Crystal Lattices

"The true test of crystallinity is not the superficial appearance of a large specimen of crystal, but whether on the microscopic scale, the atoms (or ions) are arranged in a periodic array."

References:

1) Solid State Physics –
   By N. W. Ashcroft and N. D. Mermin

2) Crystallography Applied To Solid State Physics –
   By A. R. Verma and O. N. Srivastava

3) The Oxford Solid State Basics
   By Steven H. Simon

Reciprocal Lattice

- Consider a plane wave $e^{i\mathbf{k}.\mathbf{r}}$ and a Bravais lattice **R**
- For general ***k***, the plane wave will not have the periodicity of the Bravais Lattice, but for some special choices of ***k*** it will
- The set of all wavevectors **K** that yield plane waves with the periodicity of a given Bravais lattice is known as its reciprocal lattice

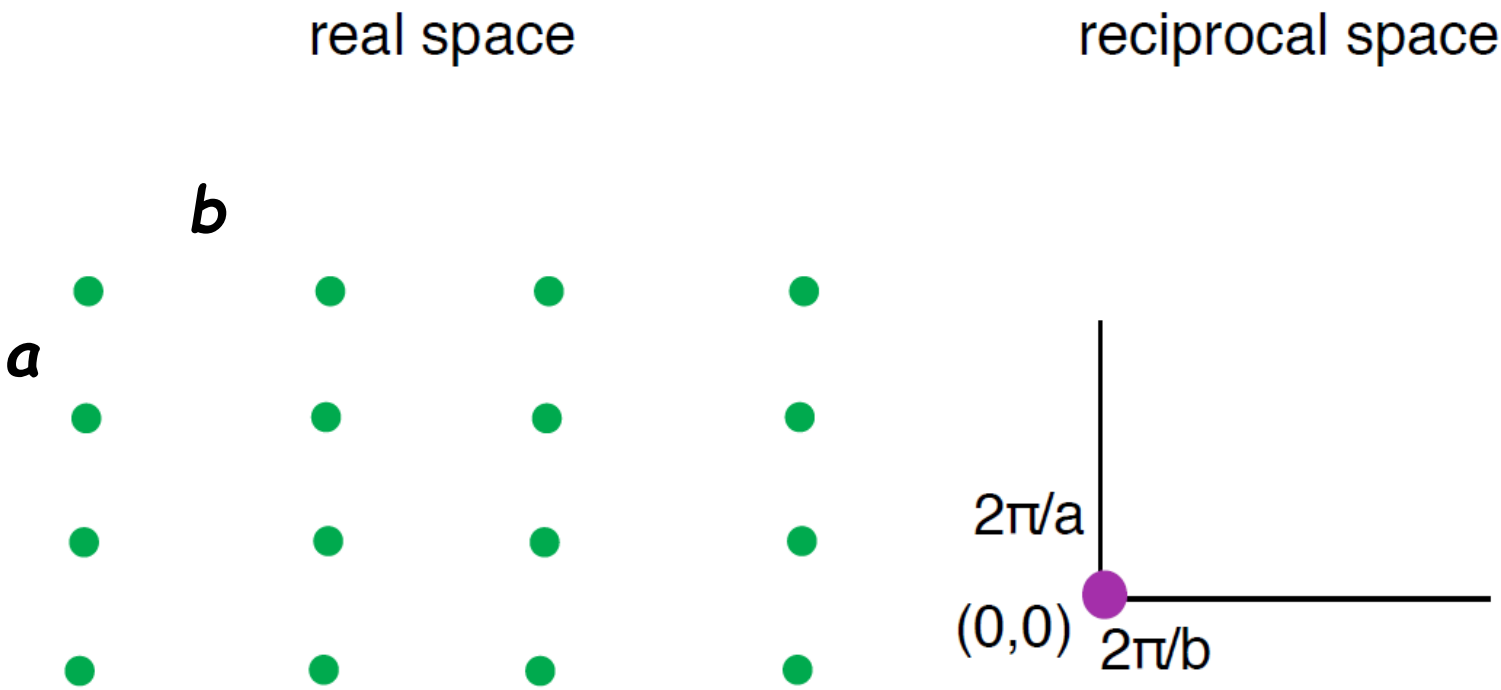
Analytically if **K** satisfies condition

$$e^{i\mathbf{K}.(\mathbf{r}+\mathbf{R})} = e^{i\mathbf{K}.\mathbf{r}}$$

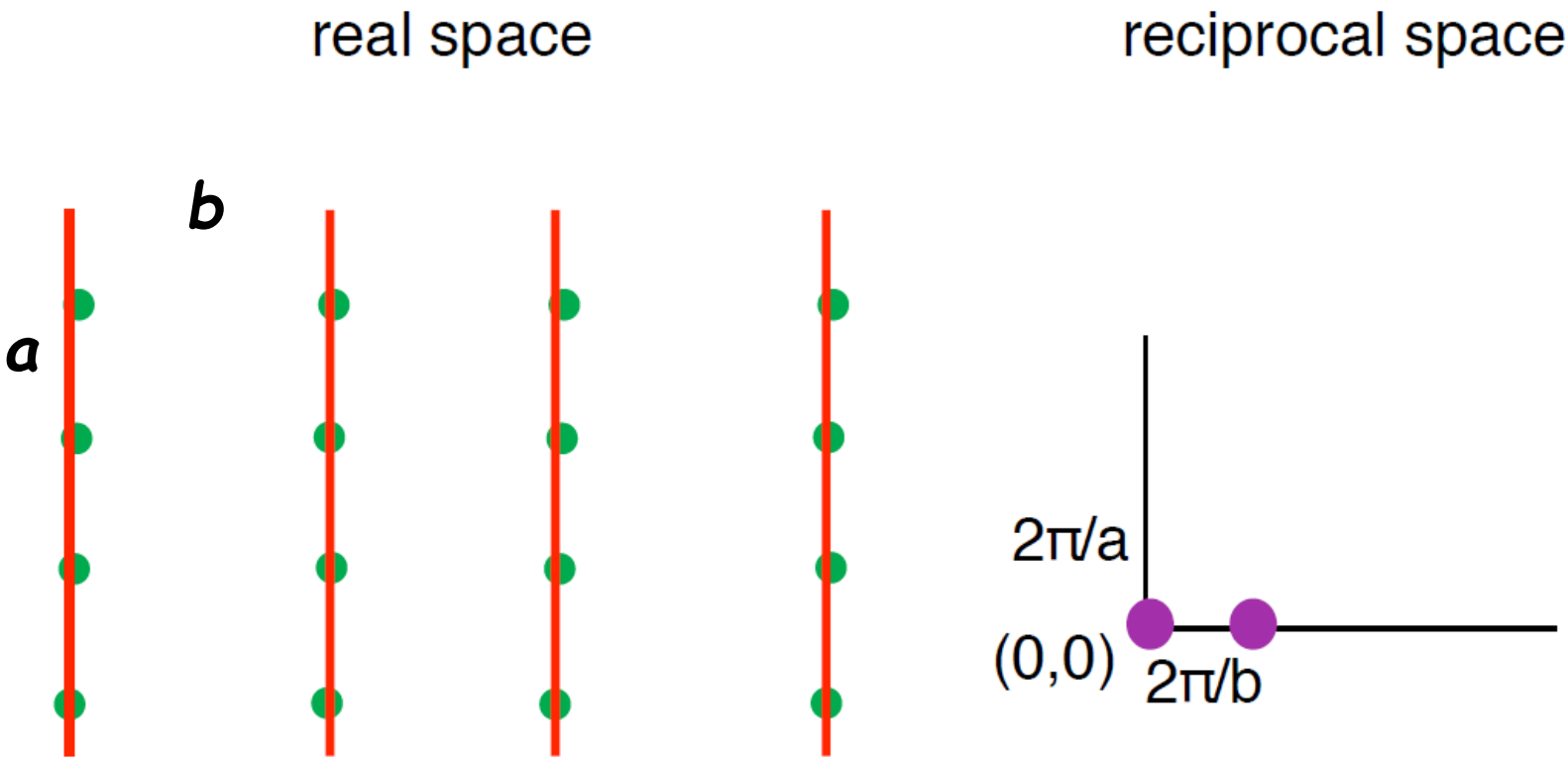
which implies $e^{i\mathbf{K}.\mathbf{R}} = 1$ for all **R** in the Bravais lattice

for any ***r*** and all **R** then **K** belongs to the reciprocal lattice of the Bravais lattice **R**

Lattice waves



Lattice waves



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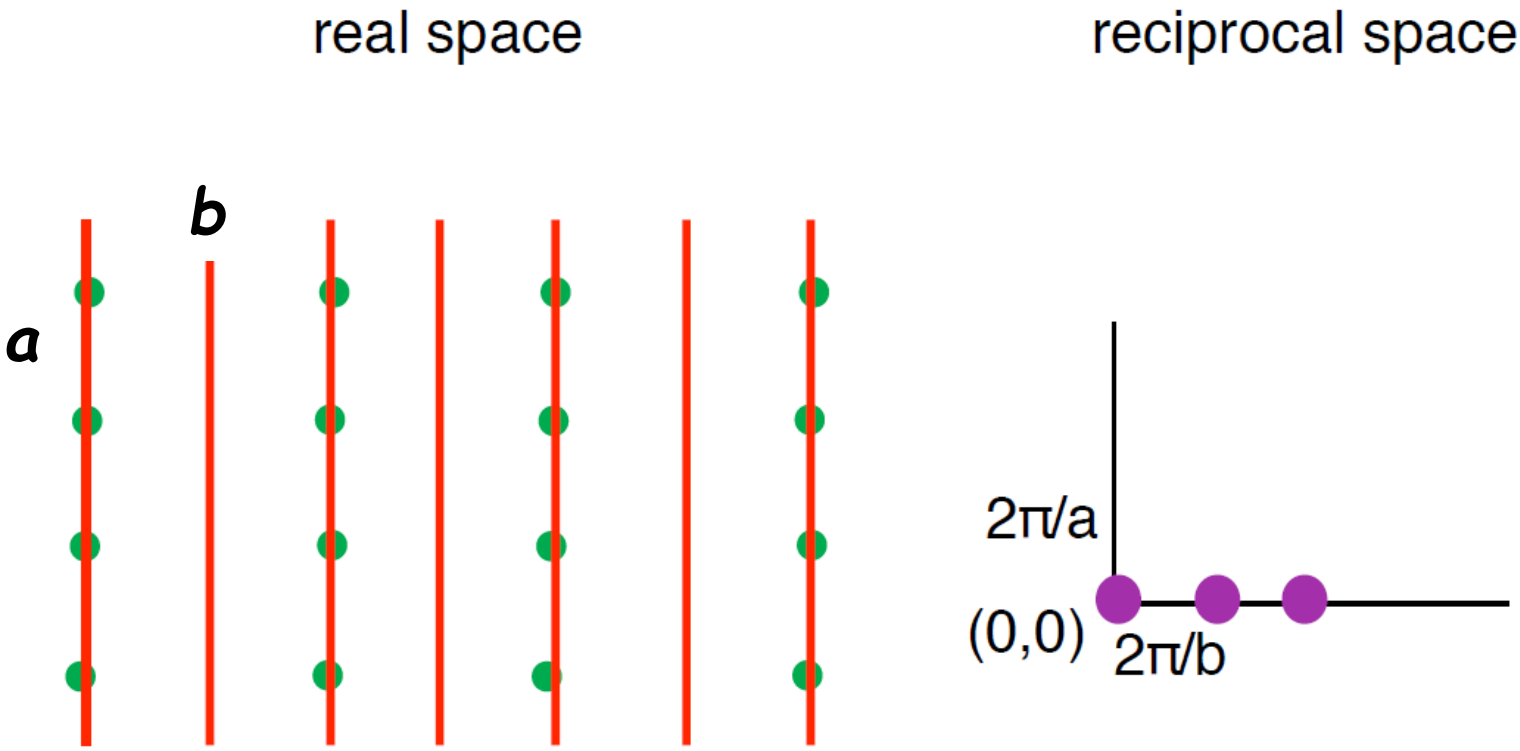
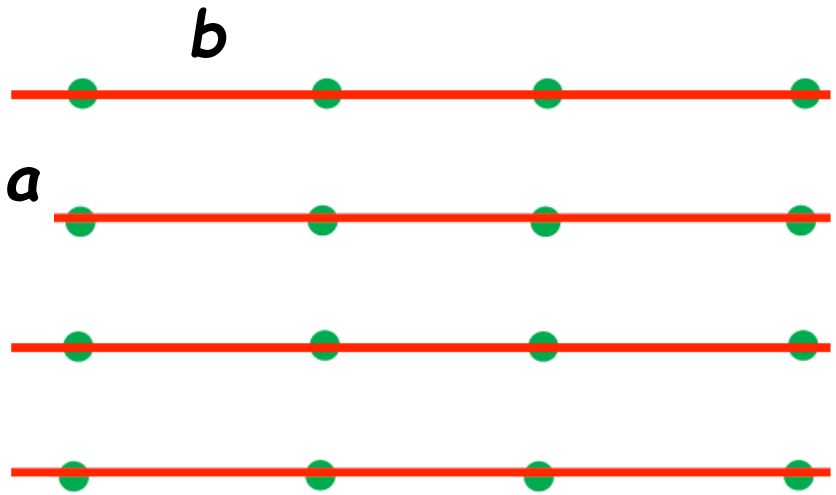
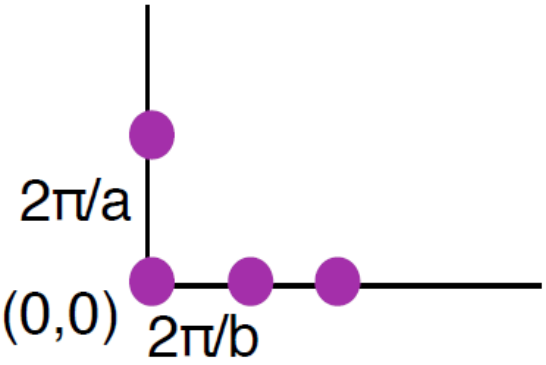


Lattice waves

real space

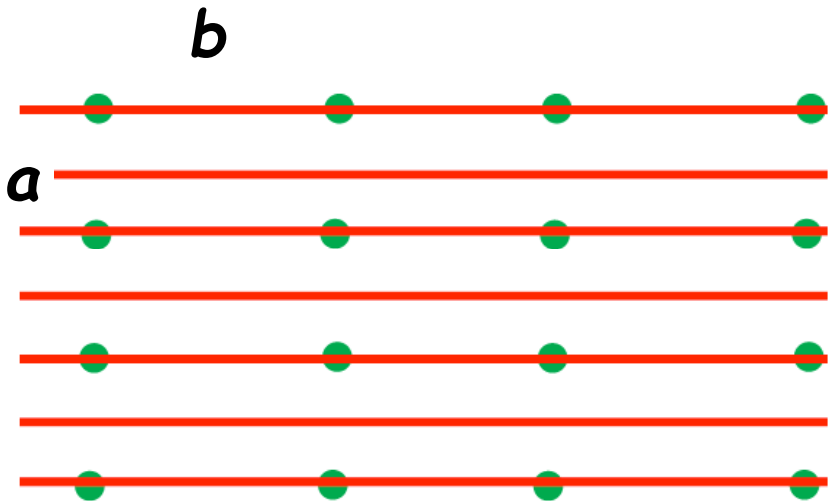


reciprocal space

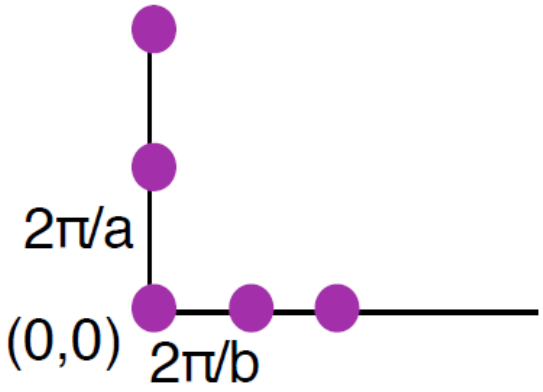


Lattice waves

real space



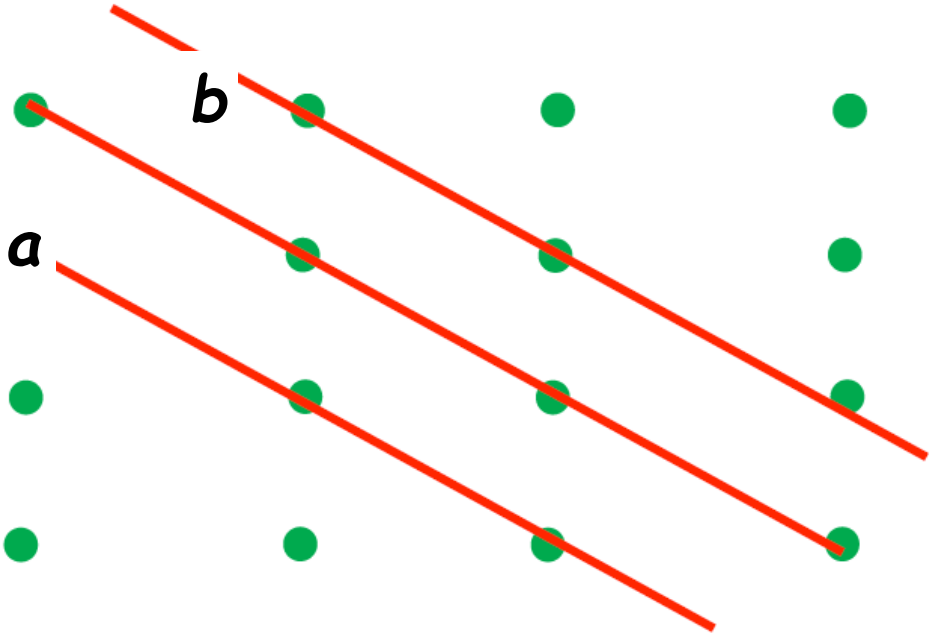
reciprocal space

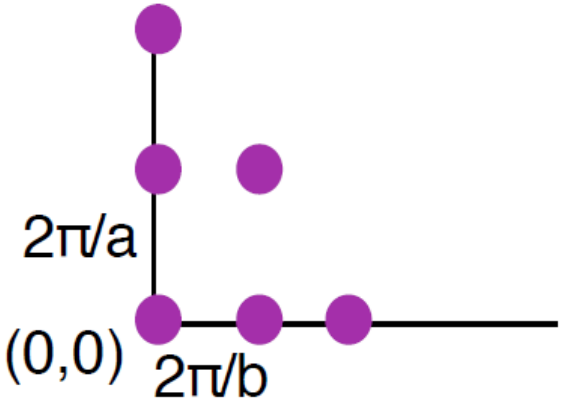


Lattice waves

real space

reciprocal space





Reciprocal Lattice

- Reciprocal lattice itself is a Bravais lattice in k space

- If $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$ are a set of primitive vectors for the direct lattice,
  then the reciprocal lattice can be generated by three primitive vectors –

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

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

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

Reciprocal Lattice

- The primitive vectors $\mathbf{b}_i$ satisfy -

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

$$\delta_{ij} = 0, \quad i \neq j$$
$$\delta_{ij} = 1, \quad i = j.$$

- Any $\mathbf{k}$ can be written as -

$$\mathbf{k} = k_1\mathbf{b}_1 + k_2\mathbf{b}_2 + k_3\mathbf{b}_3$$

- If $\mathbf{R}$ is any direct lattice vector, for integers $\mathbf{n}_i$

$$\mathbf{R} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3$$

$$\mathbf{k} \cdot \mathbf{R} = 2\pi(k_1n_1 + k_2n_2 + k_3n_3).$$

- For $e^{i\mathbf{K}.\mathbf{R}} = 1$ for all $\mathbf{R}$, the coefficients $\mathbf{k}_i$ should be integers

- The condition for Reciprocal lattice vector is satisfied by only those k which can be expressed as a linear superposition of $\mathbf{b}_i$ with integer coefficients $\mathbf{k}_i$

Reciprocal Lattice – Some examples

- The simple-cubic Bravais lattice of side "**a**" has a reciprocal lattice which is also simple-cubic of side "$\frac{2\pi}{a}$"

$$\mathbf{a}_1 = a\hat{\mathbf{x}}, \quad \mathbf{a}_2 = a\hat{\mathbf{y}}, \quad \mathbf{a}_3 = a\hat{\mathbf{z}},$$

$$\mathbf{b}_1 = \frac{2\pi}{a}\hat{\mathbf{x}}, \quad \mathbf{b}_2 = \frac{2\pi}{a}\hat{\mathbf{y}}, \quad \mathbf{b}_3 = \frac{2\pi}{a}\hat{\mathbf{z}}.$$

- Reciprocal of a FCC Bravais lattice is a BCC lattice

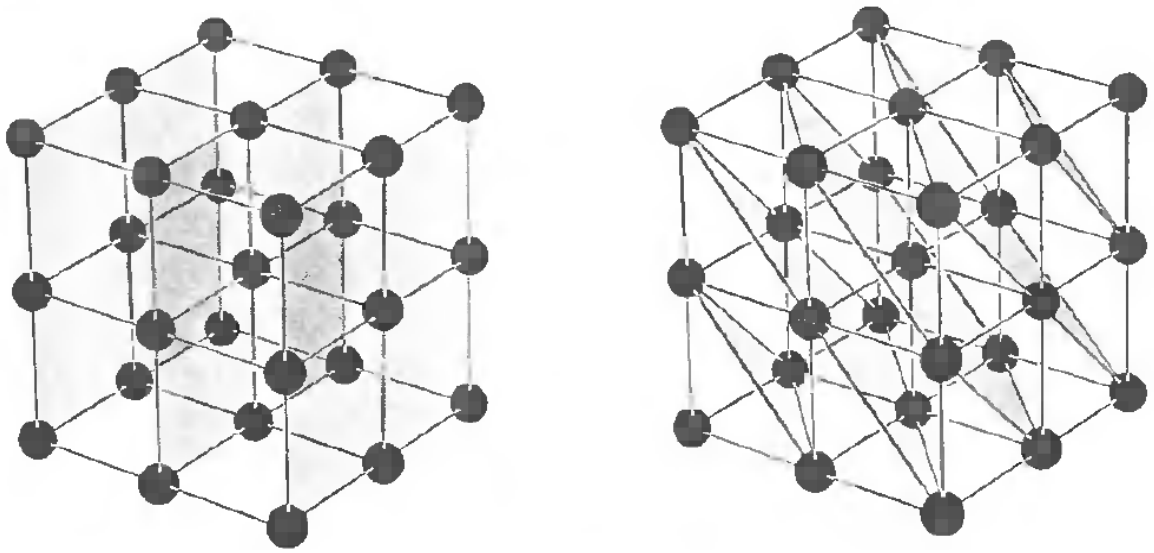
$$\mathbf{b}_1 = \frac{4\pi}{a}\frac{1}{2}(\hat{\mathbf{y}} + \hat{\mathbf{z}} - \hat{\mathbf{x}}), \quad \mathbf{b}_2 = \frac{4\pi}{a}\frac{1}{2}(\hat{\mathbf{z}} + \hat{\mathbf{x}} - \hat{\mathbf{y}}), \quad \mathbf{b}_3 = \frac{4\pi}{a}\frac{1}{2}(\hat{\mathbf{x}} + \hat{\mathbf{y}} - \hat{\mathbf{z}})$$

The Wigner-Seitz primitive unit cell of a reciprocal lattice is known as the **First Brillouin Zone**

Lattice planes

- There is an intimate connection between vectors in reciprocal lattice and planes of points in direct lattice

- A lattice plane in a 3D Bravais lattice will contain infinite number of lattice points which will form a 2D Bravais lattice within the plane

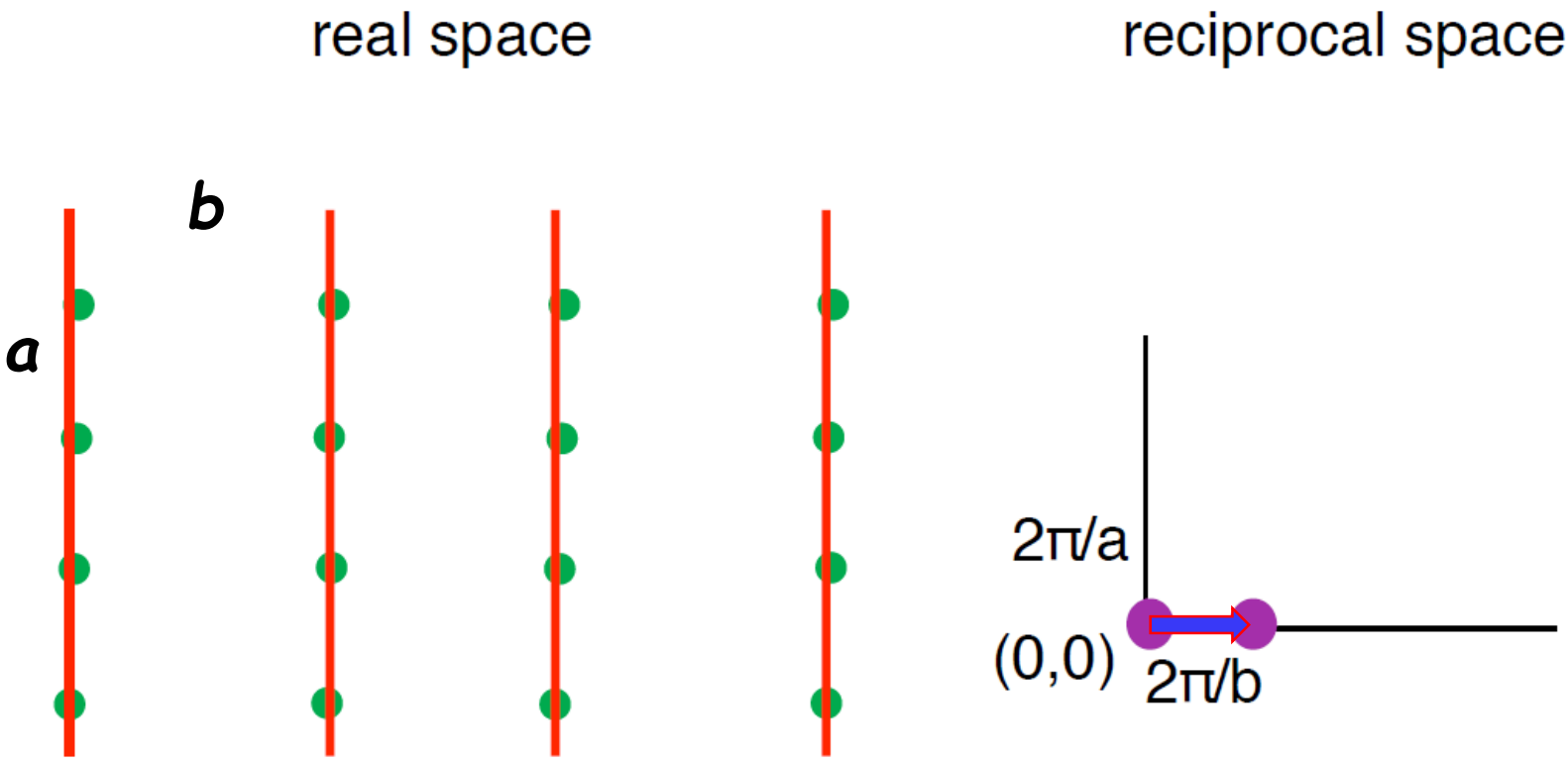


- A family of lattice plane stands for parallel, equally spaced lattice planes which together cover the entire 3D Bravais lattice

Lattice-Planes

- For any family of lattice planes separated by distance ***d***, there are reciprocal lattice vectors perpendicular to the planes, the shortest of which has a length $\frac{2\pi}{d}$

(The converse is also true)

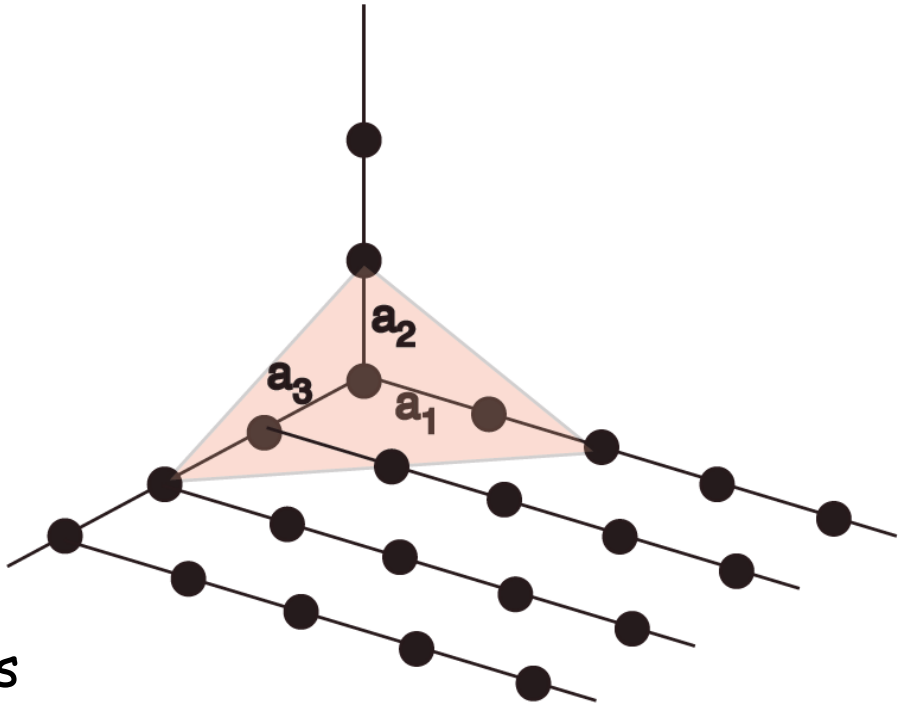


Labelling Lattice-Planes

- For a given plane, first its intercepts with the axes in units of lattice vectors need to be determined
  (2 1 2)

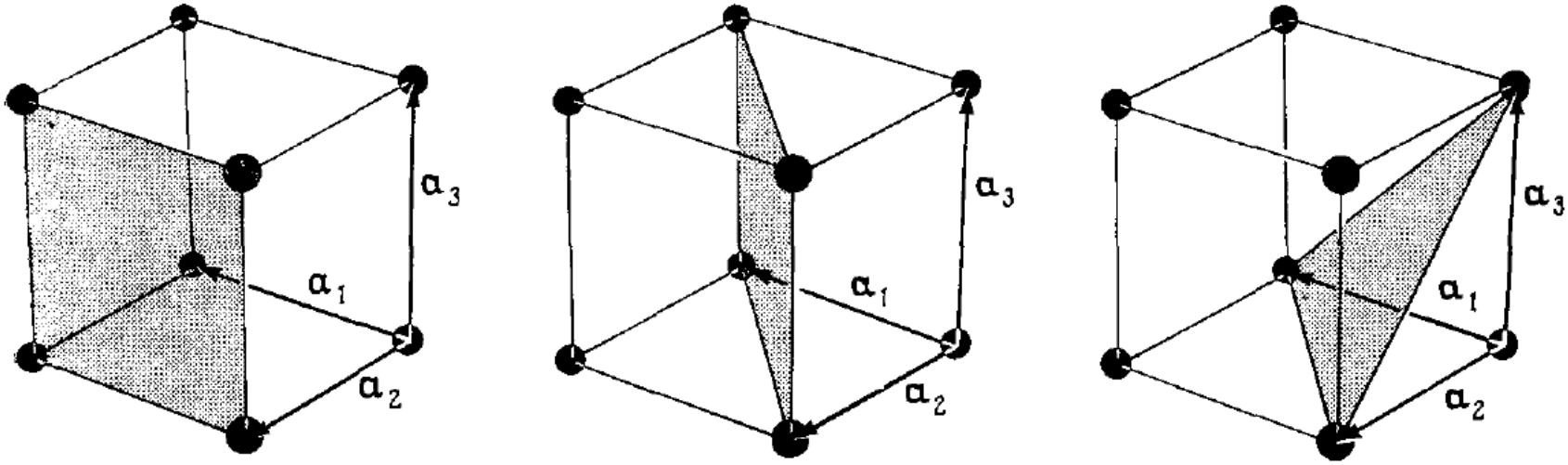
- Reciprocal of these numbers are to be taken
  $(\frac{1}{2}, 1, \frac{1}{2})$

- Reduction of numbers to the smallest set of integers having the same ratio. These are called Miller indices
  (1 2 1)



Labelling Lattice-Planes

Three lattice planes and their Miller indices for a Simple-Cubic Bravais lattice



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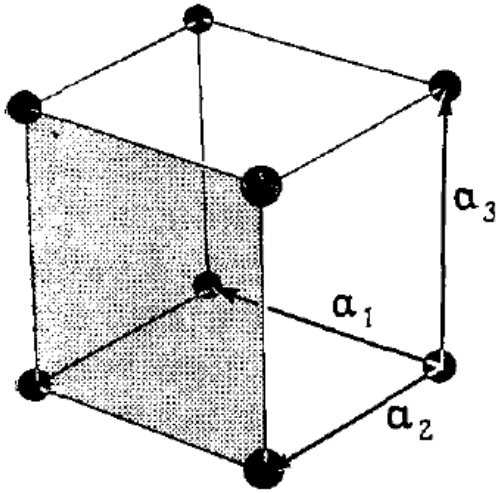

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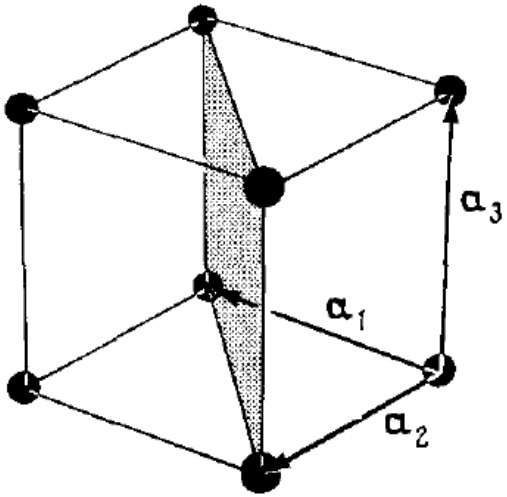

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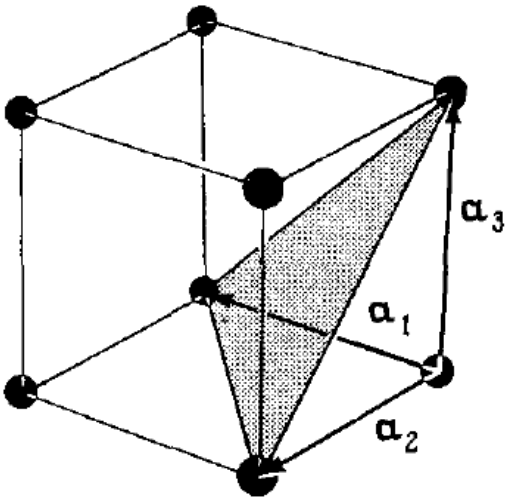

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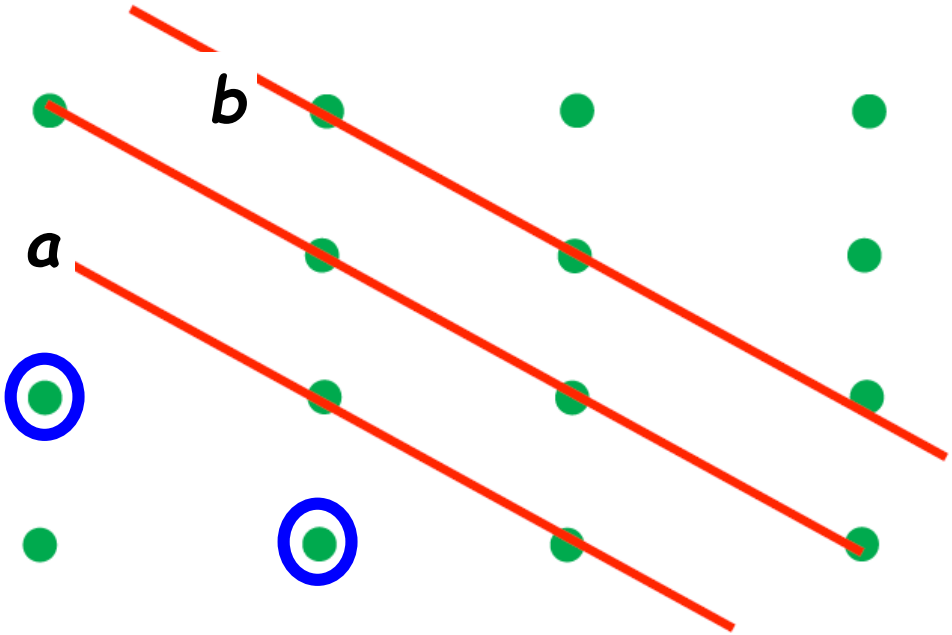
Labelling Lattice-Planes

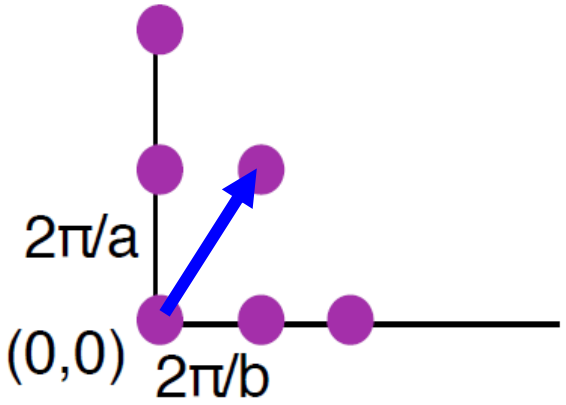
A plane with Miller indices (***h k l***) is normal to the reciprocal lattice vector (***h*** $\mathbf{b}_1$ + ***k*** $\mathbf{b}_2$ + ***l*** $\mathbf{b}_3$)

$$d_{(hkl)} = \frac{2\pi}{|\mathbf{G}|} = \frac{2\pi}{\sqrt{h^2|\mathbf{b_1}|^2 + k^2|\mathbf{b_2}|^2 + l^2|\mathbf{b_3}|^2}}$$

real space



reciprocal space



Reciprocal Lattice as a Fourier transform

One can think of the reciprocal lattice as the Fourier transform of the direct lattice

Let us consider the example of one-dimension. Direct lattice is given by - $R_n = an$

Density of lattice points - $\rho(r) = \sum_n \delta(r - an)$

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Fourier transforming this function gives -

$$\mathcal{F}[\rho(r)] = \int dr e^{ikr} \rho(r) = \sum_n \int dr e^{ikr} \delta(r - an)$$

$$= \sum_n e^{ikan} = 2\pi \sum_m \delta(k - 2\pi m/a)$$

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Generalizing to two or three - dimensions-

$$\mathcal{F}[\rho(\mathbf{r})] = \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} = (2\pi)^D \sum_{\mathbf{G}} \delta^D(\mathbf{k} - \mathbf{G})$$

Fourier Transform of a Periodic Function

Let us consider any function which satisfies - $\rho(\mathbf{r}) = \rho(\mathbf{r}+\mathbf{R})$

We than want to calculate - $\mathcal{F}[\rho(\mathbf{r})] = \int \mathbf{dr}\; e^{i\mathbf{k}\cdot\mathbf{r}}\rho(\mathbf{r})$

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$$\mathcal{F}[\rho(\mathbf{r})] = \sum_{\mathbf{R}} \int_{unit-cell} \mathbf{dx}\; e^{i\mathbf{k}\cdot(\mathbf{x}+\mathbf{R})}\rho(\mathbf{x}+\mathbf{R}) = \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} \int_{unit-cell} \mathbf{dx}\; e^{i\mathbf{k}\cdot\mathbf{x}}\rho(\mathbf{x})$$

r as a sum of the lattice point ***R*** and a vector "***x***" within the unit cell

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The first term yields a sum of Delta functions

$$\mathcal{F}[\rho(\mathbf{r})] = (2\pi)^D \sum_{\mathbf{G}} \delta^D(\mathbf{k}-\mathbf{G})S(\mathbf{k})$$

Where *S*(k) is the structure factor

$$S(\mathbf{k}) = \int_{unit-cell} \mathbf{dx}\; e^{i\mathbf{k}\cdot\mathbf{x}}\rho(\mathbf{x})$$

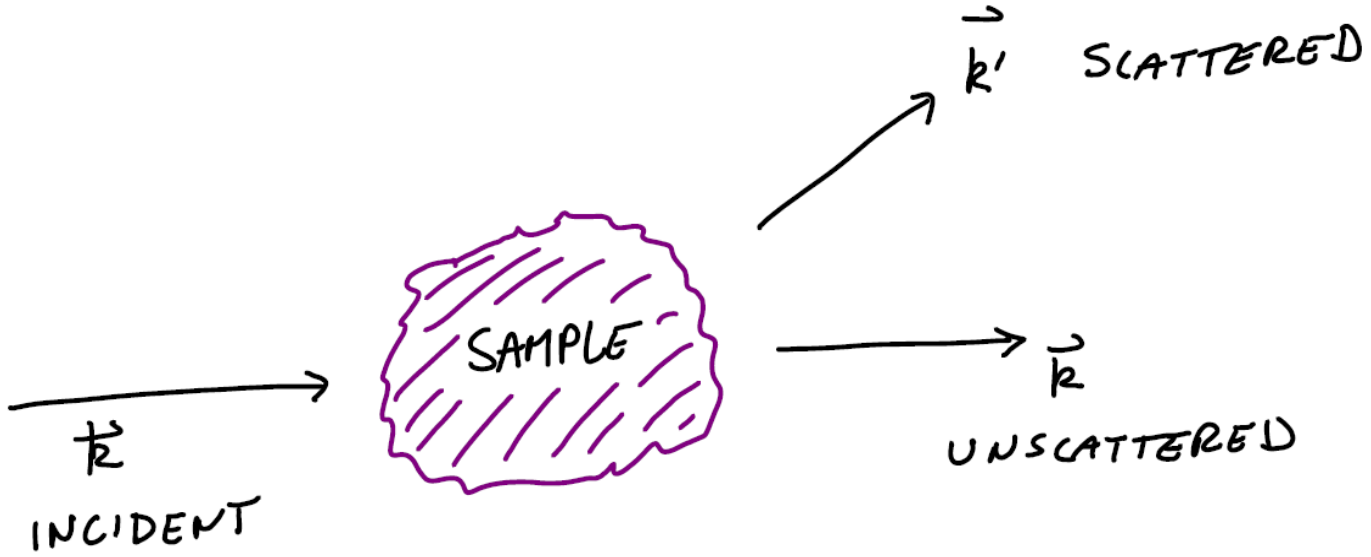
X-ray Diffraction

How to probe the underlying crystal structures?

Typical inter-atomic distances are of the order of Angstroms, thus the em probe should also have a sensitivity in that scale.

$$\hbar\omega = \frac{hc}{\lambda} = \frac{hc}{10^{-8}\ \text{cm}} \approx 12.3 \times 10^3\ \text{eV}$$

which are typical X-ray energies



The Laue condition

Fermi's Golden Rule Approach

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The transition rate per unit time for the particle scattering from *k* to *k'* is given by -

$$\Gamma(\mathbf{k}', \mathbf{k}) = \frac{2\pi}{\hbar} \left|\langle \mathbf{k}'|V|\mathbf{k}\rangle\right|^2 \delta(E_{\mathbf{k}'} - E_{\mathbf{k}})$$

$$\langle \mathbf{k}'|V|\mathbf{k}\rangle = \int \mathbf{dr}\, \frac{e^{-i\mathbf{k}'\cdot\mathbf{r}}}{\sqrt{L^3}}\, V(\mathbf{r})\, \frac{e^{i\mathbf{k}\cdot\mathbf{r}}}{\sqrt{L^3}} = \frac{1}{L^3} \int \mathbf{dr}\, e^{-i(\mathbf{k}'-\mathbf{k})\cdot\mathbf{r}}\, V(\mathbf{r})$$

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The first term vanishes unless - $\mathbf{k}' - \mathbf{k} = \mathbf{G}$

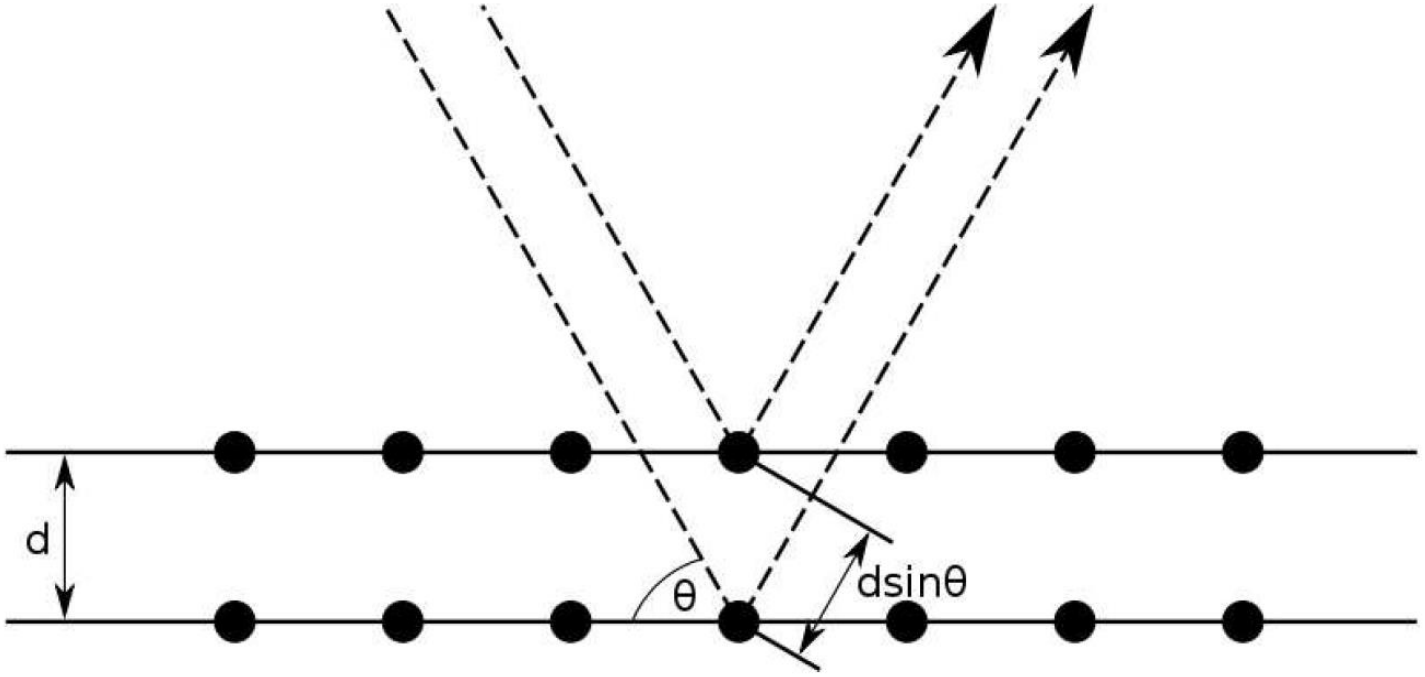
This is Laue's condition

Conservation of energy requires - $|\mathbf{k}| = |\mathbf{k}'|$

Bragg formulation

Diffraction Approach

An incoming wave is reflected of two adjacent layers of atoms separated by distance "d"



Additional distance travelled due to reflection from the layer further down is "2dSinθ"

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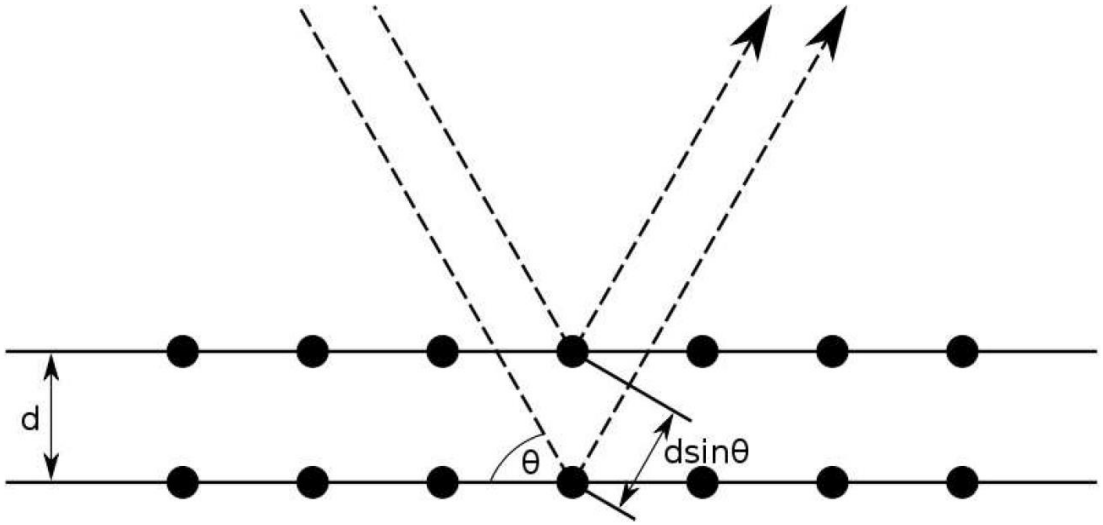

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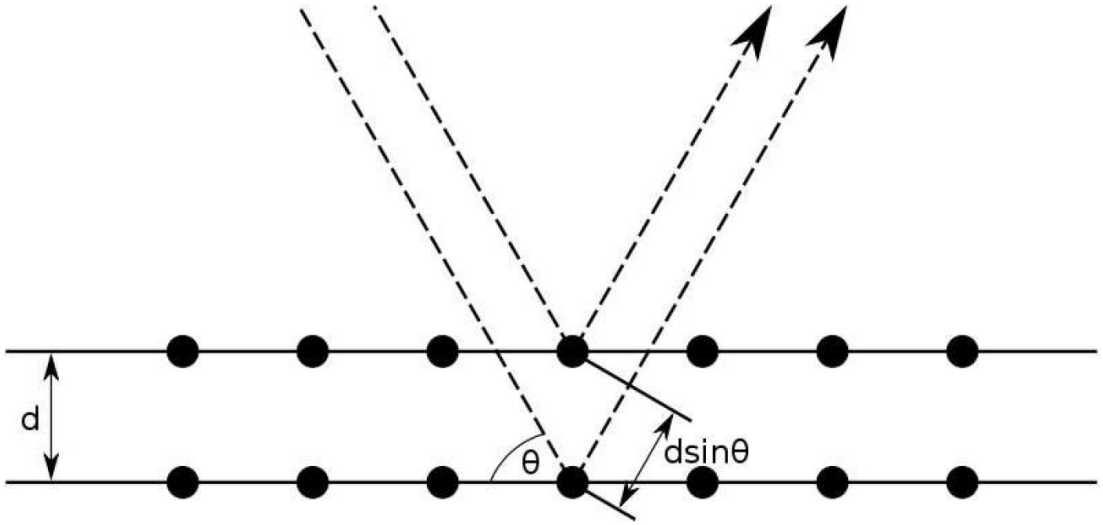


Condition for constructive interference

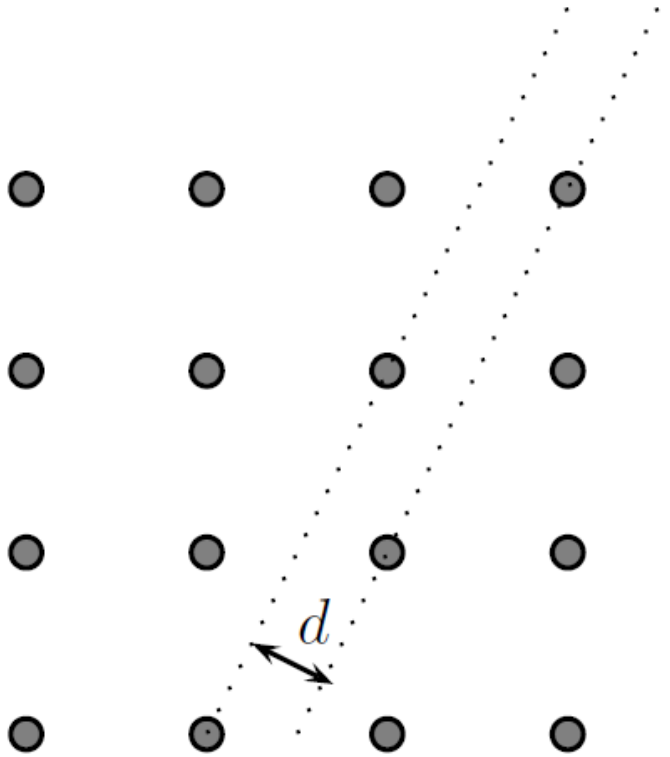
$$2dSin\theta = n\lambda$$

Bragg's law (William Henry Bragg and William Lawrence Bragg, Nobel Prize 1915)

Bragg formulation

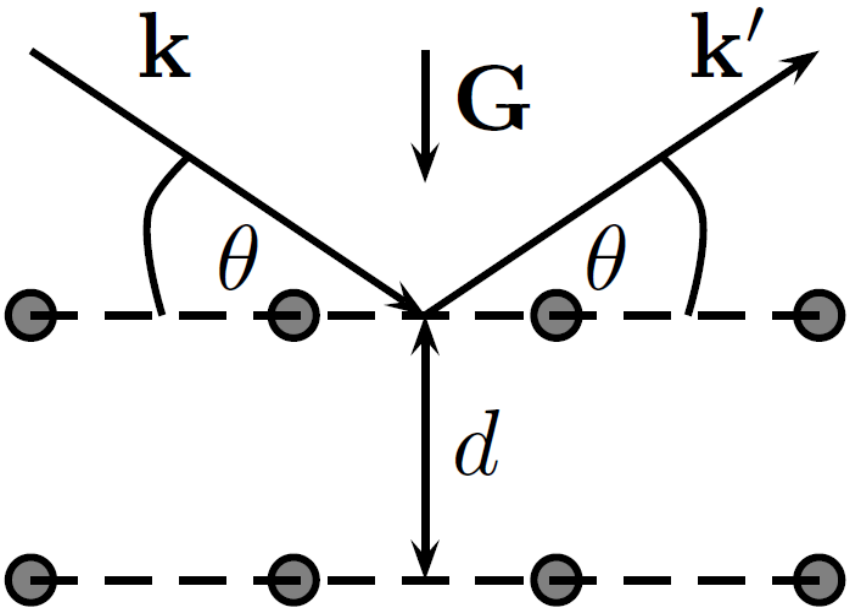
Diffraction Approach

We can have diffraction from any parallel planes of atoms



Equivalent Laue and Bragg formulations

Here "**G**" is the reciprocal lattice vector which corresponds to the family of lattice planes



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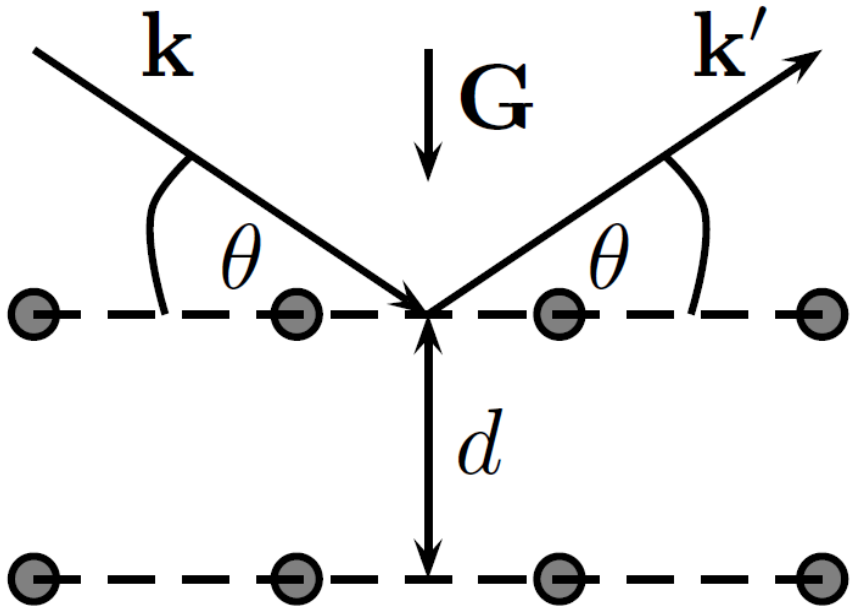

$$d = 2\pi/|\mathbf{G}|$$

From geometry we have -

$$\hat{\mathbf{k}} \cdot \hat{\mathbf{G}} = \sin\theta = -\hat{\mathbf{k}}' \cdot \hat{\mathbf{G}}$$

Equivalent Laue and Bragg formulations

Now when the Laue condition is satisfied -

$$\mathbf{k} - \mathbf{k}' = \mathbf{G} \text{ with } |\mathbf{k}| = |\mathbf{k}'| = 2\pi/\lambda$$

Or, $$\frac{2\pi}{\lambda}(\hat{\mathbf{k}} - \hat{\mathbf{k}}') = \mathbf{G}$$

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Or, $$\frac{2\pi}{\lambda}(\hat{\mathbf{k}} - \hat{\mathbf{k}}') = \mathbf{G}$$

Taking dot product on both sides -

$$\hat{\mathbf{G}} \cdot \frac{2\pi}{\lambda}(\hat{\mathbf{k}} - \hat{\mathbf{k}}') = \hat{\mathbf{G}} \cdot \mathbf{G}$$

$$\frac{2\pi}{\lambda}(\sin\theta + \sin\theta) = |\mathbf{G}|$$

Since $\hat{\mathbf{k}} \cdot \hat{\mathbf{G}} = \sin\theta = -\hat{\mathbf{k}}' \cdot \hat{\mathbf{G}}$

Equivalent Laue and Bragg formulations

Now when the Laue condition is satisfied -

$$\hat{\mathbf{G}} \cdot \frac{2\pi}{\lambda}(\hat{\mathbf{k}} - \hat{\mathbf{k}}') = \hat{\mathbf{G}} \cdot \mathbf{G}$$

$$\frac{2\pi}{\lambda}(\sin\theta + \sin\theta) = |\mathbf{G}|$$

$$\frac{2\pi}{|\mathbf{G}|}(2\sin\theta) = \lambda$$

$$2d\sin\theta = \lambda$$

Bragg condition is also satisfied

Thus, Laue and Bragg conditions are equivalent