Intro. to Electro-physics

The theory of X-ray diffraction (II)

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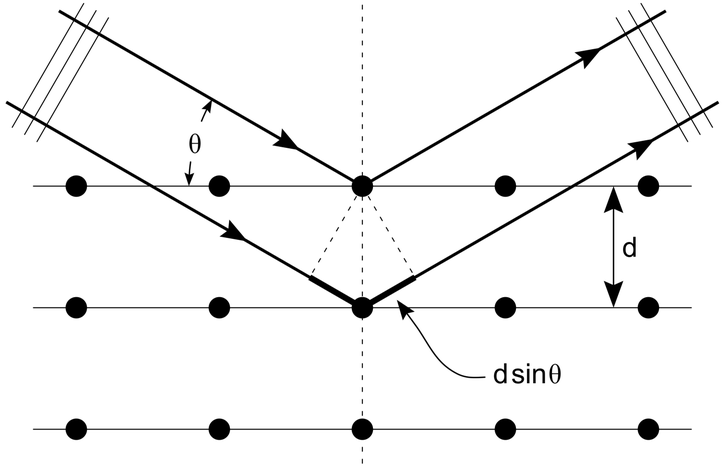
The amplitude of x-ray diffraction

- **Bragg's law**

$$2d\sin\theta = n\lambda, \quad (n = 1, 2, \cdots)$$

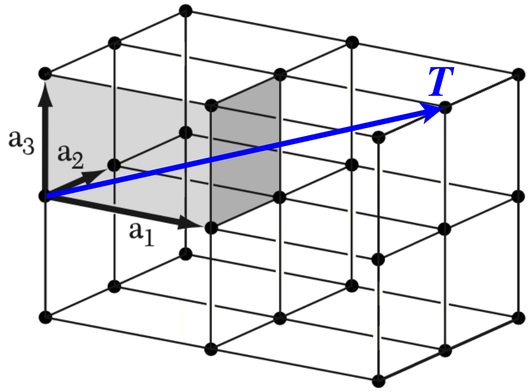
  - The condition for the constructive interference of scattered waves from the lattice points of a crystal
  - High-intensity reflected waves occurs at only certain values of θ



- **The amplitude of scattered wave**
  - Determined by the spatial distribution of electrons within each lattice point
  - Electron density

$$n(\boldsymbol{r} + \boldsymbol{T}) = n(\boldsymbol{r}), \text{ where } \boldsymbol{T} = u_1\boldsymbol{a}_1 + u_2\boldsymbol{a}_2 + u_3\boldsymbol{a}_3$$

    - $n(\boldsymbol{r})$ is invariant under any translation of the form $\boldsymbol{T}$
    - $n(\boldsymbol{r})$ is a periodic function of $\boldsymbol{r}$ with periods $\boldsymbol{a}_1, \boldsymbol{a}_2, \boldsymbol{a}_3$ in the directions of three crystal axes
    - An ideal situation for Fourier analysis!



1D Fourier analysis for XRD (1/2)

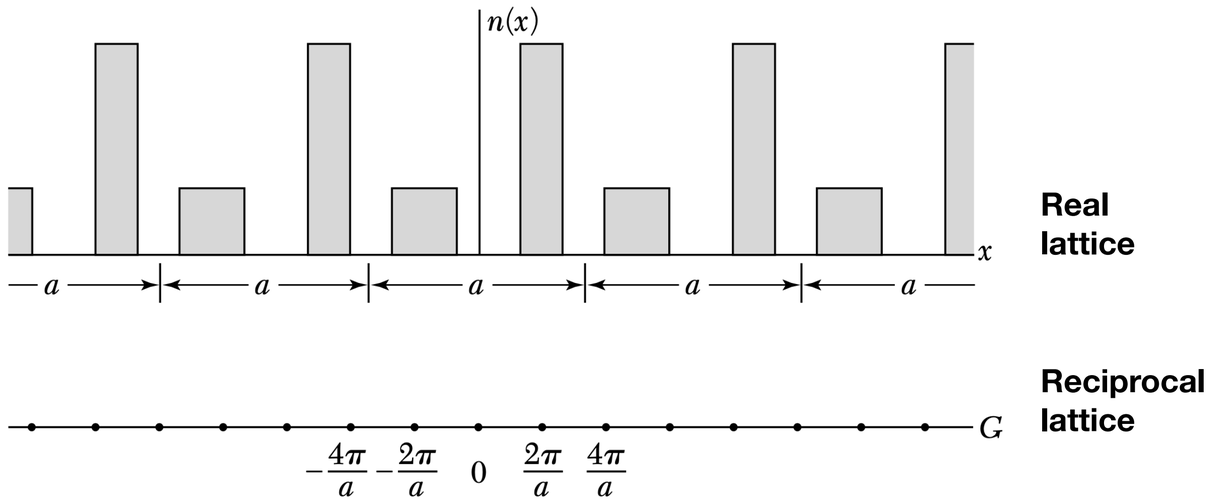
- Fourier analysis in 1D
  - Fourier series of sines and cosines for $n(x)$ with period a :

$$n(x) = n_0 + \sum_{p>0} \left[C_p \cos\left(\frac{2\pi p}{a} x\right) + S_p \sin\left(\frac{2\pi p}{a} x\right) \right],$$

    - C_p, S_p : Fourier coefficients of the expansion (real-valued), p : positive inegers
    - $2\pi/a$ represents that $n(x)$ has the period of a. That is,

$$\left[n(x+a) = n_0 + \sum_{p>0} \left[C_p \cos\left(\frac{2\pi p}{a} x + 2\pi p\right) + S_p \sin\left(\frac{2\pi p}{a} x + 2\pi p\right) \right] \right] = n(x)$$

  - $2\pi p/a \ (p = 1, 2, \cdots)$: points in the **reciprocal lattice**
    - The allowed terms in the Fourier series
    - Other terms are not allowed



1D Fourier analysis for XRD (2/2)

- Fourier analysis in 1D
  - Transformation in an exponential form

$$n(x) = n_0 + \sum_{p>0} \left[C_p \cos\left(\frac{2\pi p}{a}x\right) + S_p \sin\left(\frac{2\pi p}{a}x\right) \right] = \boxed{\sum_p n_p \exp\left(i\frac{2\pi p}{a}x\right)}$$

    - p now being all integers (positive, negative and zero)
    - n_p being complex numbers

✳ Condition to ensure that $n(x)$ is still a real function : $n^*_{-p} = n_p$

If we let $\varphi = 2\pi p x/a$, the sum of the terms in p and $-p$ is written by:

$$n_p(\cos\varphi + i\sin\varphi) + n_{-p}(\cos\varphi - i\sin\varphi) = \left(n_p + n_{-p}\right)\cos\varphi + i\left(n_p - n_{-p}\right)\sin\varphi = 2\Re\left(n_p\right)\cos\varphi - 2\Im\left(n_p\right)\sin\varphi$$

  - Inversion of Fourier series

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

3D Fourier analysis and reciprocal lattice vector

- Fourier analysis in 1D vs. 3D

	1D	3D
Fourier series	$n(x) = \sum_p n_p \exp\left(i\frac{2\pi p}{a}x\right)$	$n(\boldsymbol{r}) = \sum_{\boldsymbol{G}} n_{\boldsymbol{G}} \exp\left(i\boldsymbol{G}\cdot\boldsymbol{r}\right)$
Inversion of Fourier series	$n_p = \frac{1}{a}\int_0^a n(x)\exp\left(-i\frac{2\pi p}{a}x\right)dx$	$n_{\boldsymbol{G}} = \frac{1}{V_c}\int n(\boldsymbol{r})\exp\left(-i\boldsymbol{G}\cdot\boldsymbol{r}\right)dV$

- Reciprocal lattice vector, $\boldsymbol{G}$
  - $\boldsymbol{G} = \upsilon_1\boldsymbol{b}_1 + \upsilon_2\boldsymbol{b}_2 + \upsilon_3\boldsymbol{b}_3 \quad \left(\upsilon_1, \upsilon_2, \upsilon_3 : \text{integers}\right)$
  - Construction rule for $\boldsymbol{b}_1, \boldsymbol{b}_2, \boldsymbol{b}_3$

$$\boxed{\boldsymbol{b}_1 = 2\pi\frac{\boldsymbol{a}_2\times\boldsymbol{a}_3}{\boldsymbol{a}_1\cdot\boldsymbol{a}_2\times\boldsymbol{a}_3}; \qquad \boldsymbol{b}_2 = 2\pi\frac{\boldsymbol{a}_3\times\boldsymbol{a}_1}{\boldsymbol{a}_1\cdot\boldsymbol{a}_2\times\boldsymbol{a}_3}; \qquad \boldsymbol{b}_3 = 2\pi\frac{\boldsymbol{a}_1\times\boldsymbol{a}_2}{\boldsymbol{a}_1\cdot\boldsymbol{a}_2\times\boldsymbol{a}_3}}$$

$\left(\boldsymbol{a}_1, \boldsymbol{a}_2, \boldsymbol{a}_3 : \text{primitive lattice vectors}\right)$

  - Relationship between reciprocal vs. real lattice vectors

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

Reciprocal lattice vector

Fourier series

$$n(\boldsymbol{r}) = \sum_{\boldsymbol{G}} n_{\boldsymbol{G}} \exp\left(i\boldsymbol{G}\cdot\boldsymbol{r}\right)$$

Inversion of Fourier series

$$n_{\boldsymbol{G}} = \frac{1}{V_c}\int n(\boldsymbol{r}) \exp\left(-i\boldsymbol{G}\cdot\boldsymbol{r}\right) dV$$

- Reciprocal lattice vector, $\boldsymbol{G}$ (contd.)

$$\boldsymbol{G} = v_1\boldsymbol{b}_1 + v_2\boldsymbol{b}_2 + v_3\boldsymbol{b}_3 \quad \left(v_1, v_2, v_3 : \text{integers}\right)$$

  - $\boldsymbol{G}$ Represent the allowed points in the reciprocal lattice
  - **The vectors G in Fourier series = The reciprocal lattice vectors G**

Proof

Since $n(\boldsymbol{r})$ is invariant under any crystal translation $\boldsymbol{T} = u_1\boldsymbol{a}_1 + u_2\boldsymbol{a}_2 + u_3\boldsymbol{a}_3$,

$$\left[n(\boldsymbol{r}+\boldsymbol{T}) = \sum_{\boldsymbol{G}} n_{\boldsymbol{G}} \exp\left(i\boldsymbol{G}\cdot\boldsymbol{r}\right)\exp\left(i\boldsymbol{G}\cdot\boldsymbol{T}\right)\right] = \left[\sum_{\boldsymbol{G}} n_{\boldsymbol{G}} \exp\left(i\boldsymbol{G}\cdot\boldsymbol{r}\right) = n(\boldsymbol{r})\right]$$

$$\left(\because \exp\left(i\boldsymbol{G}\cdot\boldsymbol{T}\right) = \exp\left[i\left(v_1\boldsymbol{b}_1 + v_2\boldsymbol{b}_2 + v_3\boldsymbol{b}_3\right)\cdot\left(u_1\boldsymbol{a}_1 + u_2\boldsymbol{a}_2 + u_3\boldsymbol{a}_3\right)\right] = \exp\left[i2\pi\left(v_1u_1 + v_2u_2 + v_3u_3\right)\right] = 1\right)$$

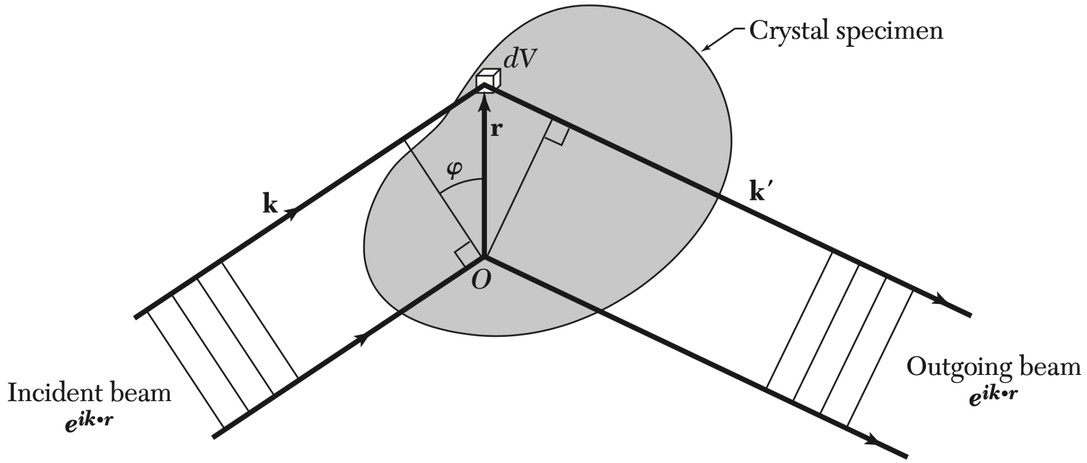
  - Every crystal structure has two lattices associated with it
    - A diffraction pattern of a crystal = A map of the reciprocal lattice of the crystal
    - A microscope image of a crystal = A map of the crystal structure in real space

Diffraction condition in reciprocal lattice (1/3)

- Diffraction condition in reciprocal lattice
  - The possible XRD can occur if the following relation satisfies:

$$\boxed{\boldsymbol{k} - \boldsymbol{k}' = \boldsymbol{G}}$$

($\boldsymbol{k}$: incident wave, $\boldsymbol{k}'$: diffracted wave)



- Proof
  - The difference in phase factors between beams scattered from the volume elements that are $\boldsymbol{r}$ apart :

$$\exp\left[i\left(\boldsymbol{k} - \boldsymbol{k}'\right)\cdot\boldsymbol{r}\right] \triangleq \exp\left[-i\Delta\boldsymbol{k}\cdot\boldsymbol{r}\right], \quad \text{where } \boxed{-\Delta\boldsymbol{k} = \boldsymbol{k} - \boldsymbol{k}' : \text{Scattering vector}}$$

  - Amplitude of the wave scattered from a volume element $\propto n\left(\boldsymbol{r}\right) dV$
  - Total amplitude of the scattered wave in the direction $\boldsymbol{k}'$:

$$F = \int \exp\left[-i\Delta\boldsymbol{k}\cdot\boldsymbol{r}\right] n\left(\boldsymbol{r}\right) dV$$

Diffraction condition in reciprocal lattice (2/3)

- Proof (contd.)
  - Total amplitude of the scattered wave in the direction $\boldsymbol{k}'$:

$$F = \int \exp\left[-i\Delta\boldsymbol{k}\cdot\boldsymbol{r}\right] n(\boldsymbol{r})\, dV \quad \text{and since } n(\boldsymbol{r}) = \sum_{\boldsymbol{G}} n_{\boldsymbol{G}} \exp\left(i\boldsymbol{G}\cdot\boldsymbol{r}\right),$$

$$F = \sum_{\boldsymbol{G}} \int n_{\boldsymbol{G}} \exp\left[i\left(\boldsymbol{G}-\Delta\boldsymbol{k}\right)\cdot\boldsymbol{r}\right] dV \begin{cases} = Vn_G, & \text{if } \Delta\boldsymbol{k} = \boldsymbol{G} \\ \approx 0, & \text{if } \Delta\boldsymbol{k} \neq \boldsymbol{G} \end{cases}. \qquad \therefore \Delta\boldsymbol{k} = \boldsymbol{G}$$

- Diffraction condition in reciprocal lattice
  - Energy conservation of an X-ray in elastic scattering :

$$\left[E = \hbar\omega = \hbar ck\right] = \left[E' = \hbar\omega' = \hbar ck'\right] \longrightarrow k = k'$$

$$\Delta\boldsymbol{k} = \boldsymbol{G} \longrightarrow \boldsymbol{k}+\boldsymbol{G} = \boldsymbol{k}' \longrightarrow \left(\boldsymbol{k}+\boldsymbol{G}\right)^2 = k^2 \longrightarrow 2\boldsymbol{k}\cdot\boldsymbol{G} + G^2 = 0$$

  - If $\boldsymbol{G}$ is a reciprocal lattice vector, so is $-\boldsymbol{G}$

$$\boxed{\therefore 2\boldsymbol{k}\cdot\boldsymbol{G} = G^2}$$

Diffraction condition in reciprocal lattice (3/3)

- Implication of the diffraction condition

$$\boxed{2\boldsymbol{k}\cdot\boldsymbol{G} = G^2}$$

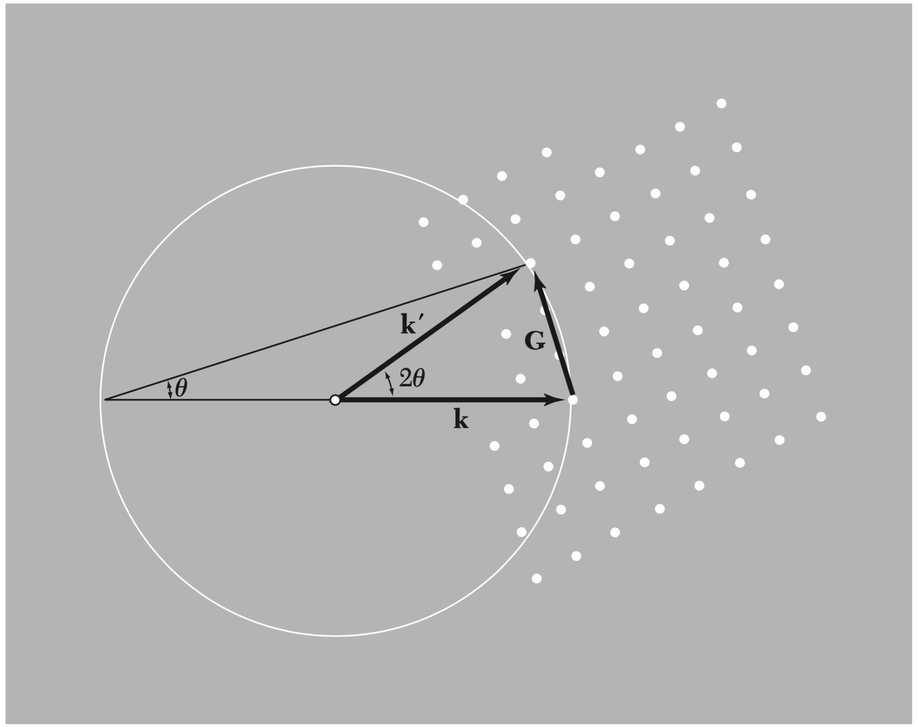
  - Consider an arbitrary plane hkl in a crystal lattice.
  - Then, the reciprocal lattice vector $\boldsymbol{G} = h\boldsymbol{b}_1 + k\boldsymbol{b}_2 + l\boldsymbol{b}_3$ should be perpendicular to this plane. **(HW)**
  - The distance between two adjacent parallel planes is given by $d\left(hkl\right) = \dfrac{2\pi}{\left|\boldsymbol{G}\right|}$. **(HW)**
  - Thus, $2\boldsymbol{k}\cdot\boldsymbol{G} = G^2 \quad\longrightarrow\quad 2\dfrac{2\pi}{\lambda}G\sin\theta = G^2 \quad\longrightarrow\quad 2d\left(hkl\right)\sin\theta = \lambda$
  - Note that integers hkl are not necessarily identical with Miller indices, since hkl may contain a common factor n.
  - Hence, $\boxed{\therefore\ 2d\sin\theta = n\lambda,}$ where d the spacing between adjacent parallel planes with indices $\left(\dfrac{h}{n}\dfrac{k}{n}\dfrac{l}{n}\right)$

The Ewald construction

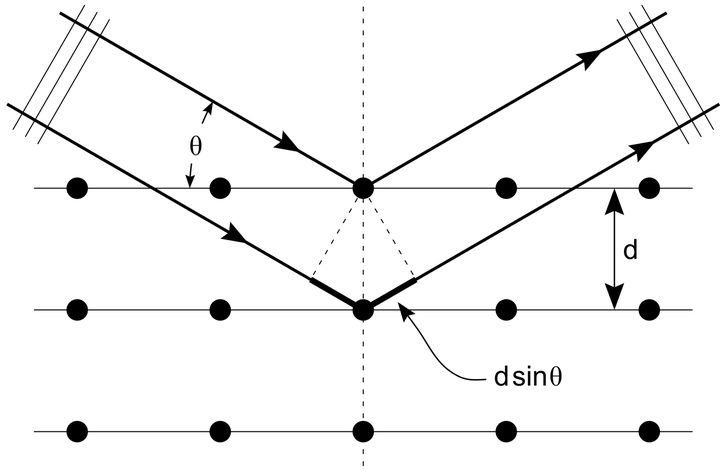
A graphical way of finding the **diffraction condition**

- The white points represent reciprocal lattice points
- The incident x-ray beam has the wave-vector $\boldsymbol{k}$
- The origin is chosen such that $\boldsymbol{k}$ terminates at any reciprocal point.
- We draw a sphere of a radius $k = 2\pi/\lambda$ about the origin of $\boldsymbol{k}$.
- **The diffracted beam will be formed if the sphere intersects any other reciprocal lattice points.**
- The diffracted beam is formed in the direction $\boldsymbol{k}' = \boldsymbol{k} + \boldsymbol{G}$ with particular reciprocal vectors $\boldsymbol{G}$.

  (θ : The Bragg angle of diffraction)



<Diffraction depicted in reciprocal lattice>



<Diffraction depicted in real lattice>

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The theory of X-ray diffraction (III)

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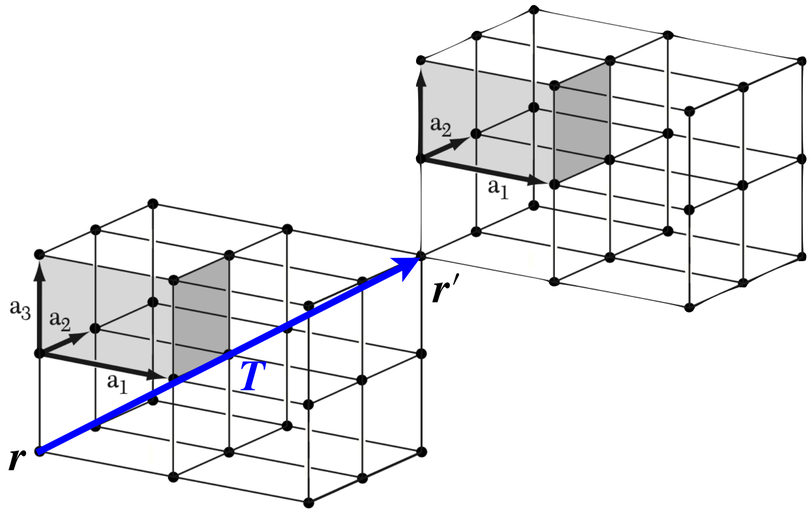
Review of the lattice and primitive cell

- Definition of the lattice and primitive cell

  $\boldsymbol{r}' = \boldsymbol{r} + \boldsymbol{T}$ ($\boldsymbol{r}$: lattice point, $\boldsymbol{T} = u_1\boldsymbol{a}_1 + u_2\boldsymbol{a}_2 + u_3\boldsymbol{a}_3$: translation vector)

  - If arbitrary lattice point $\boldsymbol{r}'$ can be described by $\boldsymbol{T}$ with any integers (u_1, u_2, u_3),
    - $(\boldsymbol{a}_1, \boldsymbol{a}_2, \boldsymbol{a}_3)$: **Primitive translation vectors**
    - The unit cell defined by $(\boldsymbol{a}_1, \boldsymbol{a}_2, \boldsymbol{a}_3)$: **Primitive cell**



- The important properties of primitive cell
  - The primitive cell is a minimum-volume cell with a volume $\boldsymbol{a}_1 \cdot \boldsymbol{a}_2 \times \boldsymbol{a}_3$
  - There is only “one” lattice point per primitive cell
  - The definition of the primitive cell is not unique!

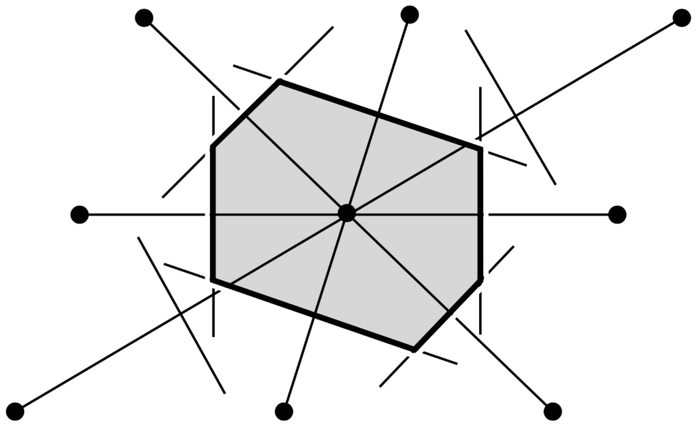
Wigner-Seitz primitive cell

- **Wigner-Seitz primitive cell**
  - Another way of choosing the primitive cell
  - Procedure of defining it:

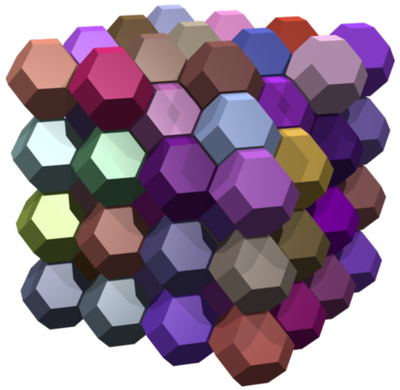
    (1) Draw lines to connect a given lattice point to all nearby lattice points.

    (2) At the midpoint and normal to these lines, draw new lines or planes.

    (3) The smallest volume enclosed in this way is the Wigner-Seitz primitive cell.
  - One lattice point at the center of the cell
  - All space can be filled by Wigner-Seitz cells as other primitive cells



2D Wigner-Seitz primitive cell



Wigner-Seitz cell of bcc lattice (truncated octahedron)

Wigner-Seitz cell of fcc lattice (rhombic dodecahedron)

Brillouin zone (1/2)

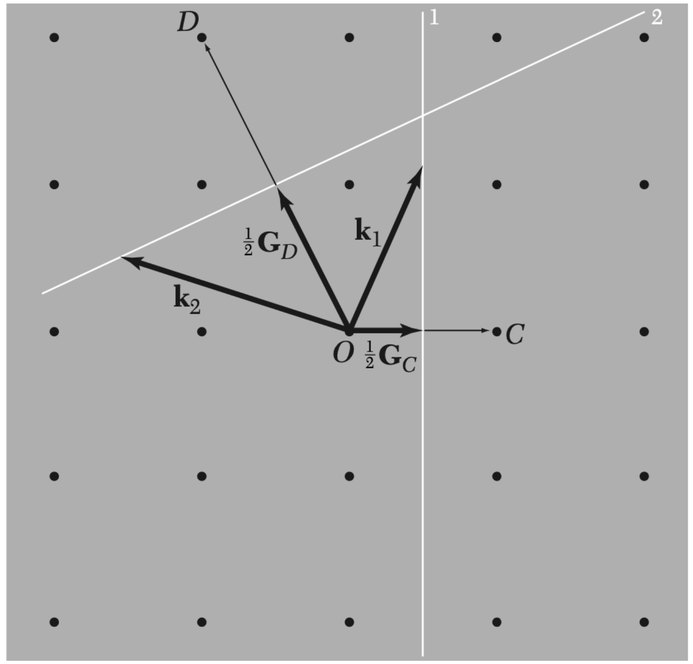
- Brillouin zone
  - Definition : a Wigner-Seitz primitive cell in reciprocal lattice
  - Provides a geometrical interpretation of diffraction condition

Diffraction condition	
Real lattice	Reciprocal lattice
Bragg's law	Laue equation
$2d\sin\theta = n\lambda$	$\boldsymbol{k}' - \boldsymbol{k} = \Delta\boldsymbol{k} = \boldsymbol{G}$ $2\boldsymbol{k}\cdot\boldsymbol{G} = G^2$

- Procedure of finding the Brillouin zone

$$2\boldsymbol{k}\cdot\boldsymbol{G} = G^2 \underset{\div 4}{\rightarrow} \boldsymbol{k}\cdot\left(\frac{1}{2}\boldsymbol{G}\right) = \left(\frac{1}{2}G\right)^2 \quad \cdots\text{(eq.1)}$$

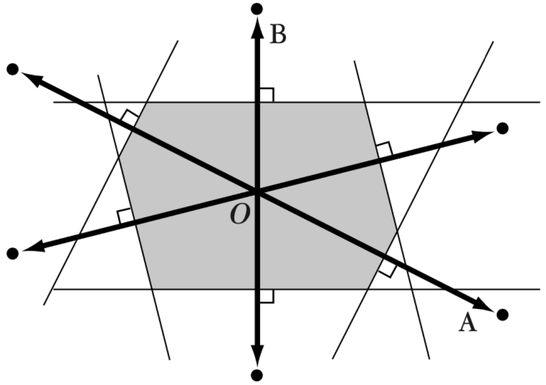
  - Select a vector $\boldsymbol{G}$ from the origin to a reciprocal lattice point
  - Construct a plane normal to this vector $\boldsymbol{G}$ at its midpoint $(1$ or $2)$
  - This plane forms a part of a Brillouin zone boundary
  - X-ray with $\boldsymbol{k}$ will be diffracted by a crystal if this $\boldsymbol{k}$ satisfies (eq. 1)
  - The diffracted beam will emerge in the direction $\boldsymbol{k}' = \boldsymbol{k} + \boldsymbol{G}$

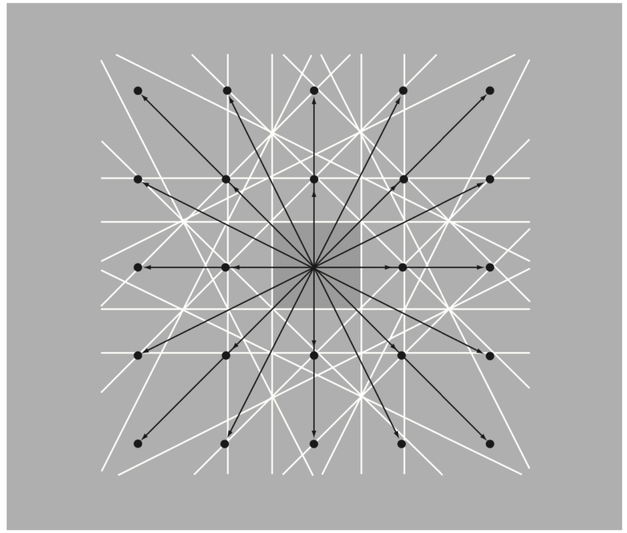


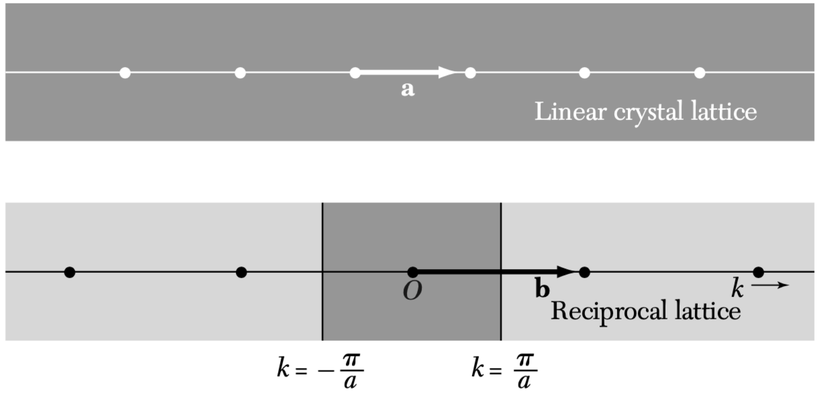
Brillouin zone (2/2)

- Brillouin zone (contd.)
  - Formed by the set of planes that are the perpendicular bisects of the reciprocal lattice vectors
  - A wave whose $\boldsymbol{k}$ terminates on any of Brillouin zone boundaries will undergo diffraction by the crystal

- **the first Brillouin zone**
  - The smallest volume entirely enclosed by planes that are the perpendicular bisectors of the reciprocal lattice vectors drawn from the origin
  - a Wigner-Seitz cell of the reciprocal lattice







Brillouin zone of simple-cubic lattice

- Primitive reciprocal lattice vectors

  (for given primitive lattice vectors $\boldsymbol{a}_1, \boldsymbol{a}_2, \boldsymbol{a}_3$)

$$\boldsymbol{b}_1 = 2\pi \frac{\boldsymbol{a}_2 \times \boldsymbol{a}_3}{\boldsymbol{a}_1 \cdot \boldsymbol{a}_2 \times \boldsymbol{a}_3}; \qquad \boldsymbol{b}_2 = 2\pi \frac{\boldsymbol{a}_3 \times \boldsymbol{a}_1}{\boldsymbol{a}_1 \cdot \boldsymbol{a}_2 \times \boldsymbol{a}_3}; \qquad \boldsymbol{b}_3 = 2\pi \frac{\boldsymbol{a}_1 \times \boldsymbol{a}_2}{\boldsymbol{a}_1 \cdot \boldsymbol{a}_2 \times \boldsymbol{a}_3}$$

- Simple-cubic (sc) lattice

  - The primitive lattice vectors *w.r.t.* the conventional cube with a side a

$$\boldsymbol{a}_1 = a\hat{\boldsymbol{x}}; \qquad \boldsymbol{a}_2 = a\hat{\boldsymbol{y}}; \qquad \boldsymbol{a}_3 = a\hat{\boldsymbol{z}} \quad \left(V = \boldsymbol{a}_1 \cdot \boldsymbol{a}_2 \times \boldsymbol{a}_3 = a^3\right)$$

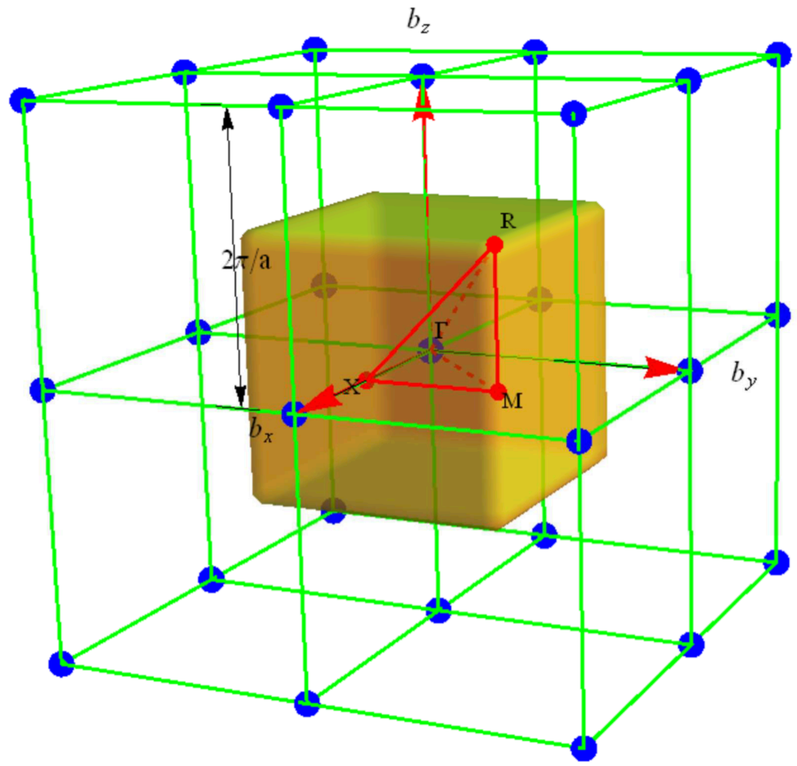
  - The primitive reciprocal lattice vector

$$\boldsymbol{b}_1 = \frac{2\pi}{a}\hat{\boldsymbol{x}}; \qquad \boldsymbol{b}_2 = \frac{2\pi}{a}\hat{\boldsymbol{y}}; \qquad \boldsymbol{b}_3 = \frac{2\pi}{a}\hat{\boldsymbol{z}} \quad \left(V = \boldsymbol{b}_1 \cdot \boldsymbol{b}_2 \times \boldsymbol{b}_3 = (2\pi/a)^3\right)$$

$\therefore$ The primitive reciprocal lattice of a sc-lattice is also a sc-lattice!

  - Brillouin zone is formed by 6 planes that are normal to

$$\pm\frac{1}{2}\boldsymbol{b}_1 = \pm\frac{\pi}{a}\hat{\boldsymbol{x}}; \qquad \pm\frac{1}{2}\boldsymbol{b}_2 = \pm\frac{\pi}{a}\hat{\boldsymbol{y}}; \qquad \pm\frac{1}{2}\boldsymbol{b}_3 = \pm\frac{\pi}{a}\hat{\boldsymbol{z}}$$



Brillouin zone of sc, fcc, and bcc structures
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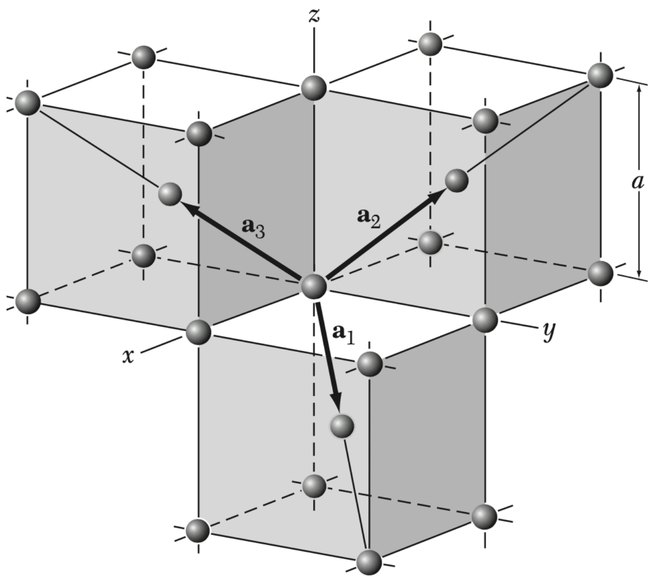
(Date: March 24, 2012)

Brillouin zone of body-centered cubic lattice

- Body-centered cubic (bcc) lattice
  - The primitive lattice vector *w.r.t.* the conventional cube with a side a

$$\boldsymbol{a}_1 = \frac{1}{2}a\left(\hat{\boldsymbol{x}} + \hat{\boldsymbol{y}} - \hat{\boldsymbol{z}}\right); \qquad \boldsymbol{a}_2 = \frac{1}{2}a\left(-\hat{\boldsymbol{x}} + \hat{\boldsymbol{y}} + \hat{\boldsymbol{z}}\right); \qquad \boldsymbol{a}_3 = \frac{1}{2}a\left(\hat{\boldsymbol{x}} - \hat{\boldsymbol{y}} + \hat{\boldsymbol{z}}\right)$$



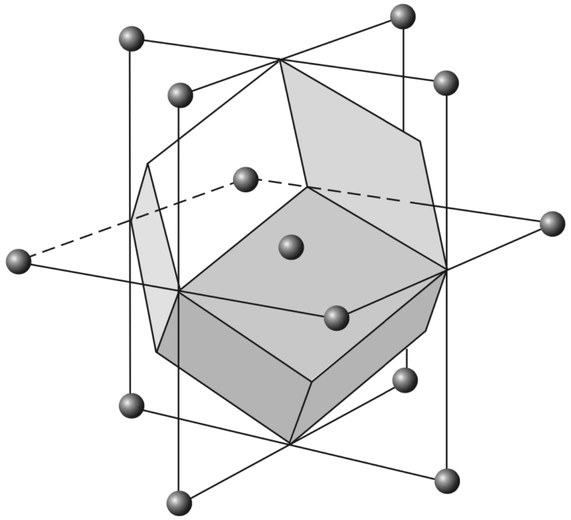
  - The primitive reciprocal lattice vector

$$\boldsymbol{b}_1 = \frac{2\pi}{a}\left(\hat{\boldsymbol{y}} + \hat{\boldsymbol{z}}\right); \qquad \boldsymbol{b}_2 = \frac{2\pi}{a}\left(\hat{\boldsymbol{x}} + \hat{\boldsymbol{z}}\right); \qquad \boldsymbol{b}_3 = \frac{2\pi}{a}\left(\hat{\boldsymbol{x}} + \hat{\boldsymbol{y}}\right) \quad (fcc!)$$

$\therefore$ The primitive reciprocal lattice of a bcc-lattice is a fcc-lattice!

  - The shortest $\boldsymbol{G}$ are the following 12 vectors:

$$\left(\frac{2\pi}{a}\right)\left(\pm\hat{\boldsymbol{y}} \pm \hat{\boldsymbol{z}}\right); \qquad \left(\frac{2\pi}{a}\right)\left(\pm\hat{\boldsymbol{x}} \pm \hat{\boldsymbol{z}}\right); \qquad \left(\frac{2\pi}{a}\right)\left(\pm\hat{\boldsymbol{x}} \pm \hat{\boldsymbol{y}}\right);$$



  - A Brillouin zone is formed by planes that are perpendicular bisectors of above vectors → 12-faced rhombic dodecahedron (사방 십이면체)

Brillouin zone of face-centered cubic lattice

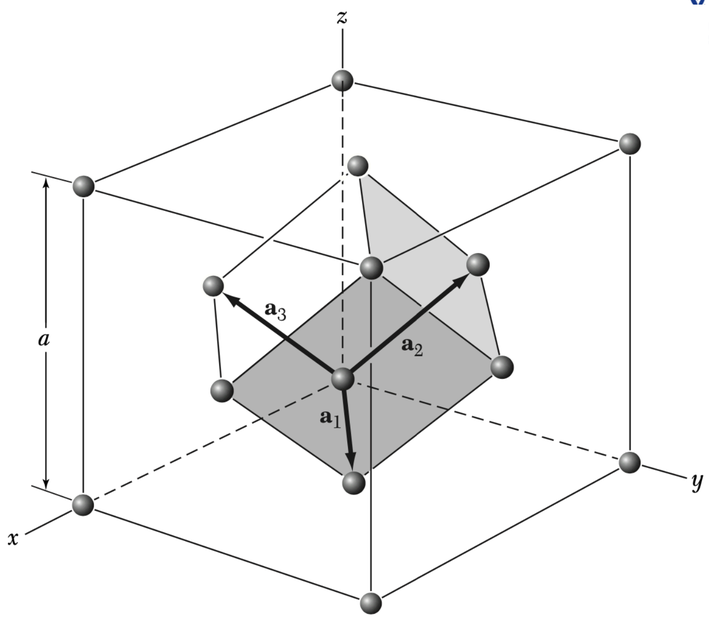
- Face-centered lattice (fcc)
  - The primitive lattice vector *w.r.t.* the conventional cube with a side a

$$\boldsymbol{a}_1 = \frac{1}{2}a\left(\hat{\boldsymbol{y}} + \hat{\boldsymbol{z}}\right); \qquad \boldsymbol{a}_2 = \frac{1}{2}a\left(\hat{\boldsymbol{x}} + \hat{\boldsymbol{z}}\right); \qquad \boldsymbol{a}_3 = \frac{1}{2}a\left(\hat{\boldsymbol{x}} + \hat{\boldsymbol{y}}\right);$$

  - The primitive reciprocal lattice vector

$$\boldsymbol{b}_1 = \frac{2\pi}{a}\left(-\hat{\boldsymbol{x}} + \hat{\boldsymbol{y}} + \hat{\boldsymbol{z}}\right); \qquad \boldsymbol{b}_2 = \frac{2\pi}{a}\left(\hat{\boldsymbol{x}} - \hat{\boldsymbol{y}} + \hat{\boldsymbol{z}}\right); \qquad \boldsymbol{b}_3 = \frac{2\pi}{a}\left(\hat{\boldsymbol{x}} + \hat{\boldsymbol{y}} - \hat{\boldsymbol{z}}\right); \ (bcc!)$$

$\therefore$ The primitive reciprocal lattice of a fcc-lattice is a bcc-lattice!



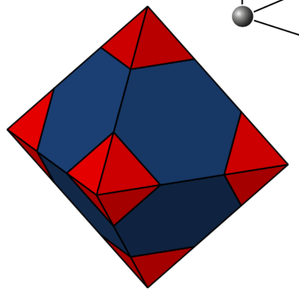
  - The shortest $\boldsymbol{G}$ are the following **8** vectors:

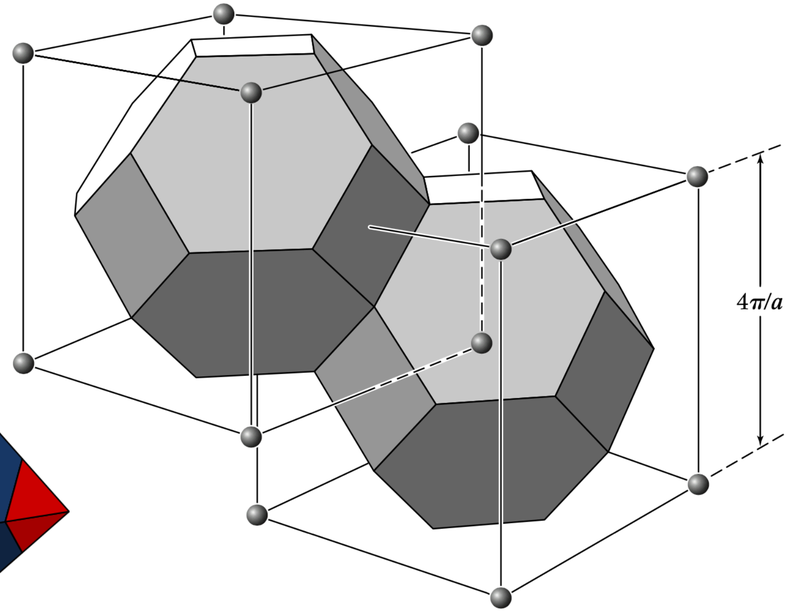
$$\left(\frac{2\pi}{a}\right)\left(\pm\hat{\boldsymbol{x}} \pm \hat{\boldsymbol{y}} \pm \hat{\boldsymbol{z}}\right);$$

  - **But,** the corners of the octahedron **(정팔면체)** thus formed are cut by the planes that are perpendicular bisectors of **6** other reciprocal lattice vectors:

$$\pm\frac{2\pi}{a}\hat{\boldsymbol{x}}; \qquad \pm\frac{2\pi}{a}\hat{\boldsymbol{y}}; \qquad \pm\frac{2\pi}{a}\hat{\boldsymbol{z}}$$

  - 14-faced "truncated" octahedron (깎은 정팔면체)





The amplitude of diffraction (1/2)

- Recall the diffraction amplitude for a crystal of N primitive cells when the diffraction condition satisfies $(\Delta \boldsymbol{k} = \boldsymbol{G})$:

$$F = N \int \exp\left[-i\boldsymbol{G}\cdot\boldsymbol{r}\right] n(\boldsymbol{r})\, dV \triangleq N S_{\boldsymbol{G}}\,, \quad \text{where} \quad \boxed{S_{\boldsymbol{G}} = \int \exp\left[-i\boldsymbol{G}\cdot\boldsymbol{r}\right] n(\boldsymbol{r})\, dV}$$

Structural factor

  - Assumptions for further analysis on $S_{\boldsymbol{G}}$
    - Each primitive cell consists of s atoms
    - j-th atom located at $\boldsymbol{r}_j$ has an "electron density function n_j" that contributes to an electron density at $\boldsymbol{r}$ $(n(\boldsymbol{r}))$:

$n_j\left(\boldsymbol{r}-\boldsymbol{r}_j\right)$: the contribution of j-th atom at $\boldsymbol{r}_j$ to the electron density at $\boldsymbol{r}$

$$n(\boldsymbol{r}) = \sum_{j=1}^{s} n_j\left(\boldsymbol{r}-\boldsymbol{r}_j\right)$$

- **Structural factor**

$$S_{\boldsymbol{G}} = \sum_{j=1}^{s} \int n_j\left(\boldsymbol{r}-\boldsymbol{r}_j\right) \exp\left(-i\boldsymbol{G}\cdot\boldsymbol{r}\right) dV. \qquad \text{Let } \boldsymbol{r}-\boldsymbol{r}_j \triangleq \boldsymbol{\rho}$$

$$= \sum_{j=1}^{s} \exp\left(-i\boldsymbol{G}\cdot\boldsymbol{r}_j\right) \boxed{\int n_j(\boldsymbol{\rho}) \exp\left(-i\boldsymbol{G}\cdot\boldsymbol{\rho}\right) dV}$$

Atomic form factor

The amplitude of diffraction (2/2)

- **Structural factor (contd.)**

Let $\int n_j(\boldsymbol{\rho}) \exp(-i\boldsymbol{G}\cdot\boldsymbol{\rho}) dV \triangleq f_j$ (atomic form factor; out of scope). Then,

$$S_{\boldsymbol{G}} = \sum_{j=1}^{s} \exp\left(-i\boldsymbol{G}\cdot\boldsymbol{r}_j\right) \int n_j(\boldsymbol{\rho}) \exp(-i\boldsymbol{G}\cdot\boldsymbol{\rho}) dV = \sum_{j=1}^{s} f_j \exp\left(-i\boldsymbol{G}\cdot\boldsymbol{r}_j\right).$$

Now, let $\begin{cases} \boldsymbol{r}_j = x_j\boldsymbol{a}_1 + y_j\boldsymbol{a}_2 + z_j\boldsymbol{a}_3 & \text{(the position of a j-th atom)} \\ \boldsymbol{G} = \upsilon_1\boldsymbol{b}_1 + \upsilon_2\boldsymbol{b}_2 + \upsilon_3\boldsymbol{b}_3 & \text{(reciprocal lattice vector)} \end{cases}.$

$$S_{\boldsymbol{G}} = \sum_{j=1}^{s} f_j \exp\left[-i\left(\upsilon_1\boldsymbol{b}_1 + \upsilon_2\boldsymbol{b}_2 + \upsilon_3\boldsymbol{b}_3\right)\cdot\left(x_j\boldsymbol{a}_1 + y_j\boldsymbol{a}_2 + z_j\boldsymbol{a}_3\right)\right]$$

$$\boxed{= \sum_{j=1}^{s} f_j \exp\left[-i2\pi\left(\upsilon_1 x_j + \upsilon_2 y_j + \upsilon_3 z_j\right)\right]}$$

- Then, the intensity of diffraction is determined by

$$I = S_{\boldsymbol{G}} \cdot S_{\boldsymbol{G}}^* = \left|S_{\boldsymbol{G}}\right|^2 \quad \left(\therefore S_{\boldsymbol{G}} \text{ not necessarily be real}\right)$$

Structural factor of the bcc lattice

- Structural factor of the bcc-lattice
  - The bcc basis referred to the cubic cell has identical atoms at

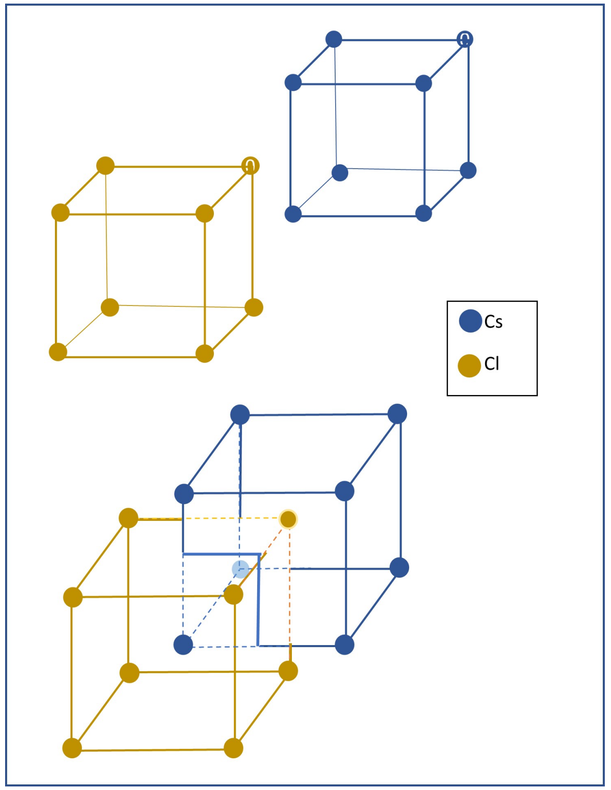
$$\left(x_1, y_1, z_1\right) = (0,0,0) \text{ and } \left(x_2, y_2, z_2\right) = \left(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}\right)$$

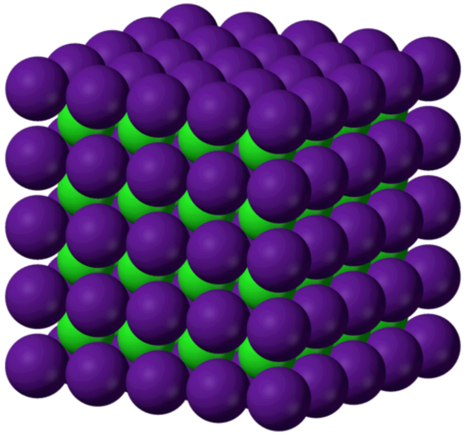
  - The structural factor is given by

$$S_{\boldsymbol{G}} = \sum_{j=1}^{s} f_j \exp\left[-i2\pi\left(v_1 x_j + v_2 y_j + v_3 z_j\right)\right]$$

$$= \sum_{j=1}^{s} f \exp\left[1 - i2\pi\left(v_1 + v_2 + v_3\right)\right]$$

$$= \begin{cases} 0, & \text{when } v_1 + v_2 + v_3 : \text{odd integers} \\ 2f, & \text{when } v_1 + v_2 + v_3 : \text{even integers} \end{cases}$$





Structural factor of the fcc lattice

- Structural factor of the fcc-lattice
  - The fcc-basis referred to the cubic cell has identical atoms at

$$\left(x_j, y_j, z_j\right) = (0,0,0),\ \left(0,\frac{1}{2},\frac{1}{2}\right),\ \left(\frac{1}{2},0,\frac{1}{2}\right),\ \left(\frac{1}{2},\frac{1}{2},0\right)$$

  - The structural factor is given by

$$S_{\boldsymbol{G}} = \sum_{j=1}^{s} f \exp\left[1 - i2\pi\left(\upsilon_1 + \upsilon_2 + \upsilon_3\right)\right]$$

$$= f\left[1 + \exp\left[-i\pi\left(\upsilon_2 + \upsilon_3\right)\right] + \exp\left[-i\pi\left(\upsilon_1 + \upsilon_3\right)\right] + \exp\left[-i\pi\left(\upsilon_1 + \upsilon_2\right)\right]\right]$$

$$= \begin{cases} 4f, & \text{when all } \upsilon_1, \upsilon_2, \upsilon_3 \text{ are even/odd integers} \\ 0, & \text{when one of } \upsilon_1, \upsilon_2, \upsilon_3 \text{ is even/odd integer} \end{cases}$$