Chapter II: Reciprocal lattice

Read chapter 2 of Kittel

# How can we study crystal structure?

- Need probe that can penetrate into crystal
- X-rays, neutrons, (high energy electrons)

- X-rays discovered by Roentgen in 1895 - instant sensation round the world - view of his wife's hand
- Neutrons (discovered in 1932) penetrate with almost no interaction with most materials

How can we study crystal structure?

- X-rays scatter from the electrons - intensity proportional to the density n($\mathbf{r}$) - Mainly the core electrons around the nucleus

- Similarly for high energy electrons

- Neutrons scatter from the nuclei (and electron magnetic moment)
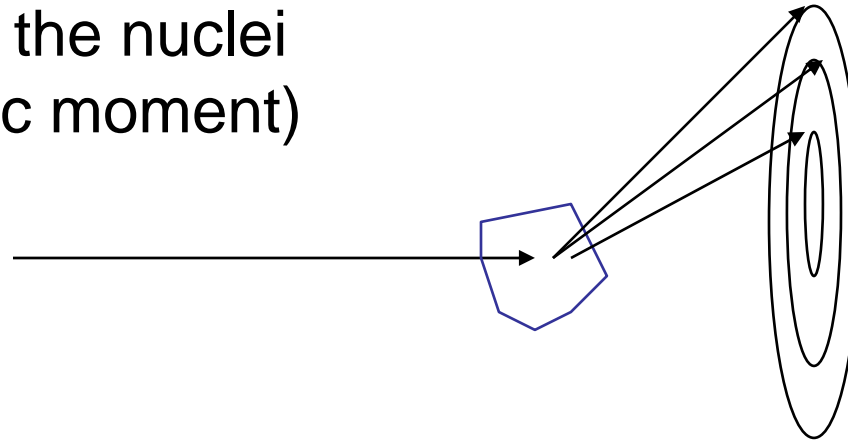
- In all cases the scattering is periodic - the same in each cell of the crystal

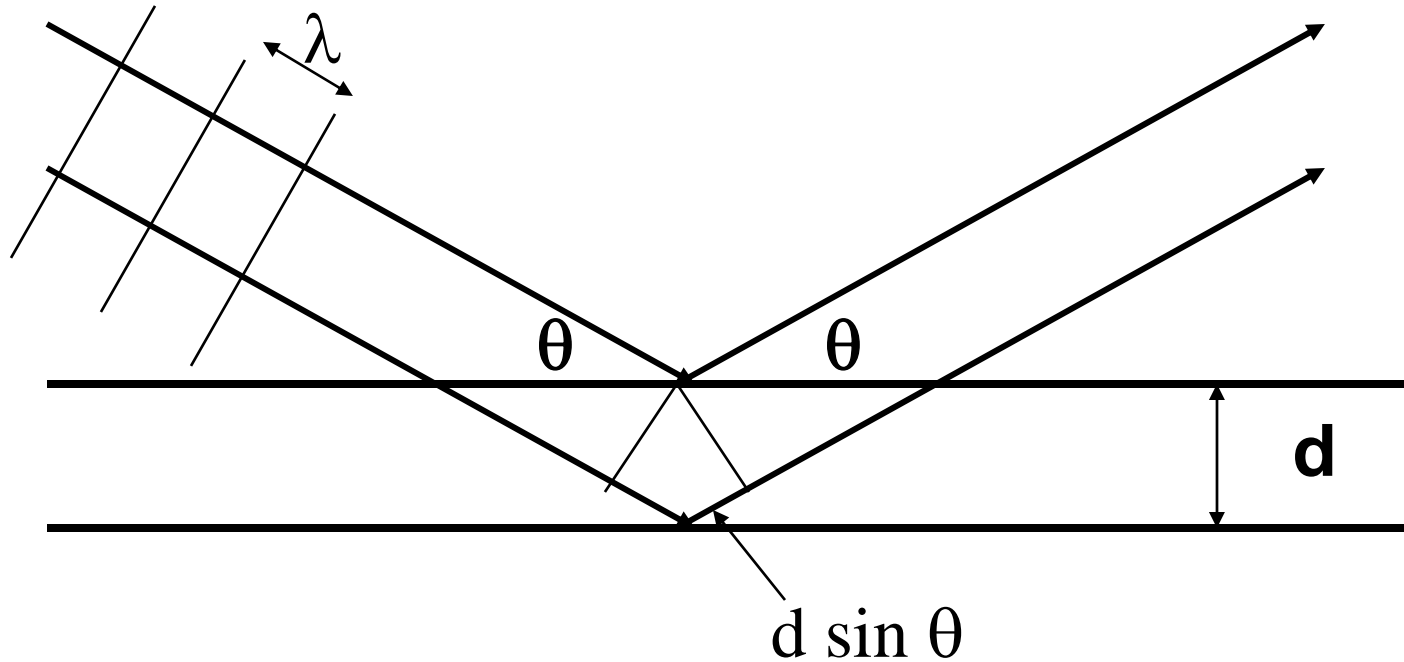- Diffraction is the constructive interference of the scattering from the very large number of cells of the crystal

The crystal can be viewed as made up of planes in different ways

Lattice



(01)

a_2

φ

a_1

(14)
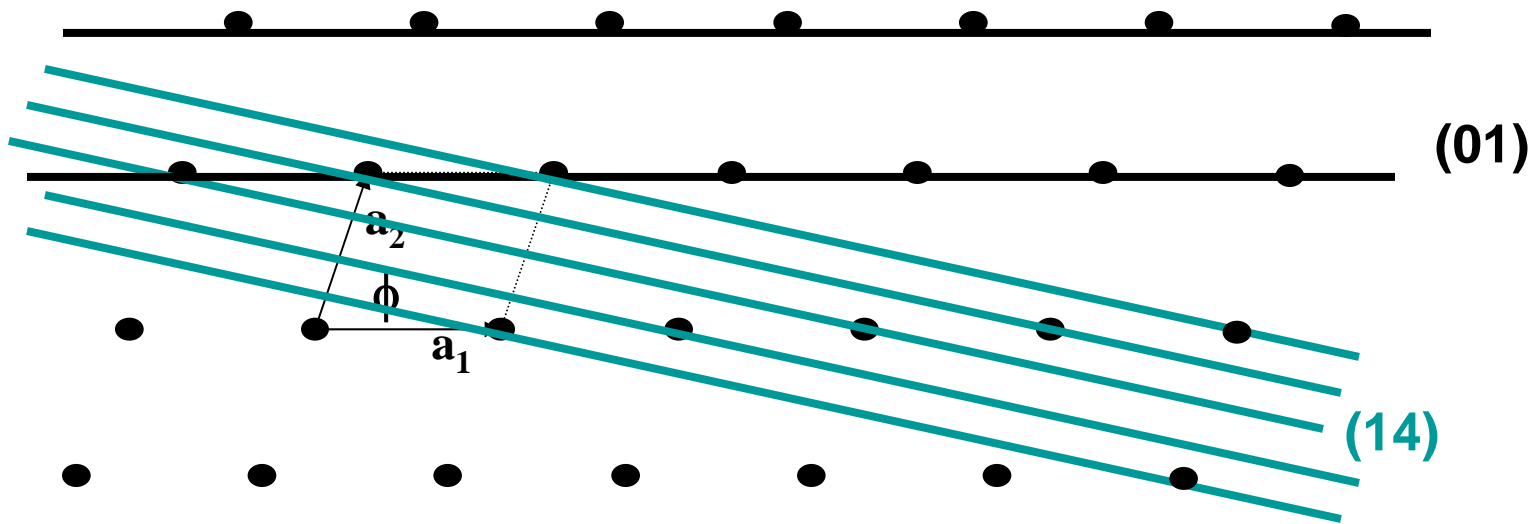
- Low index planes: more lattice points, more widely spaced
- High index planes: less lattice points, more closely spaced
- Bragg model: incident waves are reflected specularly from parallel planes
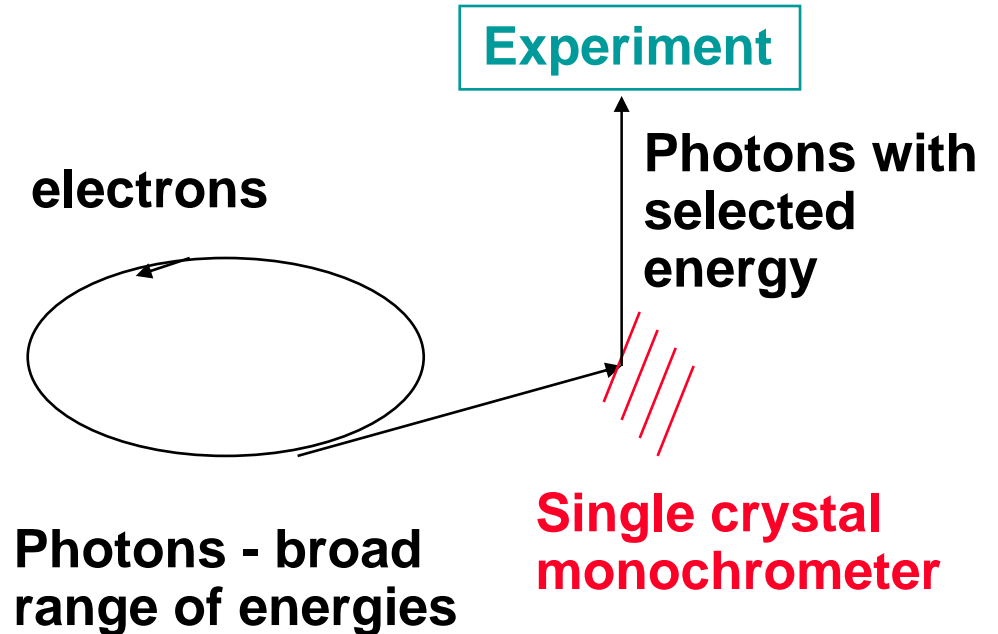
Bragg Scattering Law

- Condition for constructive interference: 2d sin θ = n λ

- Maximum λ = 2d

- Thus only waves with λ of order atomic size can have Bragg scattering from a crystal

Single crystal diffraction

Rotate both sample and detector about axis

2θ
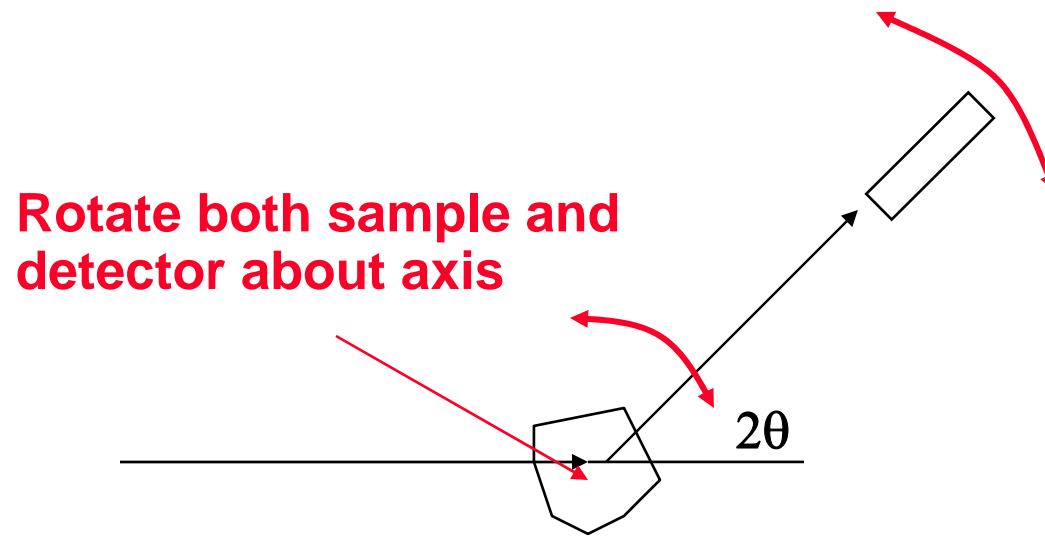
• Crystal must be oriented in all directions
in 3D space using "Gonier Spectrometer"

• Observe scattering only at Bragg angles for a fixed
wavelength x-ray or neutrons or …..

Alternative approach - energy dispersive diffraction

electrons

Experiment

Photons with selected energy

Photons - broad range of energies

Single crystal monochrometer

- For fixed angle θ , vary the energy (i.e., λ) to satisfy Bragg condition

- X-rays over broad energy range now available at synchrotrons

- Diffraction (Bragg scattering) from a single crystallite used to select X-rays with desired wavelength

Scattered wave amplitude

- The Bragg law gives the condition for the constructive interference of waves scattered from lattice planes.

- We need a deeper analysis to determine the scattering intensity from the basis of atoms, i.e. from the spatial distribution of electrons within each cell.

- We will use the periodicity of the electron number density n(**r**) to perform Fourier analysis.

- We end up with a second lattice associated with the crystal – reciprocal lattice

Periodic Functions and Fourier Analysis

- Any periodic function can be expressed in terms of its periodic Fourier components (harmonics).
- Example of density n(x) in 1D crystal:

$$n(x) = n_0 + \Sigma_{p>0}[C_p \cos (2\pi p x/a) + S_p \sin (2\pi p x/a)]$$

- Easier expression:

$$n(x) = \Sigma_p n_p \exp(i \, 2\pi p x/a)$$

(easier because $\exp(a + b) = \exp(a) \exp(b)$)

- Expression for Fourier Components:

$$n_p = a^{-1} \int_0^a dx \, n(x) \exp(- i \, 2\pi p x/a)$$

Periodic functions and Fourier Analysis

- Define vector position r = (x,y) (2D), r = (x,y,z) (3D).

- Fourier analysis

$$f(\mathbf{r}) = \Sigma_{\mathbf{G}} \, f_{\mathbf{G}} \, \exp(i \, \mathbf{G} \cdot \mathbf{r})$$

  where the **G**'s are vectors, i.e.,

$$\exp(i \, \mathbf{G} \cdot \mathbf{r}) = \exp(i \, (G_x \, x + G_y \, y + G_z \, z))$$

- A periodic function satisfies

$$f(\mathbf{r}) = f(\mathbf{r} + \mathbf{T}) \text{ where } \mathbf{T} \text{ is any translation}$$

$$\mathbf{T}(n_1, n_2, \ldots) = n_1 \, \mathbf{a_1} + n_2 \, \mathbf{a_2} \, (+ \, n_3 \, \mathbf{a_3} \text{ in 3D}),$$

  where the n's are integers

- Thus

$$f(\mathbf{r} + \mathbf{T}) = \Sigma_{\mathbf{G}} \, f_{\mathbf{G}} \, \exp(i \, \mathbf{G} \cdot \mathbf{r}) \, \exp(i \, \mathbf{G} \cdot \mathbf{T}) = f(\mathbf{r})$$

$$\Rightarrow \exp(i \, \mathbf{G} \cdot \mathbf{T}) = 1 \Rightarrow \mathbf{G} \cdot \mathbf{T} = 2\pi \times \text{integer}$$

Reciprocal Lattice

- The reciprocal lattice is the set of vectors **G** in Fourier space that satisfy the requirement

    $\mathbf{G} \cdot \mathbf{T} = 2\pi \times$ integer for any translation

    $\mathbf{T}(n_1,n_2,\ldots) = n_1 \, \mathbf{a_1} + n_2 \, \mathbf{a_2} \, (+ \, n_3 \, \mathbf{a_3}$ in 3D)

- How to find the **G**'s ??

- Define vectors $\mathbf{b_i}$ by

    $\mathbf{b_i} \cdot \mathbf{a_j} = 2\pi \, \delta_{ij}$, where $\delta_{ii} = 1$, $\delta_{ij} = 0$ if $i \neq j$

- If we define the vectors

    $\mathbf{G}(m_1,m_2,\ldots) = m_1 \, \mathbf{b_1} + m_2 \, \mathbf{b_2} \, (+ \, m_3 \, \mathbf{b_3}$ in 3D),

    where the m's are integers, then clearly

    $\mathbf{G} \cdot \mathbf{T} = 2\pi \times$ integer for any **T**

Reciprocal Lattice and Translations

- Note: Reciprocal lattice is defined only by the vectors
$$G(m_1, m_2, \ldots) = m_1 \, \mathbf{b_1} + m_2 \, \mathbf{b_2} \; (+ \, m_3 \, \mathbf{b_3} \text{ in 3D}),$$
where the m's are integers and
$$\mathbf{b_i} \cdot \mathbf{a_j} = 2\pi \, \delta_{ij}, \text{ where } \delta_{ii} = 1, \; \delta_{ij} = 0 \text{ if } i \neq j$$

- The only information about the actual basis of atoms is in the quantitative values of the Fourier components $f_\mathbf{G}$ in the Fourier analysis
$$f(\mathbf{r}) = \Sigma_\mathbf{G} \, f_\mathbf{G} \, \exp(\, i \, \mathbf{G} \cdot \mathbf{r})$$

- Inversion:
$$f_\mathbf{G} = V_{cell}^{-1} \int_{cell} d\mathbf{r} \, f(\mathbf{r}) \, \exp(- \, i \, \mathbf{G} \cdot \mathbf{r})$$
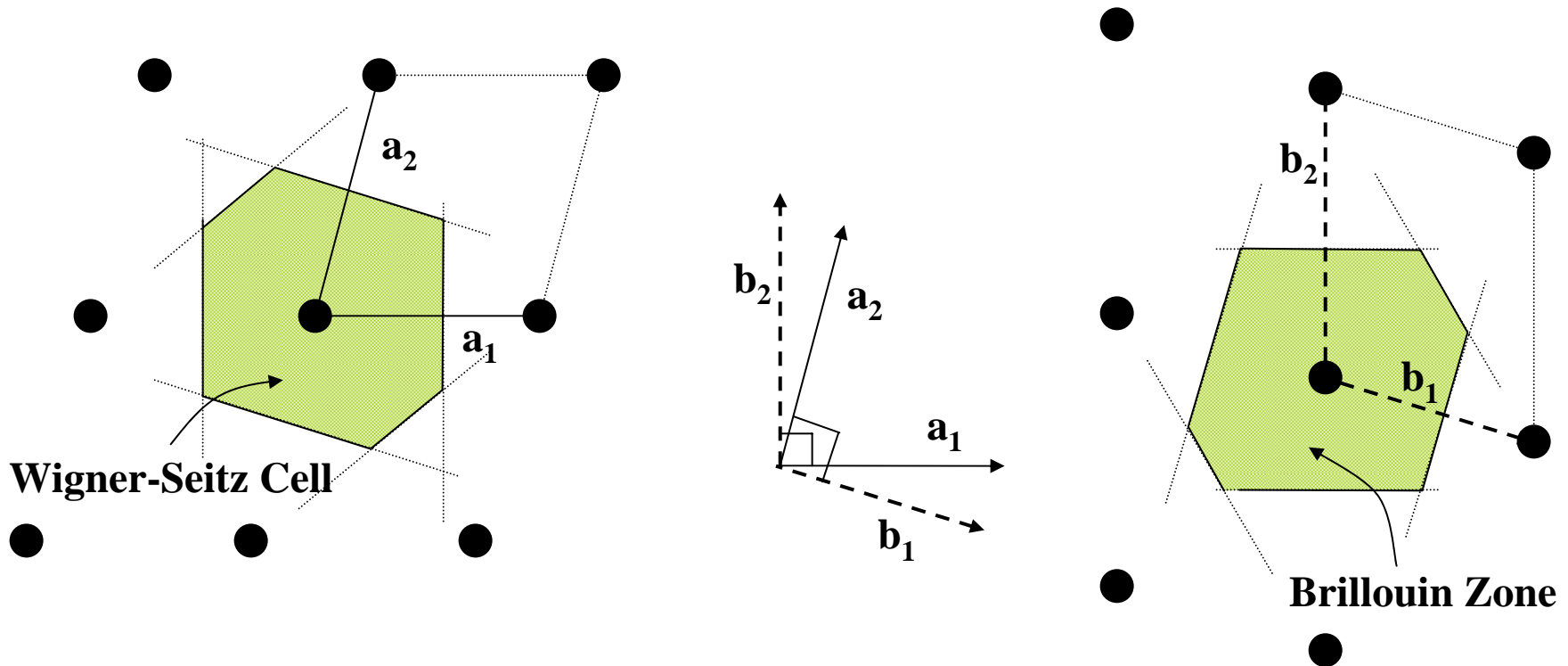
Reciprocal Lattice and Fourier Analysis in 1D

- In 1D, $b = 2\pi/a$, **b** and **a** parallel
- Periodic function $f(x)$:

$$f(x) = \Sigma_p f_p \exp(i\, 2\pi\, p\, x/a)$$
$$= \Sigma_p f_p \exp(i\, p\, b),\ p = \text{integer}$$

- The set of all integers $\times b$ are the reciprocal lattice

a
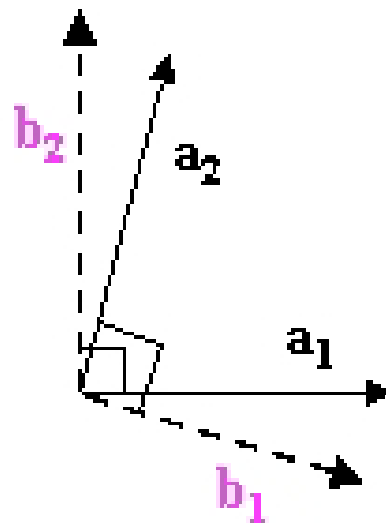
● ● ● ● ● ● ● ● ● ●

b

● ● ● ● ● ● ● ● ● ●
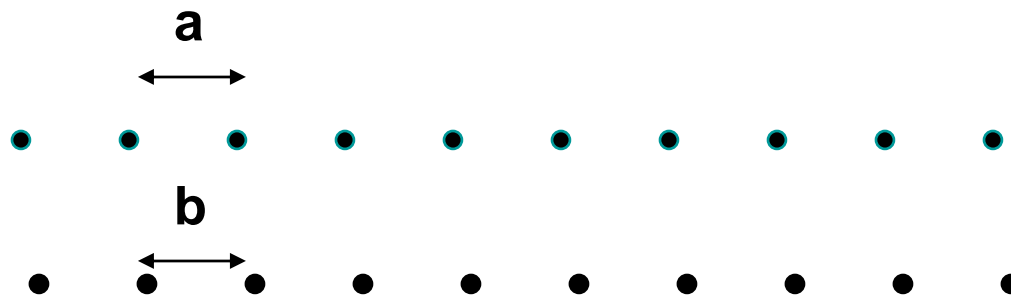
Real & Reciprocal lattices in 2 D

- Two lattices associated with crystal lattice
- b_1 perpendicular to a_2 , b_2 perpendicular to a_1
- Wigner-Seitz cell of reciprocal lattice called the "First Brillouin Zone" or just "Brillouin Zone"

Ex. What is the relationship between b_1 and b_2, if $a_1 > a_2$?

Reciprocal Lattice in 3D

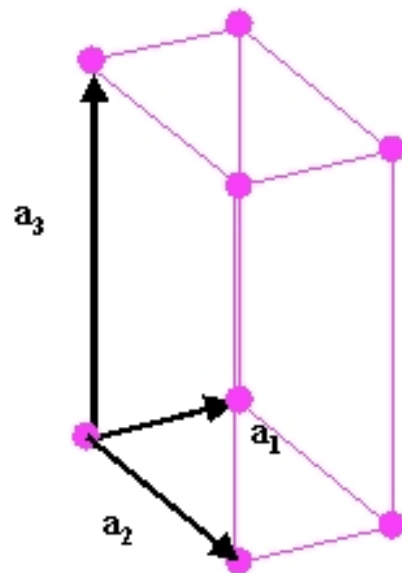- The primitive vectors of the reciprocal lattice are defined by the vectors b_i that satisfy
  $$\mathbf{b_i} \cdot \mathbf{a_j} = 2\pi\, \delta_{ij}, \text{ where } \delta_{ii} = 1, \ \delta_{ij} = 0 \text{ if } i \neq j$$

- How to find the **b**'s?

- Note: $\mathbf{b_1}$ is orthogonal to $\mathbf{a_2}$ and $\mathbf{a_3}$, etc.
- In 3D, this is found by noting that $(\mathbf{a_2} \times \mathbf{a_3})$ is orthogonal to $\mathbf{a_2}$ and $\mathbf{a_3}$
- Also volume of primitive cell $V = |\mathbf{a_1} \cdot (\mathbf{a_2} \times \mathbf{a_3})|$
- Then $\mathbf{b_i} = (2\pi / V)(\mathbf{a_j} \times \mathbf{a_k})$,
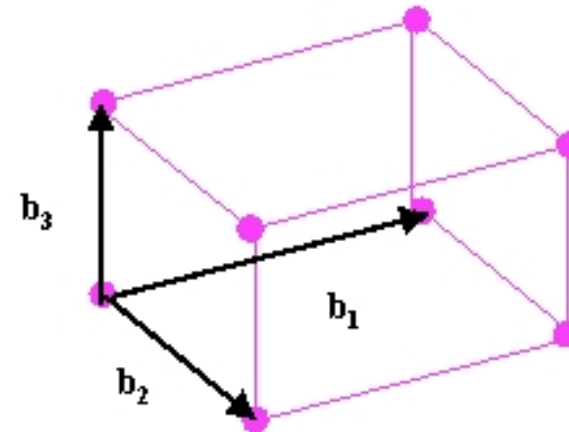 where $(i, j, k) = (1,2,3), (2,3,1)$ or $(3,1,2)$

Three Dimensional Lattices
Simplest examples

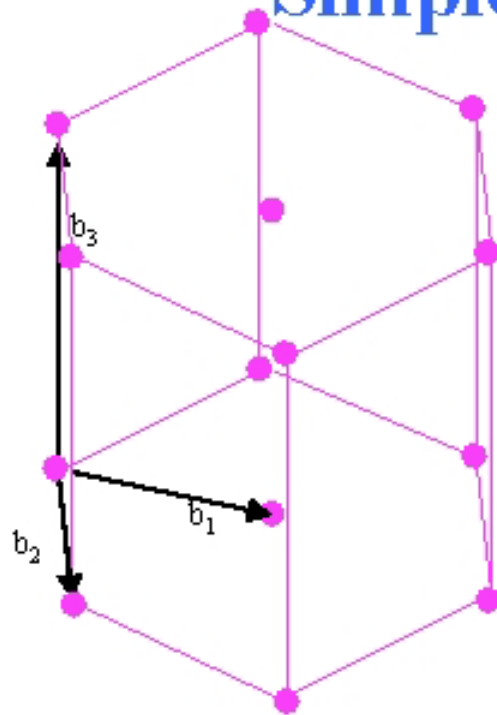
Simple Orthorhombic Bravais Lattice
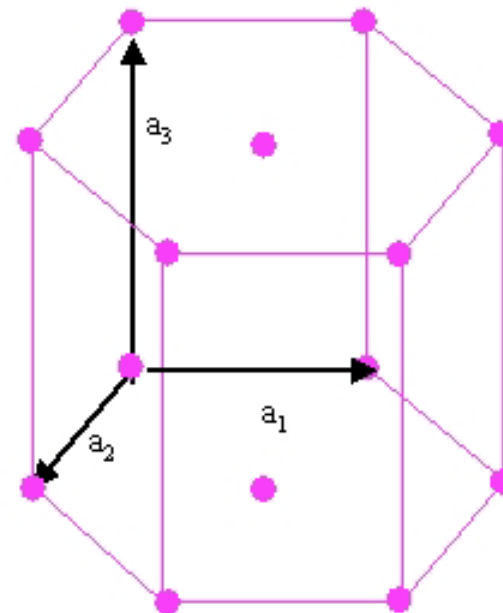with $a_3 > a_2 > a_1$

Reciprocal Lattice
Note: $b_1 > b_2 > b_3$

- **Long lengths in real space imply short lengths in reciprocal space and vice versa**

Three Dimensional Lattices
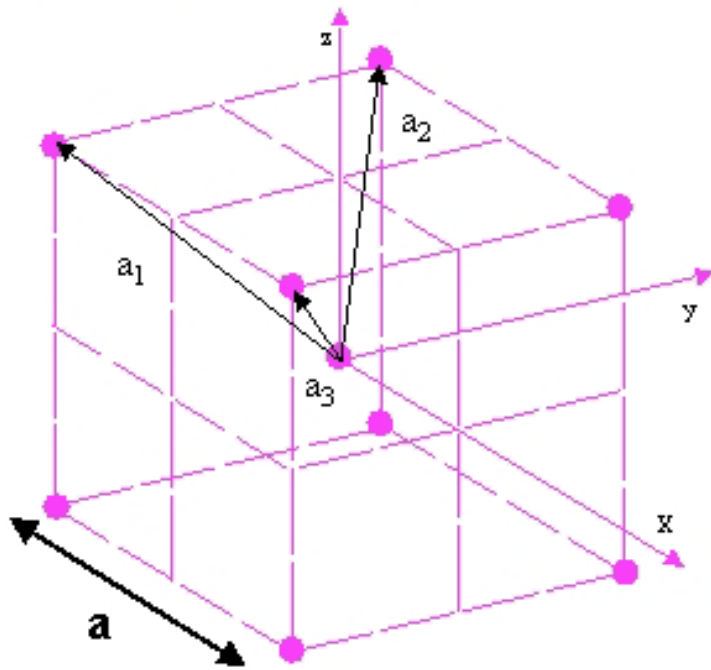# Simplest examples

Reciprocal Lattice

Hexagonal Bravais Lattice

$$a_1 = \hat{x}/2 - \hat{y}/2 + \hat{z}/2$$

$$a_2 = \hat{x}/2 + \hat{y}/2 - \hat{z}/2$$

$$a_3 = -\hat{x}/2 + \hat{y}/2 + \hat{z}/2$$

$$b_i = \frac{2\pi}{V} a_j \times a_k$$
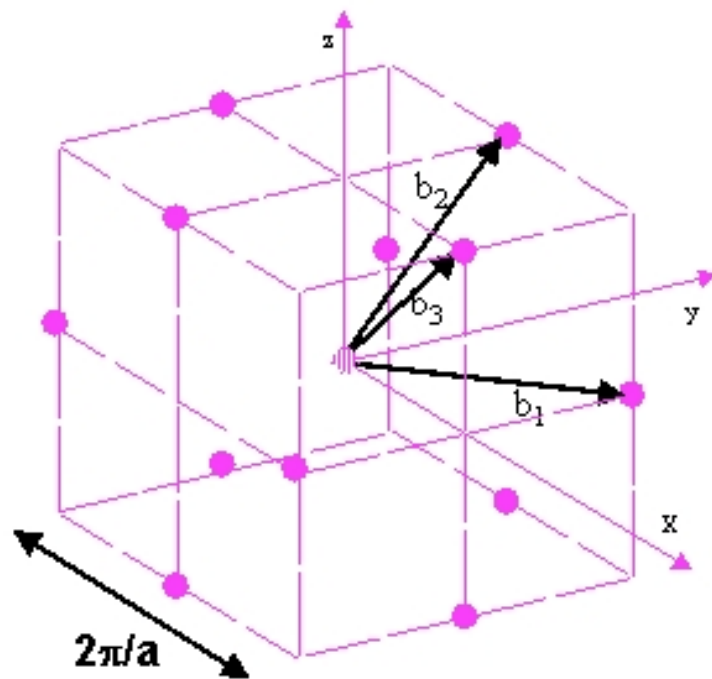

Primitive vectors and the
conventional cell of bcc lattice

Ex. Write the primitive vectors of the reciprocal lattice in terms of $\hat{x}, \hat{y}, \hat{z}$

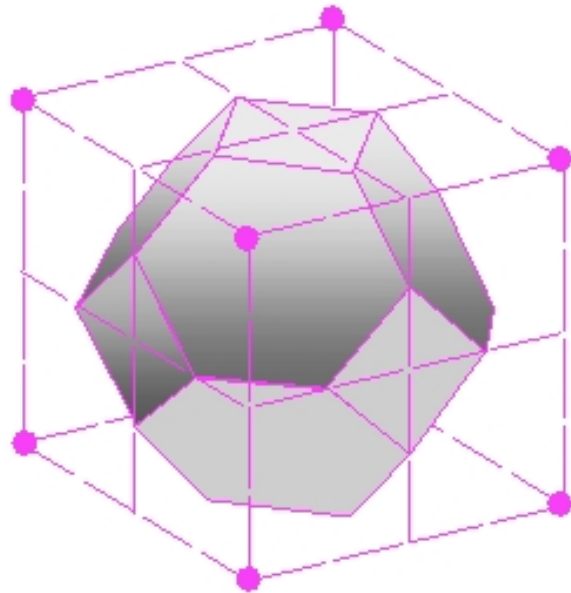# Face Centered - Body Centered Cubic Reciprocal to one another

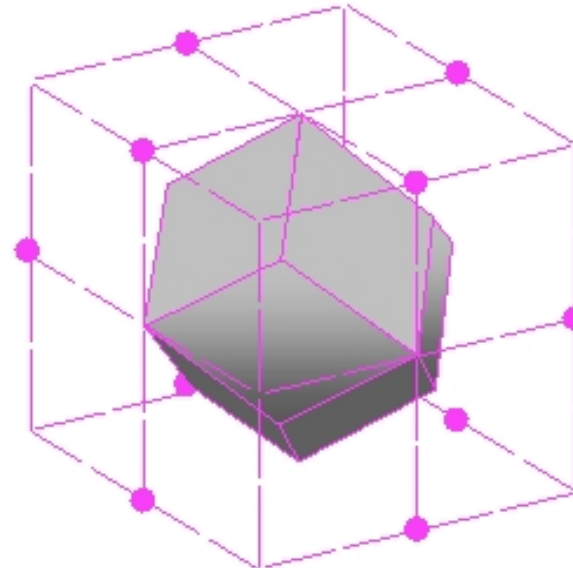Reciprocal lattice is
Face Centered Cubic
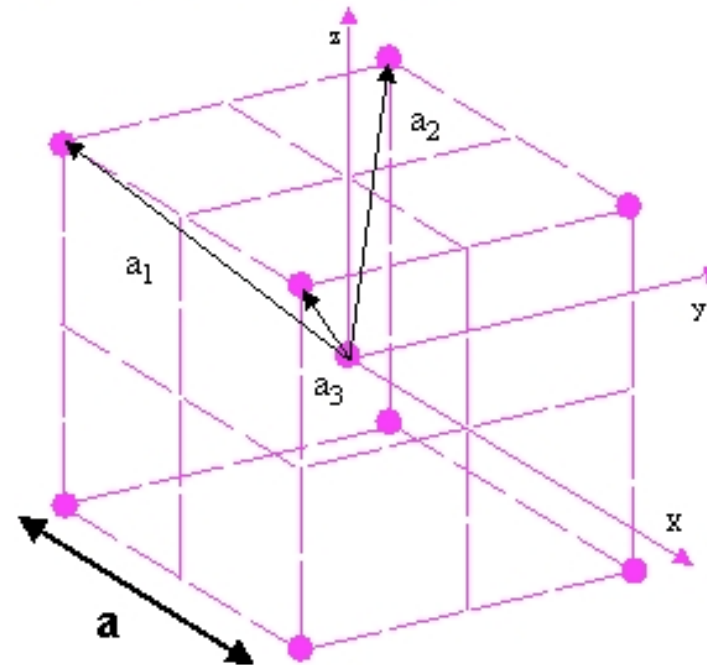
Primitive vectors and the
conventional cell of bcc lattice

Body Centered Cubic

Wigner-Seitz Cell for
Body Centered Cubic Lattice

Brillouin Zone =
Wigner-Seitz Cell for
Reciprocal Lattice

Real and reciprocal lattice
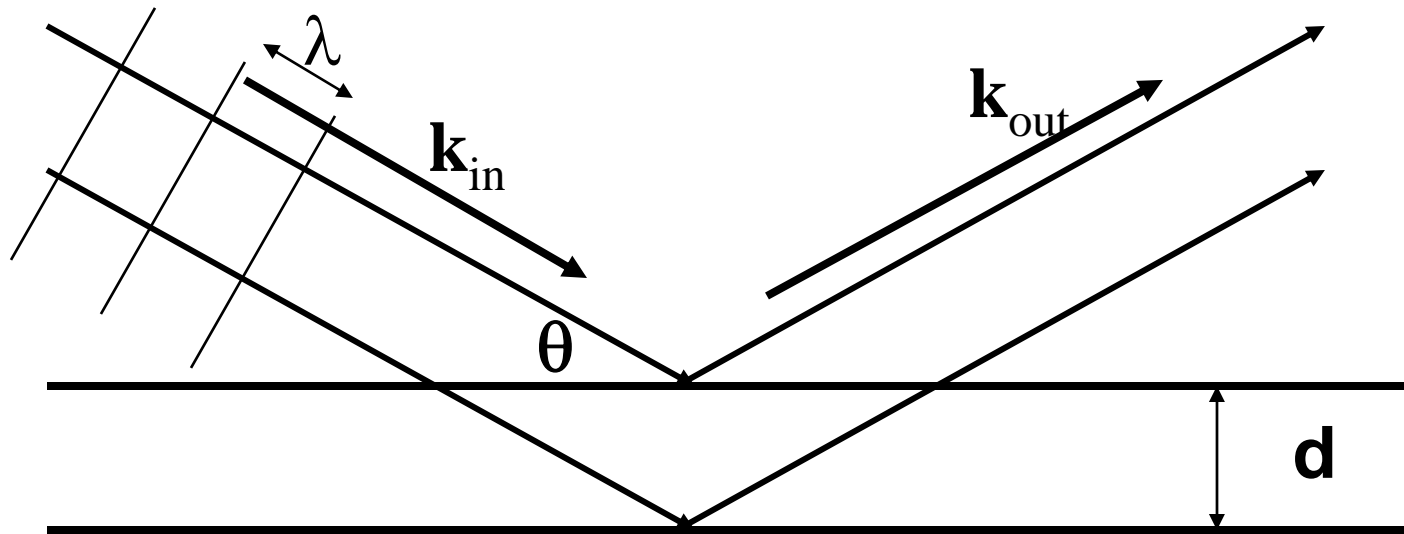# (recall Bravais exercises)

- the reciprocal vector **G**= h **b**$_1$ + k **b**$_2$ + l **b**$_3$ is perpendicular to the real lattice plane with index (h k l)

- the distance between two consecutive (h k l) planes is

$$d_{hkl} = n \frac{2\pi}{|\boldsymbol{G}|}$$
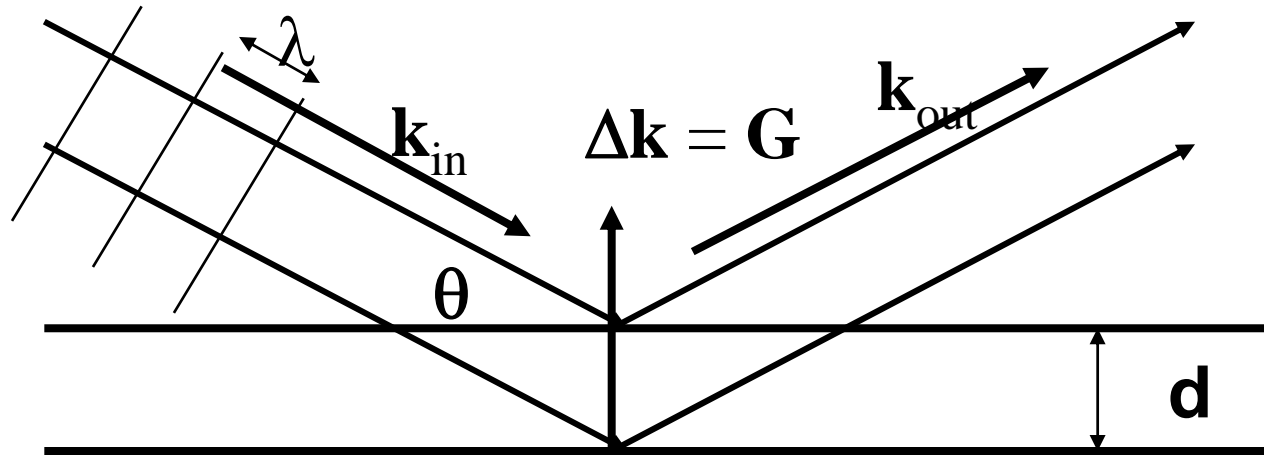
- See also Problem 2.1 in Kittel

Scattering and Fourier Analysis

- The in and out waves have the form:
  $\exp(\,i\,\mathbf{k}_{in}\cdot\,\mathbf{r} - i\,\omega t)$ and $\exp(\,i\,\mathbf{k}_{out}\cdot\,\mathbf{r} - i\,\omega t)$

- If the in wave drives the electron density, which then radiates waves, the outgoing amplitude is proportional to:

  $F = \int_{space} dr\, n(\mathbf{r})\, \exp(i\,(\mathbf{k}_{in} - \mathbf{k}_{out})\cdot\,\mathbf{r})$

Scattering and Fourier Analysis

- Define $\Delta k = k_{out} - k_{int}$
- Then we know from Fourier analysis that

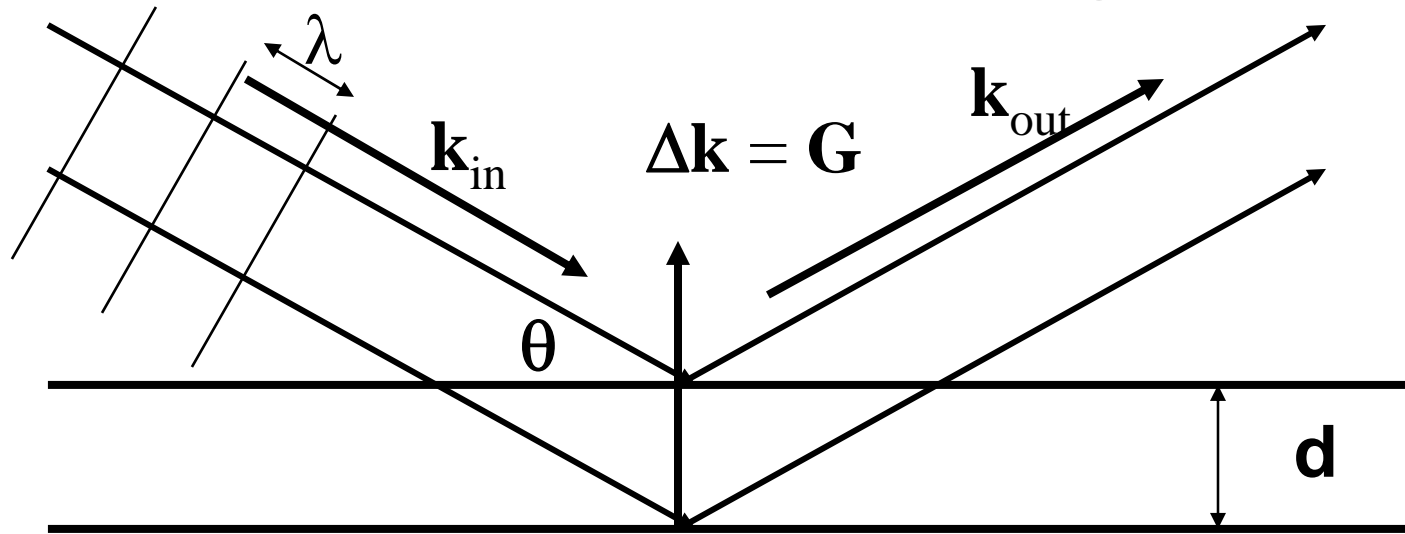$$F = \int_{space} d\mathbf{r} \, n(\mathbf{r}) \exp(- i \, \Delta\mathbf{k} \cdot \mathbf{r}) = N_{cell} \, V_{cell} \, n_G$$

only if $\Delta\mathbf{k} = \mathbf{G},$ where G = recip. lat. vector

- Otherwise integral vanishes $\Rightarrow$ no diffraction
- $n_G = V_{cell}^{-1} \int_{cell} d\mathbf{r} \, n(\mathbf{r}) \exp(- i \, \mathbf{G} \cdot \mathbf{r})$

The set of reciprocal lattice vectors determines the possible x-ray reflections

Elastic Scattering

- For elastic scattering (energy the same for in and out waves)

  $|\mathbf{k}_{in}| = |\mathbf{k}_{out}|$, or $\mathbf{k}_{in}^2 = \mathbf{k}_{out}^2 = (\mathbf{k}_{in} + \mathbf{G})^2$

- Then one arrives at the condition for diffraction:
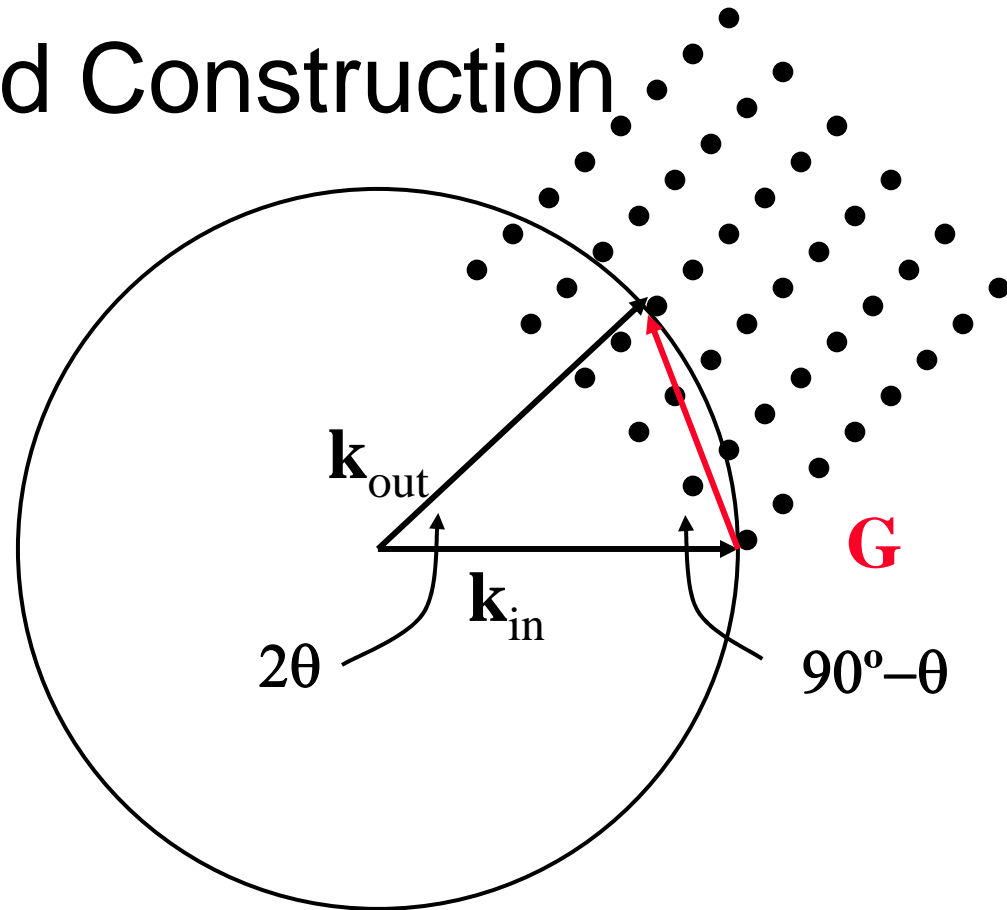
  $$2\,|\mathbf{k}_{in}\cdot \mathbf{G}| = \mathbf{G}^2$$

Ewald Construction

- Laue equations:

$$a_1 \bullet \Delta k = 2\pi h$$
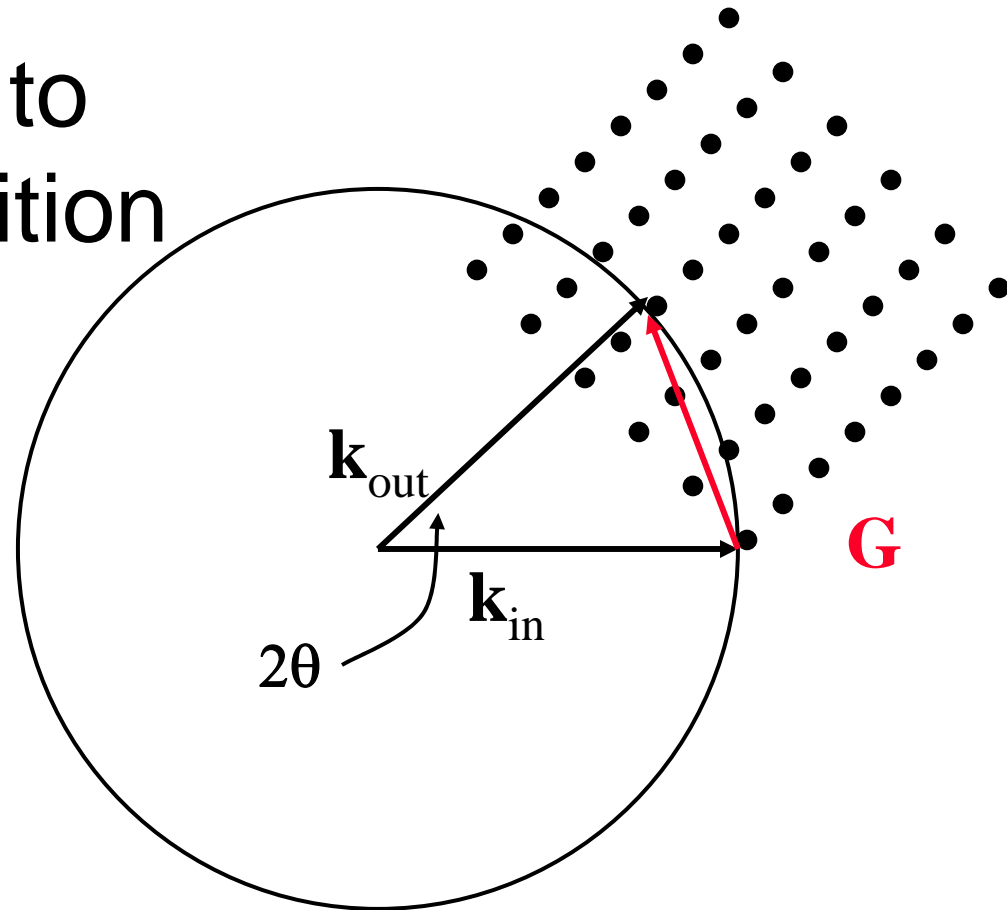
$$a_2 \bullet \Delta k = 2\pi k$$

$$a_3 \bullet \Delta k = 2\pi l$$

$\mathbf{k}_{out} = \mathbf{k}_{in} + \mathbf{G}$

$\mid 2\,\mathbf{k}_{in} \cdot \mathbf{G} \mid = 2\mid \mathbf{k}_{in}\mid\mid\mathbf{G}\mid \cos(90^{\mathbf{o}}+\theta) = 2\mid\mathbf{k}_{in}\mid\mid\mathbf{G}\mid \sin\theta$

Equivalent to Bragg Condition

- From last slide, since $\mathbf{G}^2 = |\mathbf{G}|^2$:

$$|\mathbf{G}| = 2 |\mathbf{k}_{in}| \sin \theta$$

- But $|\mathbf{k}_{in}| = 2\pi/\lambda$, and $|\mathbf{G}| = n (2\pi/d)$, where d = spacing between planes (see Kittel prob. 2.1)

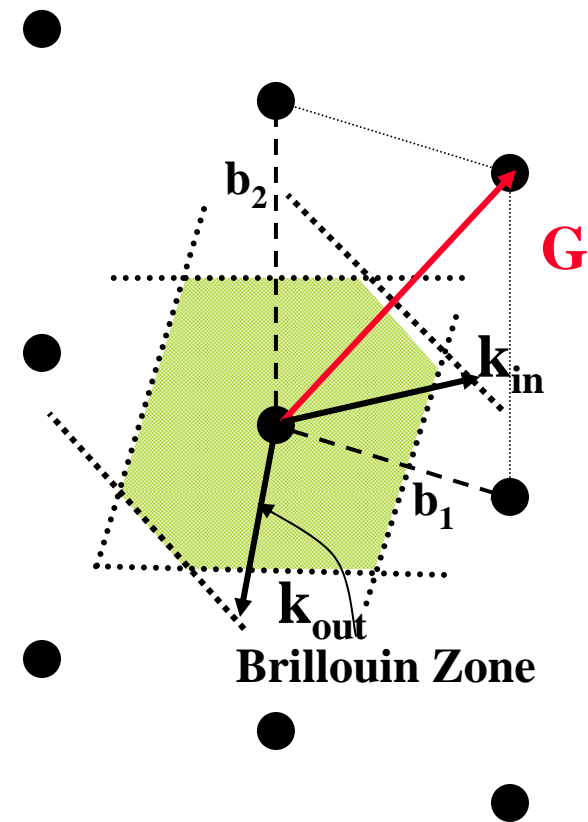- $\Rightarrow$ Bragg condition $2d \sin \theta = n \lambda$

Geometric Construction of Diffraction Conditions

- Consequence of condition
  $| 2\, \mathbf{k_{in}} \cdot \mathbf{G} | = G^2$

- $| \mathbf{k_{in}} \cdot \mathbf{G}/2 | = (G/2)^2$

- The vector $\mathbf{k_{in}}$ (also $\mathbf{k_{out}}$) lies along the perpendicular bisecting plane of a $\mathbf{G}$ vector

- One example is shown
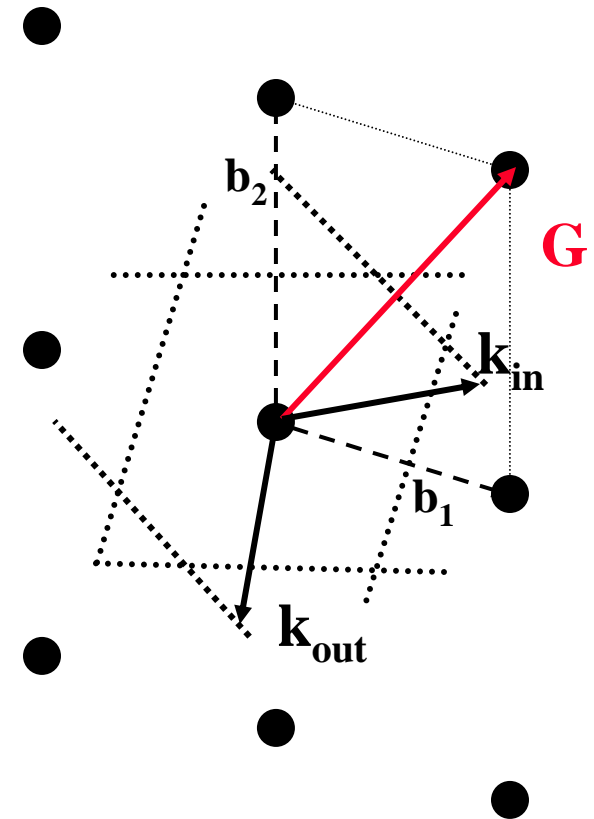
Diffraction and the Brillouin Zone

- Brillouin Zone formed by perpendicular bisectors of **G** vectors

- Consequence:
  No diffraction for any k
  inside the first Brillouin Zone

- Special role of Brillouin Zone (Wigner-Seitz cell of reciprocal lattice) as opposed to any other primitive cell

Comparison of diffraction from different lattices

- The Bragg condition can also be written
$$| \mathbf{G} | = 2 | \mathbf{k_{in}} | \sin \theta$$
$$\Rightarrow \quad \sin \theta = (\lambda / 4\pi) | \mathbf{G} |$$

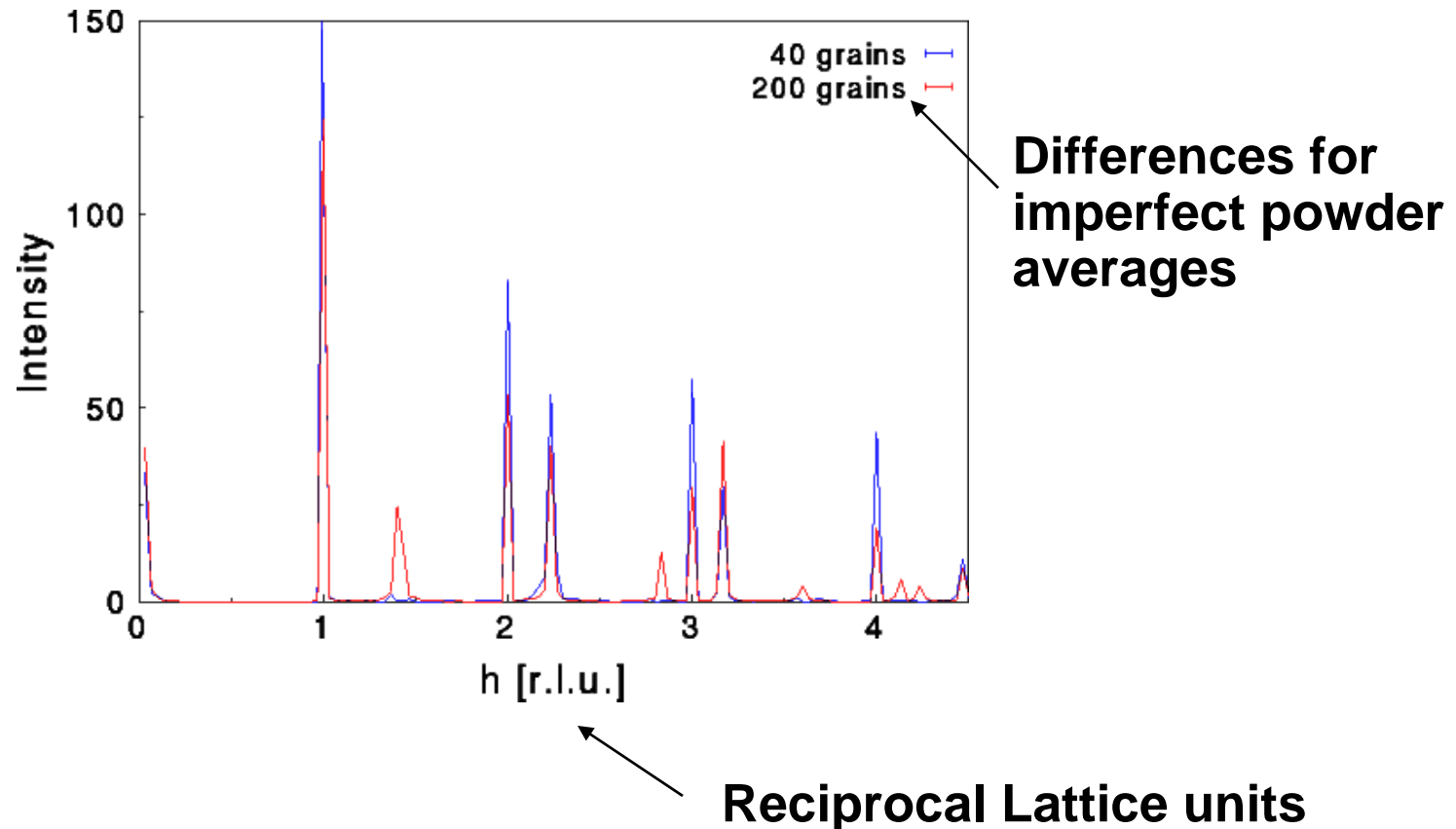- Thus the ratios of the sines of the angles for diffraction are given by:
$$\sin \theta_1 / \sin \theta_2 = | \mathbf{G_1} | / | \mathbf{G_2} |$$

- Each type of lattice has characteristic ratios the positions of diffraction peaks as a function of $\sin \theta$

- Simple scaling with λ

Experimental Powder Pattern

- Diffraction peaks at angles satisfying the Bragg condition

Differences for imperfect powder averages

Reciprocal Lattice units

Fourier analysis of the basis

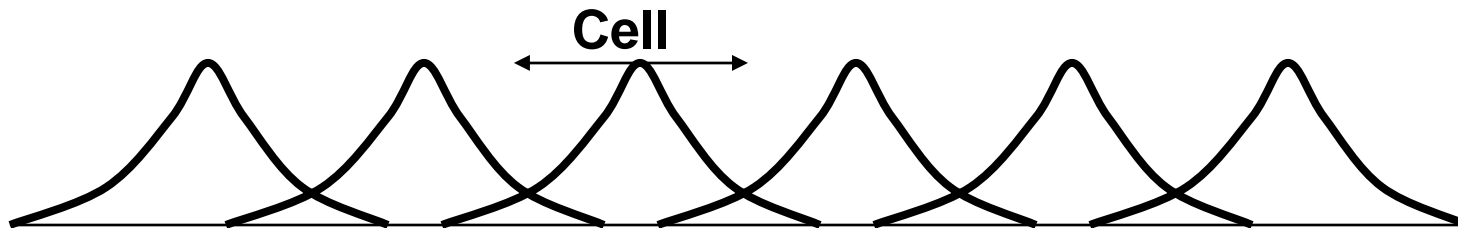- The intensity of the diffraction at each **G** is proportional to the square of the scattering amplitude

$$F = N \int_{cell} d\mathbf{r}\, n(\mathbf{r}) \exp(-i\, \mathbf{G} \cdot \mathbf{r}) = NS_{\mathbf{G}}$$

- $S_{\mathbf{G}}$ – structure factor

- Regard the crystal density $n(\mathbf{r})$ as a sum of atomic-like densities $n^{atom}(\mathbf{r} - \mathbf{R}_i)$, centered at point $\mathbf{R}_i$

$$n(\mathbf{r}) = \sum_{all\, i} n^{atom\, i}(\mathbf{r} - \mathbf{R}_i)$$

- Then also

$$S_{\mathbf{G}} = \sum_{i\, in\, cell} \int_{space} d\mathbf{r}\, n^{atom\, i}(\mathbf{r} - \mathbf{R}_i) \exp(-i\, \mathbf{G} \cdot \mathbf{r})$$

Cell

One atom per cell and Form Factor

- Then one can set $R_i = 0$ and $S_{\mathbf{G}}$ is the Fourier transform of one atom density

$$f = \int_{space} d\mathbf{r} \; n^{atom}(\mathbf{r}) \exp(-i\,\mathbf{G}\cdot\mathbf{r})$$

$$n^{atom}(\mathbf{r}) \qquad |r|$$

- Called Form Factor
- In the limit of point-like atoms $f = Z$

$$f \qquad \text{Values of } |G| \text{ for a particular crystal}$$

$$|G|$$

More than one atom per cell

- $S_\mathbf{G} = \sum_{i \text{ in cell}} \int_{\text{space}} d\mathbf{r} \, n^{\text{atom } i} (\mathbf{r} - \mathbf{R}_i) \exp(-i\,\mathbf{G} \cdot \mathbf{r})$
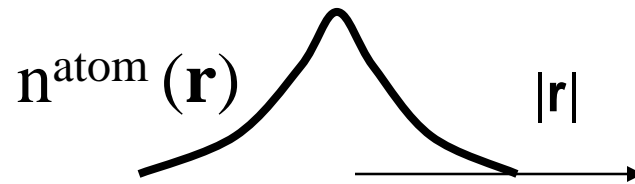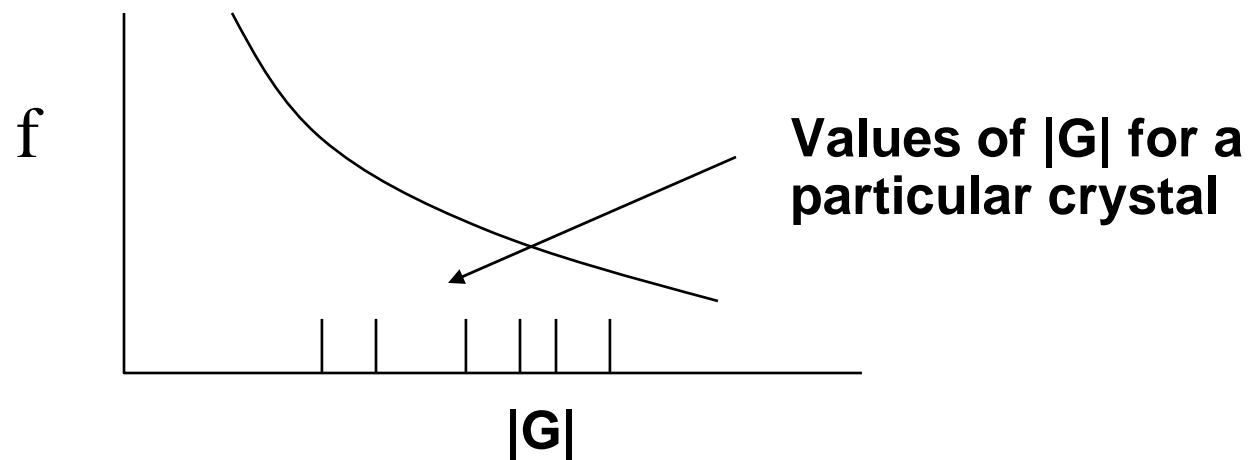
    $= \sum_{i \text{ in cell}} \exp(-i\,\mathbf{G} \cdot \mathbf{R_i})$
    $\int_{\text{space}} d\mathbf{r} \, n^{\text{atom } i} (\mathbf{r} - \mathbf{R}_i) \exp(-i\,\mathbf{G} \cdot (\mathbf{r} - \mathbf{R}_i))$

    $= \sum_{i \text{ in cell}} \exp(-i\,\mathbf{G} \cdot \mathbf{R}_i)$
    $\int_{\text{space}} d\mathbf{r} \, n^{\text{atom } i} (\mathbf{r}) \exp(-i\,\mathbf{G} \cdot \mathbf{r})$

    $= \sum_{i \text{ in cell}} \exp(-i\,\mathbf{G} \cdot \mathbf{R}_i) \, f_G^{\text{atom } i}$

- Interpretation: Form factor $f_G^{\text{atom } i}$ and phase factor $\exp(-i\,\mathbf{G} \cdot \mathbf{R_i})$ for each atom in unit cell

Structure factor and atomic form factor

- The amplitude of the scattered electromagnetic wave is

$$F_G = NS_G$$

- The structure factor of the base is

$$S_G = \sum_{i\ in\ cell} f_G^{atom\ i}\ exp(-i\boldsymbol{G}\cdot\boldsymbol{R}_i)$$

- The atomic form factor

$$f_j = f_G^{atom\ j} = \int_{unit\ cell} dV\ n_j(r)\,exp(-i\boldsymbol{G}\cdot\boldsymbol{r})$$

"Pure" Structure factor

- Often the basis contains more than one atom that is same element, e.g., diamond structure

- Then $f_G^{\text{atom } i} = f_G^{\text{atom}}$ is the same and
  $$S_G = \sum_{i \text{ in cell}} \exp(-i\,\mathbf{G}\cdot\mathbf{R_i})\; S_G^{\text{atom } i}$$

  $$= f_G^{\text{atom}} \sum_{i \text{ in cell}} \exp(-i\,\mathbf{G}\cdot\mathbf{R_i})$$

- Define "pure" structure factor
  $$S_G^0 = (1/n) \sum_{i \text{ in cell}} \exp(-i\,\mathbf{G}\cdot\mathbf{R_i})$$
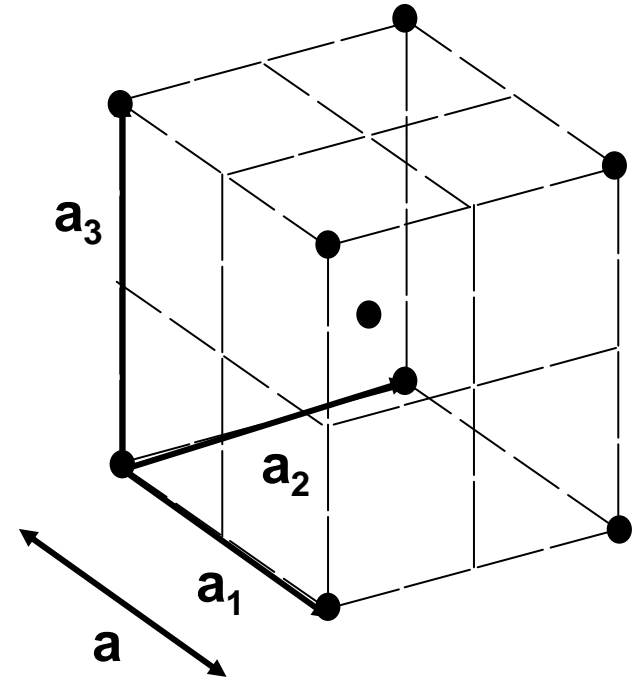
  where n = number of atoms in cell

- Then $S_G = n\; S_G^0\, f_G^{\text{atom}}$

Body Centered Cubic viewed as Simple Cubic with 2 points per cell

$S^0_G = (1/2) \sum_{i=1,2} \exp(- i\, \mathbf{G} \cdot \mathbf{R_i})$

$= (1/2) (1 + \exp(- i\, \mathbf{G} \cdot \mathbf{R_2})$

$= (1/2) \exp(- i\, \mathbf{G} \cdot \mathbf{R_2}/2)$

$[\exp(i\, \mathbf{G} \cdot \mathbf{R_2}/2) + \exp(- i\, \mathbf{G} \cdot \mathbf{R_2}/2)]$

$= \exp(- i\, \mathbf{G} \cdot \mathbf{R_2}/2) \cos (\mathbf{G} \cdot \mathbf{R_2}/2)$

Result: If $\mathbf{G} = (v_1\ v_2\ v_3)\ 2\pi/a$
$|S^0_G| = 1$ if sum of integers is even
$| S^0_G | = 0$ if sum is odd

Same as we found before!
FCC reciprocal lattice

Points at
$R_1 = (0,0,0)$
$R_2 = (1,1,1)\ a/2$

Face Centered Cubic viewed as
Simple Cubic with 4 points per cell

$S^0_G = (1/4) \sum_{i=1,4} \exp(- i \, \mathbf{G} \cdot \mathbf{R_i})$
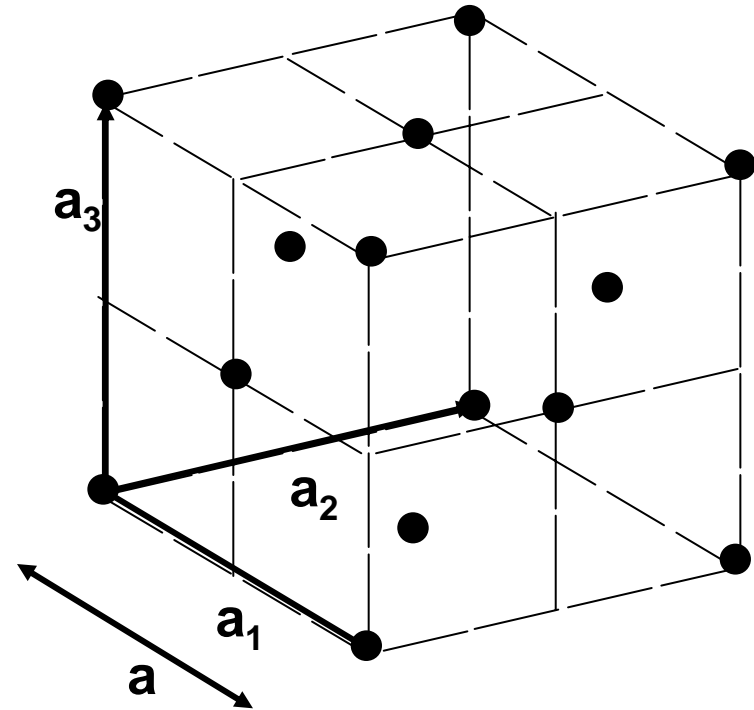
Result:

If $\mathbf{G} = (v_1 \, v_2 \, v_3) \, 2\pi/a$
then

$S^0_G = 1$ if all integers
are odd or all are even

$S^0_G = 0$ otherwise

Same as we found before!
BCC reciprocal lattice

Points at   (0,0,0) ; (1,1,0) a/2 ;
(1,0,1) a/2 ; (0,1,1) a/2

Structure factor for diamond

- Ex: diamond structure
  $$S^0_G = (1/2) \sum_{i=1,2} \exp(- i\, G \cdot R_i)$$

- $R_1 = + (1/8, 1/8, 1/8)a$
  $R_2 = - (1/8, 1/8, 1/8)a$