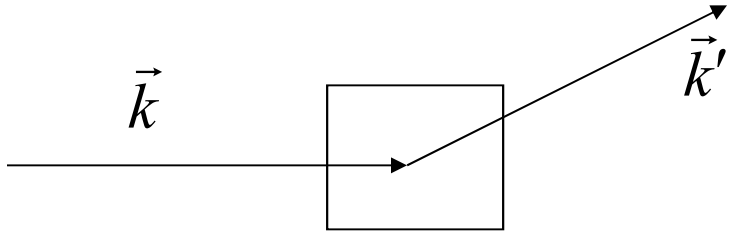
Diffraction condition (Laue condition)

$$\vec{k}' - \vec{k} = \Delta\vec{k} = \vec{G}$$



$|\vec{k}| = |\vec{k}'|$ for elastic scattering

Single crystal diffraction



Scattering wave vector

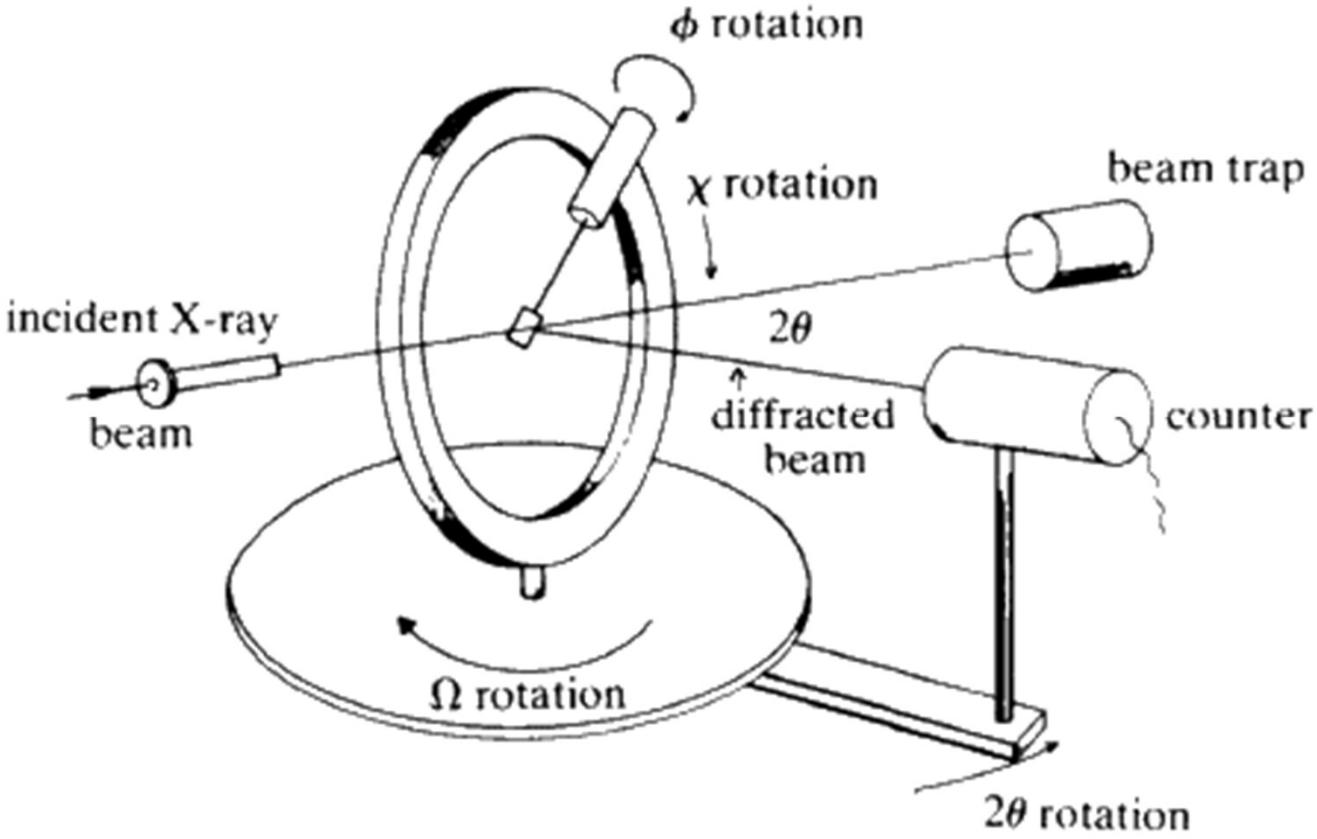
$$\vec{G} = \Delta\vec{k} = \vec{q}$$

Every time a diffraction peak is observed, record *G*. When many *G* vectors are known, determine the reciprocal lattice.

The sample and the detector must be turned to find all of the diffraction peaks.

Gx	Gy	Gz	$\lvert n_G \rvert^2$
2.4E10	2.4E10	0	10341
2.4E10	0	2.4E10	9989

$$n(\vec{r}) = \sum_{\vec{G}} n_{\vec{G}} \exp(i\vec{G}\cdot\vec{r})$$



θ sets the length of the scattering vector

http://serc.carleton.edu/research_education/geochemsheets/techniques/SXD.html

Determining real space primitive lattice vectors

$$\vec{a}_1 = 2\pi \frac{\vec{b}_2 \times \vec{b}_3}{\vec{b}_1 \cdot \left(\vec{b}_2 \times \vec{b}_3\right)}$$

$$\vec{a}_2 = 2\pi \frac{\vec{b}_3 \times \vec{b}_1}{\vec{b}_1 \cdot \left(\vec{b}_2 \times \vec{b}_3\right)}$$

$$\vec{a}_3 = 2\pi \frac{\vec{b}_1 \times \vec{b}_2}{\vec{b}_1 \cdot \left(\vec{b}_2 \times \vec{b}_3\right)}$$

$$\vec{a}_i \cdot \vec{b}_j = 2\pi\delta_{ij}$$

$\vec{b}_1, \vec{b}_2, \vec{b}_3$ determined from diffraction experiment

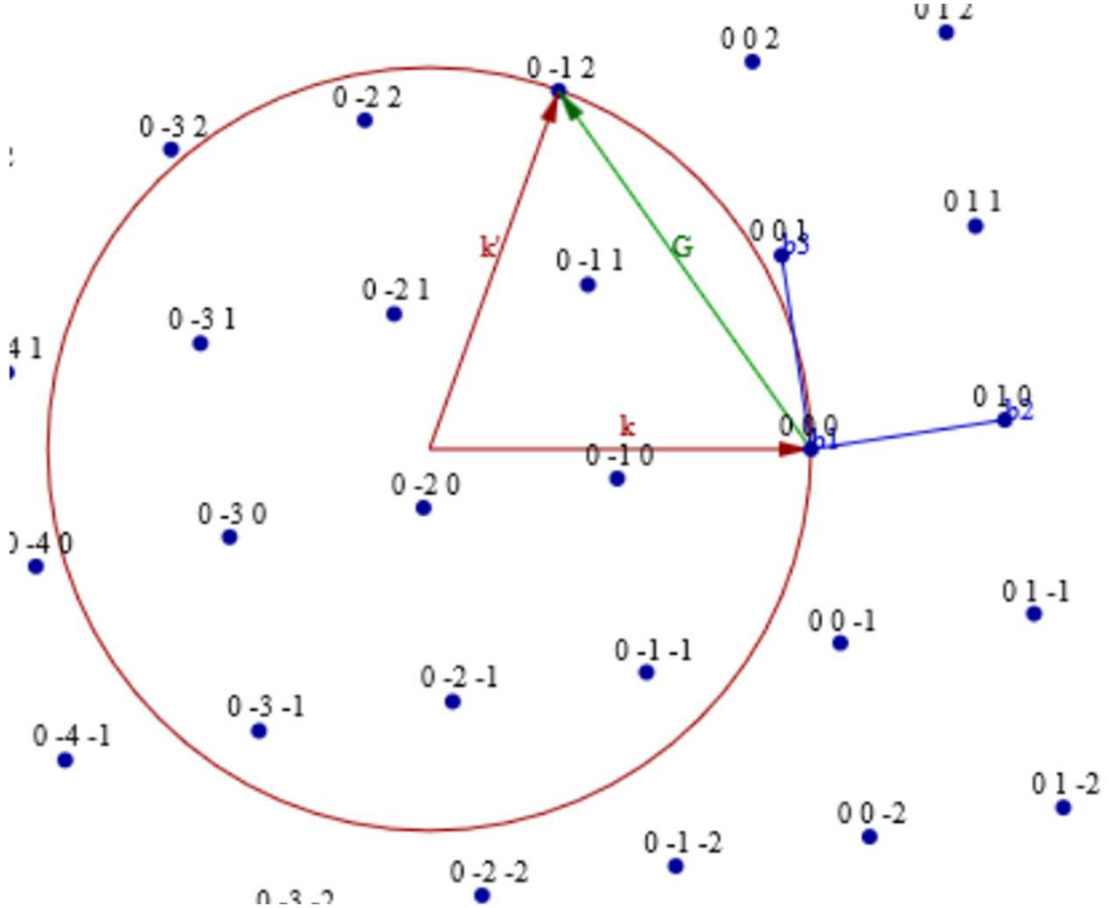
Volume of the primitive unit cell $\vec{a}_1 \cdot \left(\vec{a}_2 \times \vec{a}_3\right)$

G vectors specify the Bravais lattice.

X-ray Fluorescence spectrometer

Tells you the atomic composition of a sample to a fraction of a %

Ewald sphere $\Delta\vec{k} = \vec{G}$



Draw a vector representing the incoming radiation so that it ends at the origin. As the crystal is rotated around the origin, the condition for diffraction will be satisfied every time a reciprocal lattice point is on the sphere.

The number of diffraction peaks that will be observed in a diffraction experiment

Diffraction can occur whenever the diffraction condition, $\vec{k}' - \vec{k} = \vec{G}$, is satisfied. Here $\vec{k}$ is the wave vector of the incoming waves, $\vec{k}'$ is the wave vector of the scattered wave, and $\vec{G}$ is a reciprocal lattice vector. For elastic scattering, $|\vec{k}| = |\vec{k}'|$ and diffraction can only occur for $2|\vec{k}| > |\vec{G}|$. Thus, there are only a finite number of diffraction peaks observable. The number of diffraction peaks can be estimated by dividing the volume of a sphere of radius $2|\vec{k}|$ by the volume of a primitive unit cell in reciprocal space. A more exact number can be obtained by testing if reciprocal lattice points lie inside the sphere. The form below calculates the primitive lattice vectors in reciprocal space from the primitive lattice vectors in real space and then determines the number of reciprocal lattice points that satisfy the diffraction condition.

Primitive lattice vectors:

$\vec{a}_1 =$ 4.12 $\hat{x} +$ 0 $\hat{y} +$ 0 $\hat{z}$ [Å]
$\vec{a}_2 =$ 0 $\hat{x} +$ 4.12 $\hat{y} +$ 0 $\hat{z}$ [Å]
$\vec{a}_3 =$ 0 $\hat{x} +$ 0 $\hat{y} +$ 4.12 $\hat{z}$ [Å]

X-ray wavelength λ = 1.540598 [Å]
Cu Kα = 1.540598 Å
Cr Kα = 2.28975 Å
Mo Kα = 0.7093165 Å

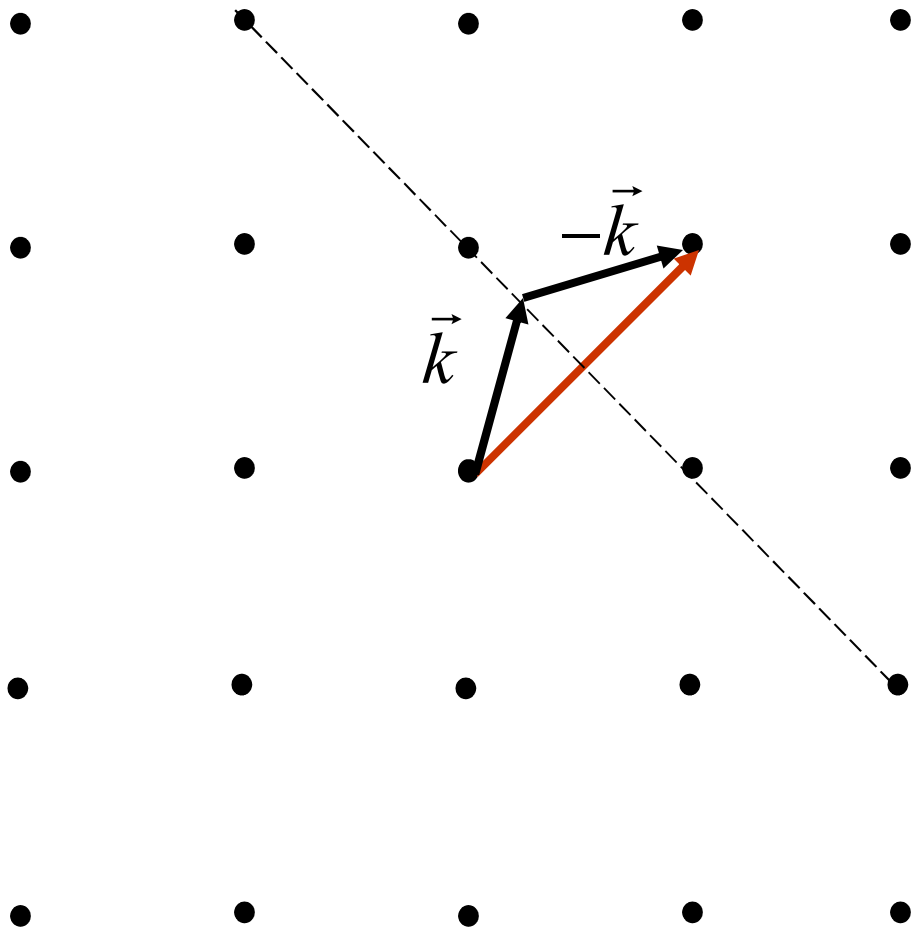
submit

Al (fcc) NaCl (fcc) CsCl (sc) SrTiO3 (perovskite, sc)
GaAs (Zincblend, fcc) GaN (Wurtzite, hex)

Primitive reciprocal lattice vectors

$$\vec{b}_1 = 2\pi \frac{\vec{a}_2 \times \vec{a}_3}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)} = 1.525\ \hat{k}_x + 0.000\ \hat{k}_y + 0.000\ \hat{k}_z\ [\text{Å}^{-1}]$$
$$\vec{b}_2 = 2\pi \frac{\vec{a}_3 \times \vec{a}_1}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)} = 0.000\ \hat{k}_x + 1.525\ \hat{k}_y + 0.000\ \hat{k}_z\ [\text{Å}^{-1}]$$
$$\vec{b}_3 = 2\pi \frac{\vec{a}_1 \times \vec{a}_2}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)} = 0.000\ \hat{k}_x + 0.000\ \hat{k}_y + 1.525\ \hat{k}_z\ [\text{Å}^{-1}]$$

Diffraction condition



$$\vec{k}\,' - \vec{k} = \vec{G}$$

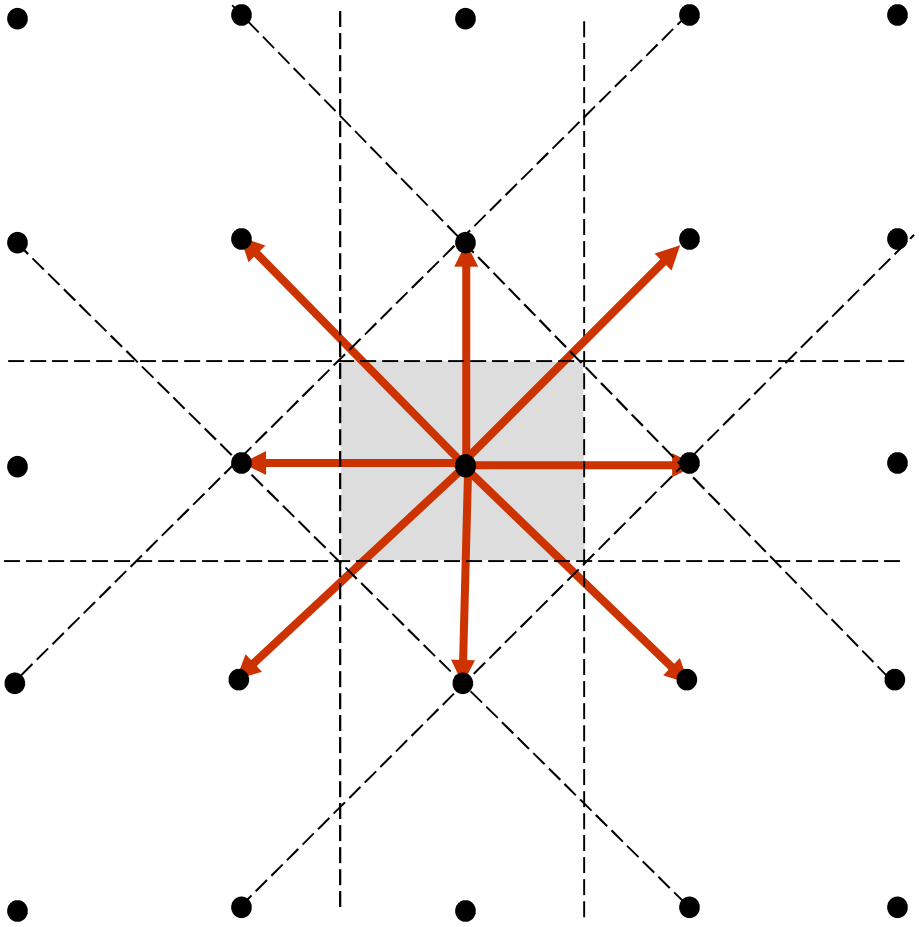
For every G there is a $-G$ so the diffraction condition can also be written as

$$\vec{k} - \vec{k}\,' = \vec{G}$$

a wave will be diffracted if the wave vector ends on one of the planes

Brillouin zones

Leon Brillouin



1st Brillouin zone consists of the *k*-states around the origin that can be reached without crossing a plane.