Crystal Diffraction

Molecular and Solid State Physics

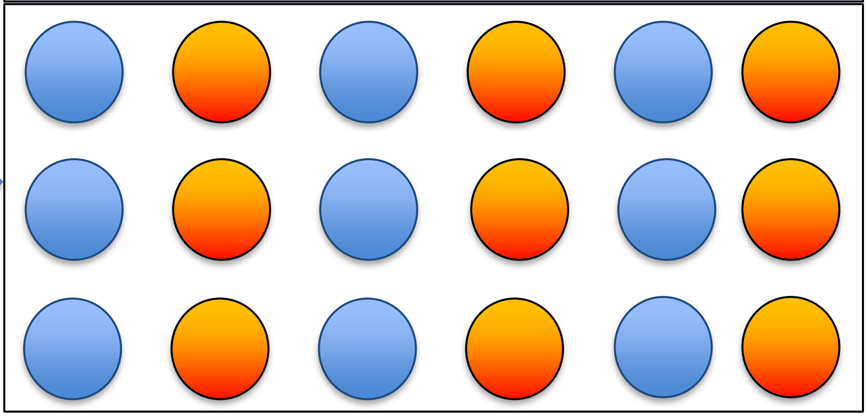
Oliver T. Hofmann, Institute of Solid State Physics

List of Symbols Used

Symbol	Meaning
d	Lattice plance distance
E	Electromagnetic field
FT(x)	Fourier transform (of x)
G	Reciprocal lattice vector
h,k,l	Miller indices (integers)
I	(wave) intensity
k	Reciprocal wave vector
n	Reflection order (integer)
r	Position (in real space)
S	Structure factor
λ	Wavelength
ρ	Scattering probability density
Θ	Scattering angle

How Do We Describe Crystals?

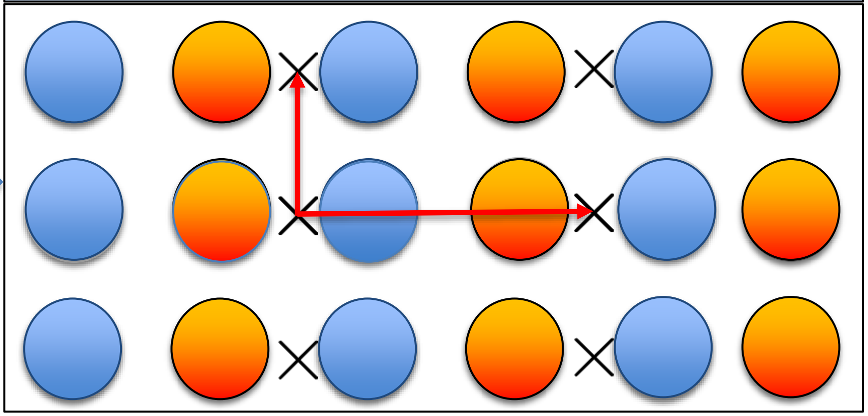
Periodic building blocks



Periodicity: Lattice	Building blocks: Basis

How Do We Describe Crystals?

Periodic building blocks



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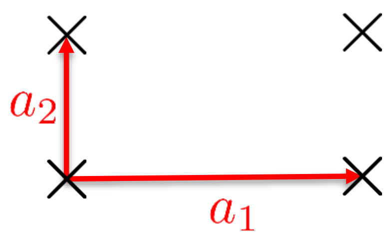
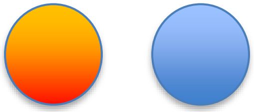
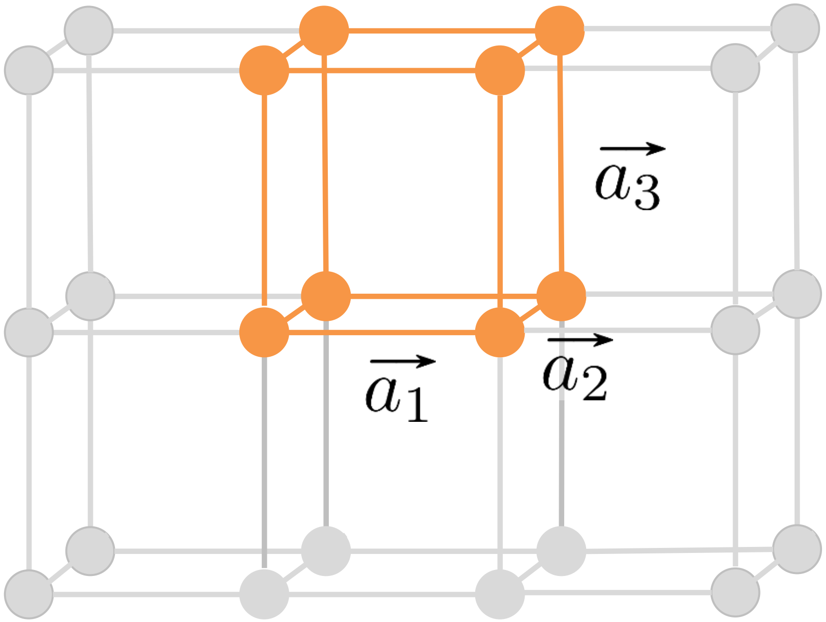
	

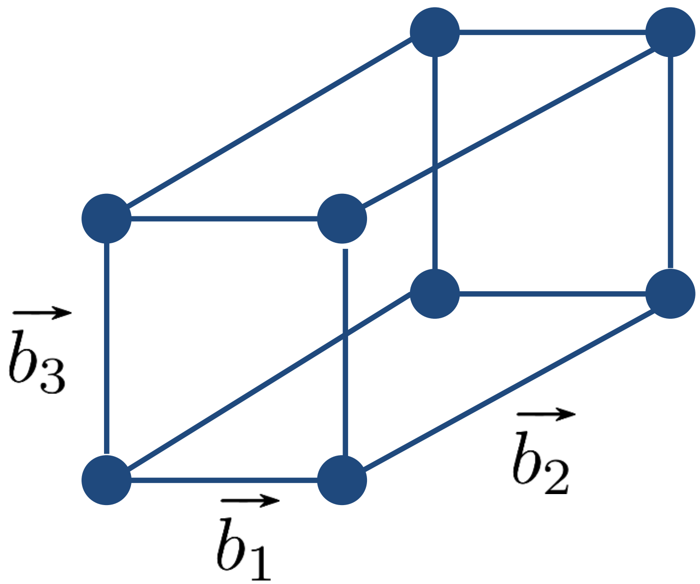
$$\text{Crystal} = \text{lattice} \otimes \text{basis}$$

Reciprocal Space

$$\vec{b_1} = 2\pi \frac{\vec{a_2} \times \vec{a_3}}{\vec{a_1}(\vec{a_2} \times \vec{a_3})} \quad \vec{b_2} = 2\pi \frac{\vec{a_3} \times \vec{a_1}}{\vec{a_1}(\vec{a_2} \times \vec{a_3})} \quad \vec{b_3} = 2\pi \frac{\vec{a_1} \times \vec{a_2}}{\vec{a_1}(\vec{a_2} \times \vec{a_3})}$$



Real Space



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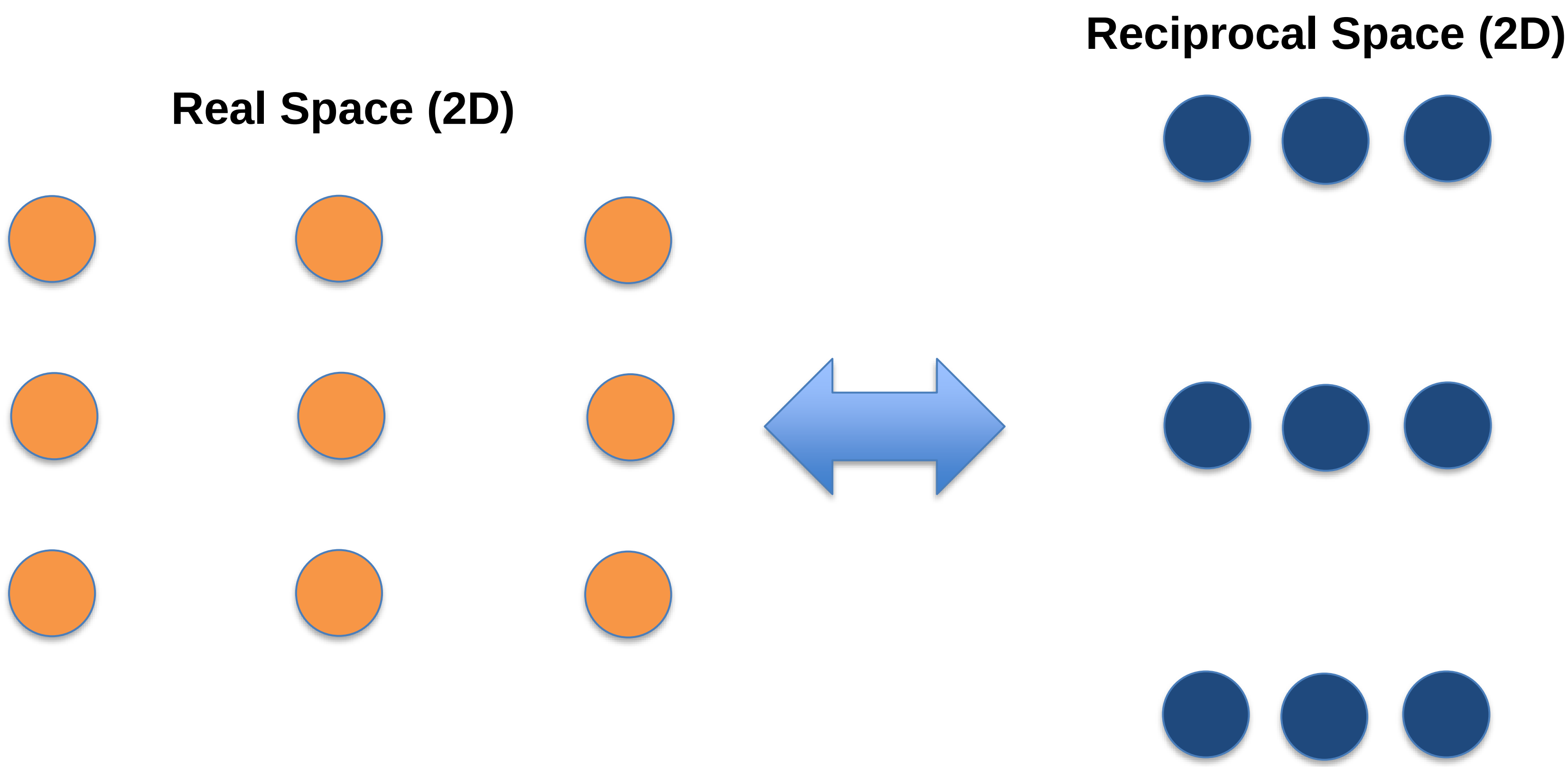


Periodic Functions

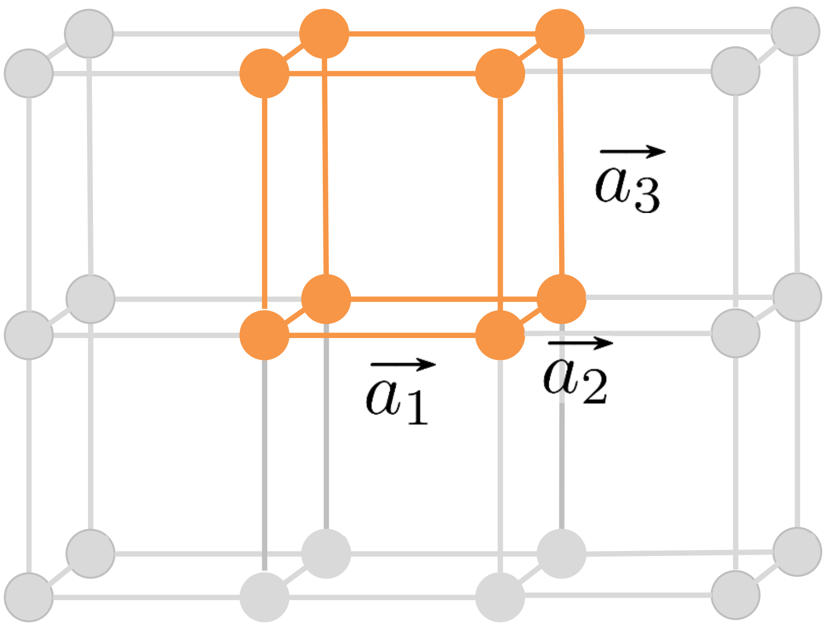
$$f(r) = \sum_{G} S \cdot e^{i\vec{G}\vec{r}}$$

$$\vec{G} = \begin{pmatrix} h \\ k \\ l \end{pmatrix} \cdot \begin{pmatrix} \vec{b_1} \\ \vec{b_2} \\ \vec{b_3} \end{pmatrix}$$

Structure factor

Reciprocal lattice vector

Miller indices



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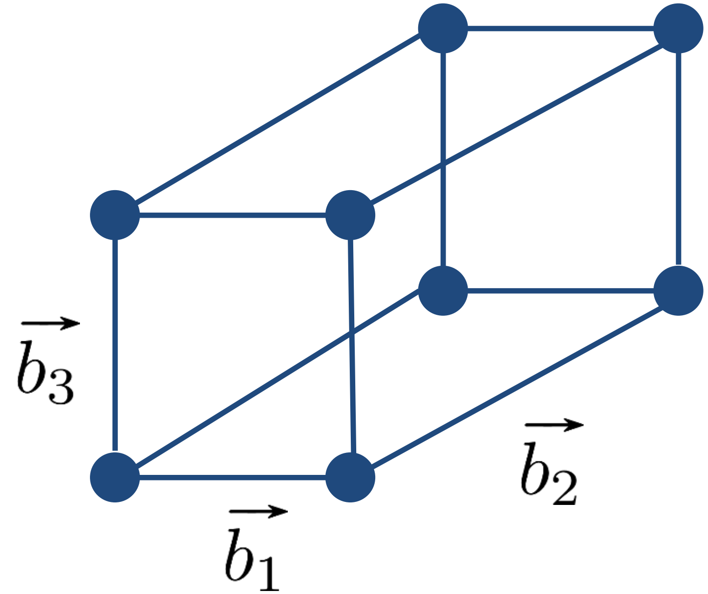

Reciprocal Space

Crystal Diffraction

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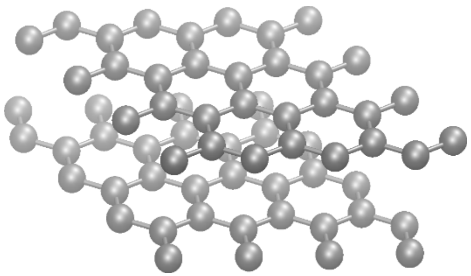
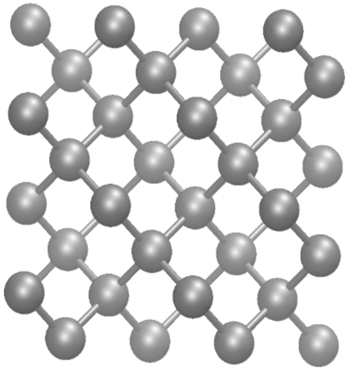
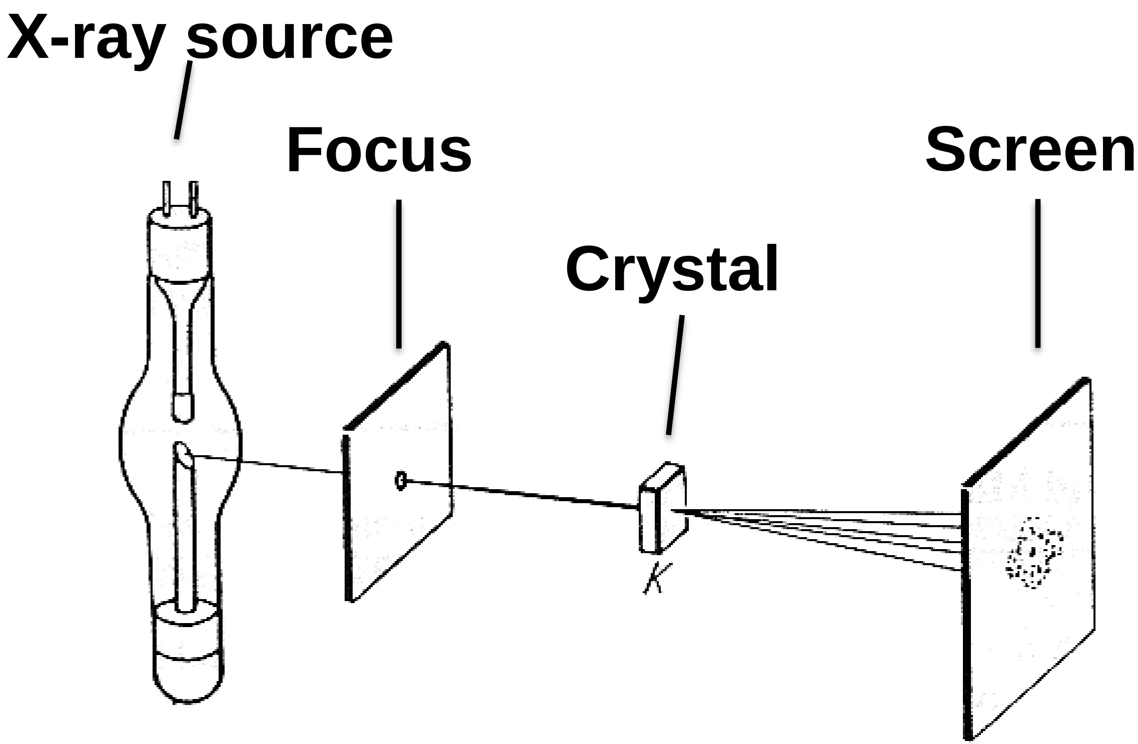
The Importance of Structure





Crystal Diffraction

Historical experiment by Max von Laue, Nobel price 1914



Modified from: http://www.chemgapedia.de/vsengine/glossary/de/laue_00045verfahren.glos.html

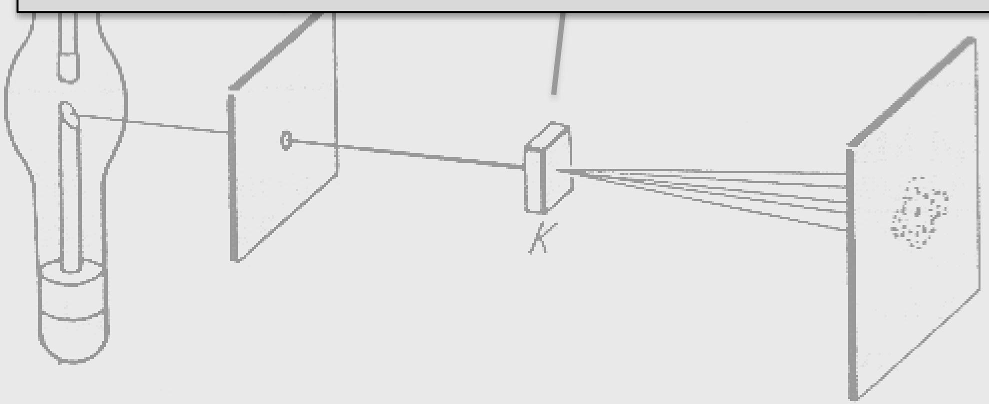
Crystal Diffraction

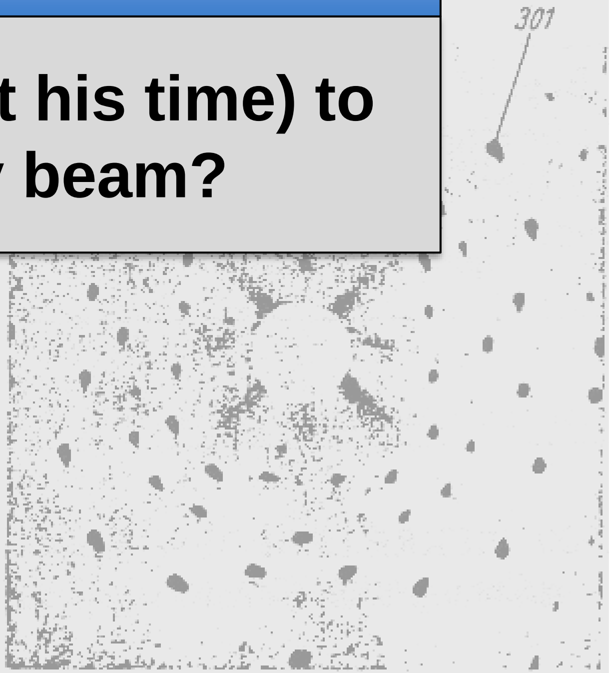
Historical experiment by Max von Laue, Nobel price 1914

X-ra

Student Challenge:

What could von Laue have done (at his time) to obtain a monochromatic x-ray beam?





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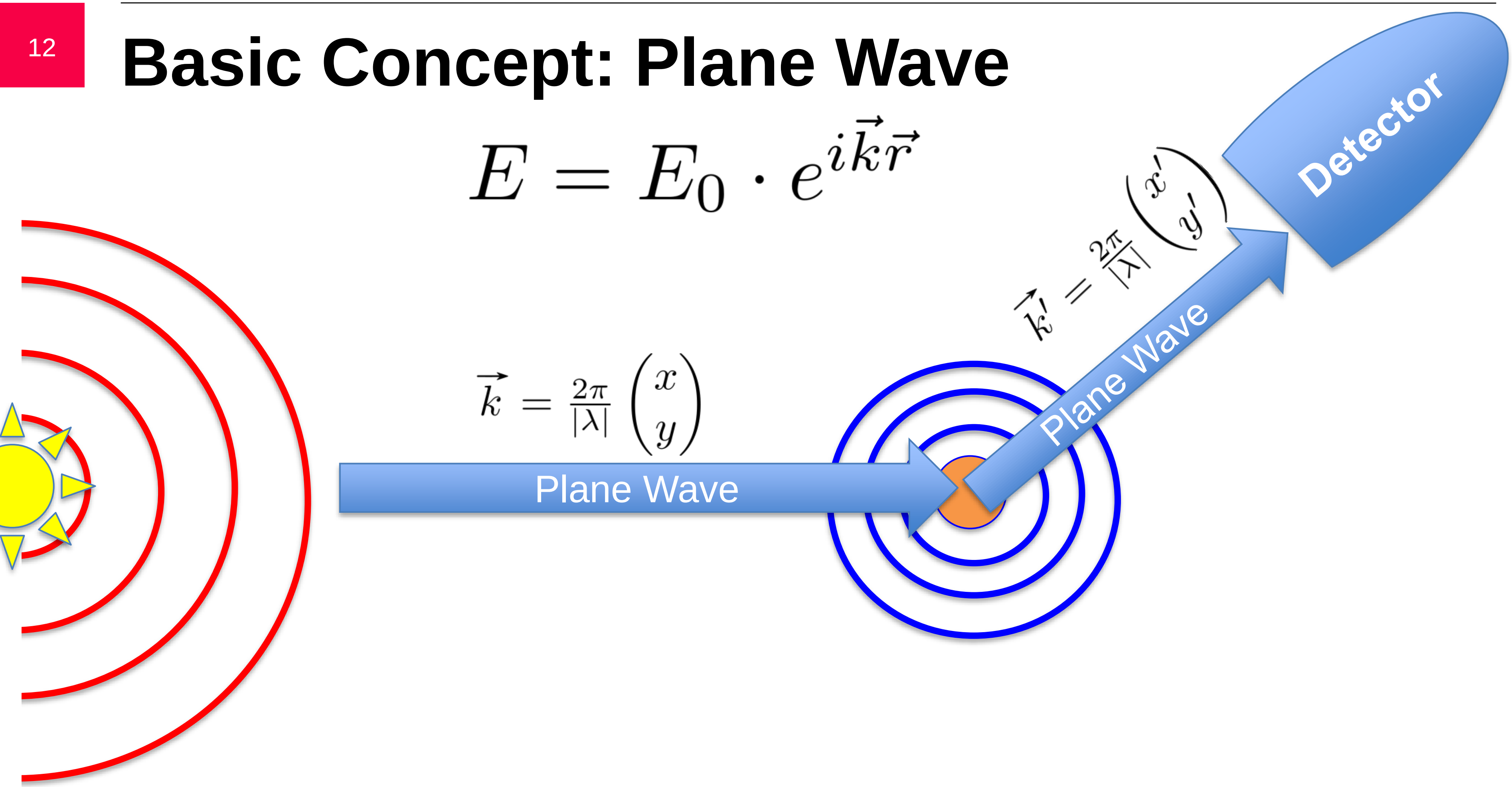
Basic Concept: Plane Wave

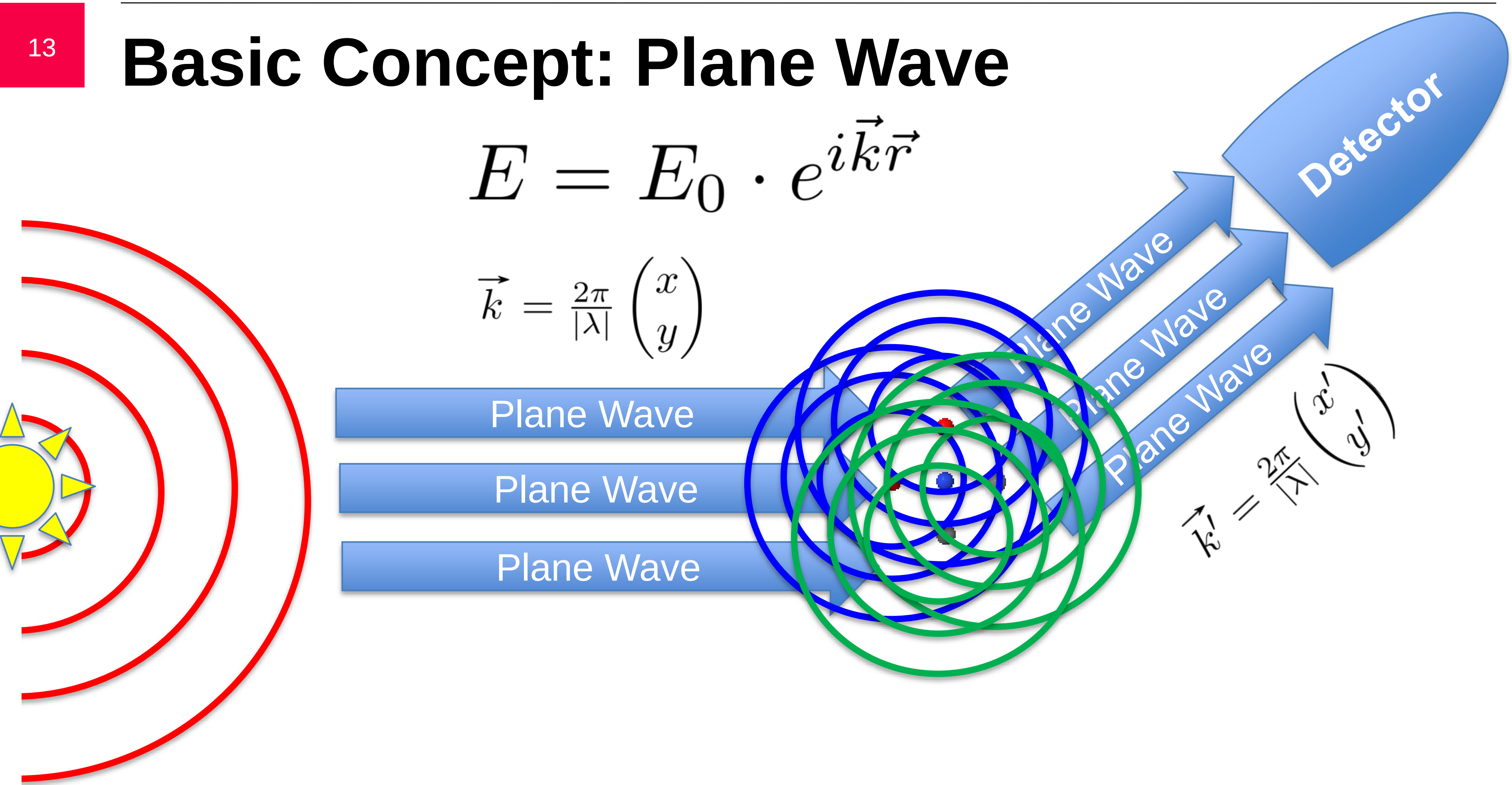
$$E = E_0 \cdot e^{i\vec{k}\vec{r}}$$



Basic Concept: Plane Wave

$$E = E_0 \cdot e^{i\vec{k}\vec{r}}$$

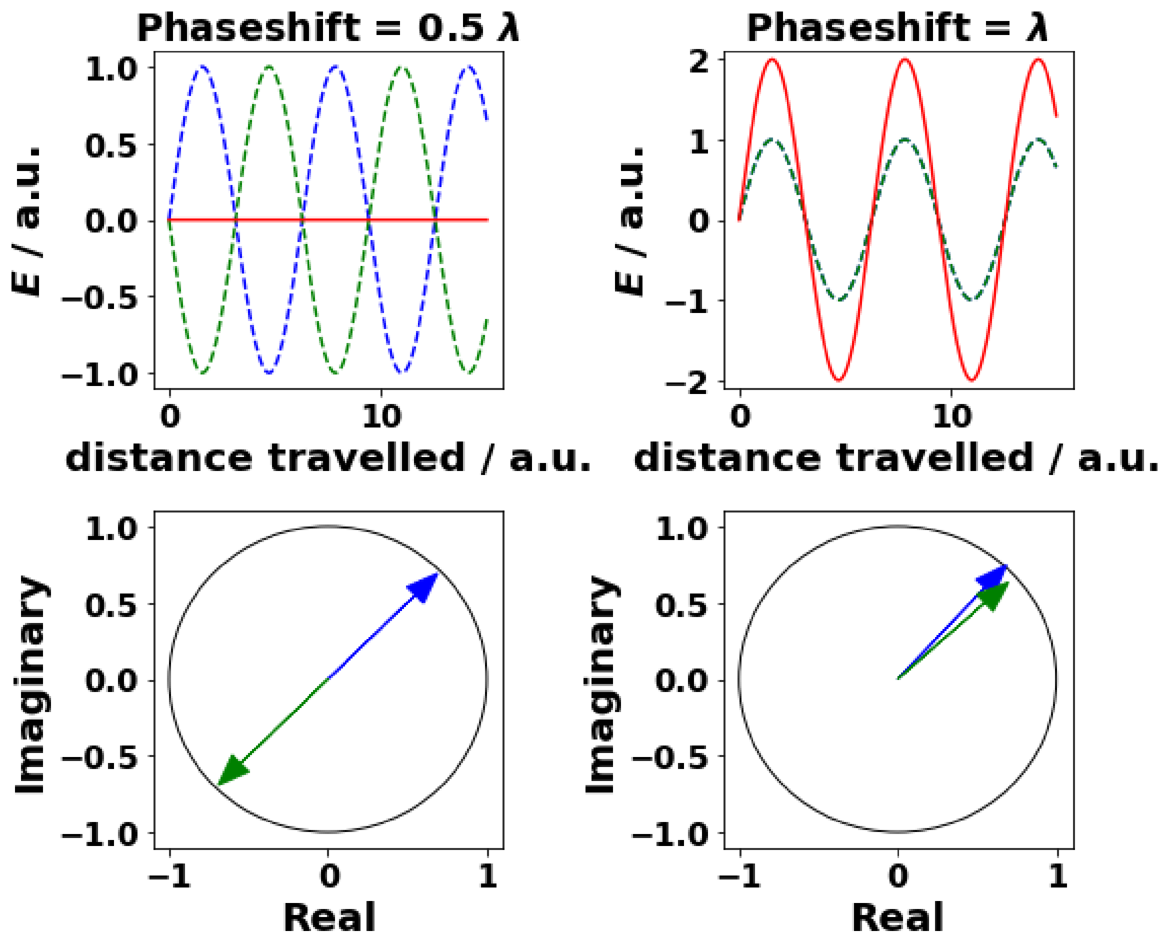
$$\vec{k} = \frac{2\pi}{|\lambda|}\begin{pmatrix} x \\ y \end{pmatrix}$$



$$E = E_0 \times \left(e^{i\vec{k}\vec{r}} + e^{i\vec{k}(\vec{r}+\Delta\vec{r})} \right)$$

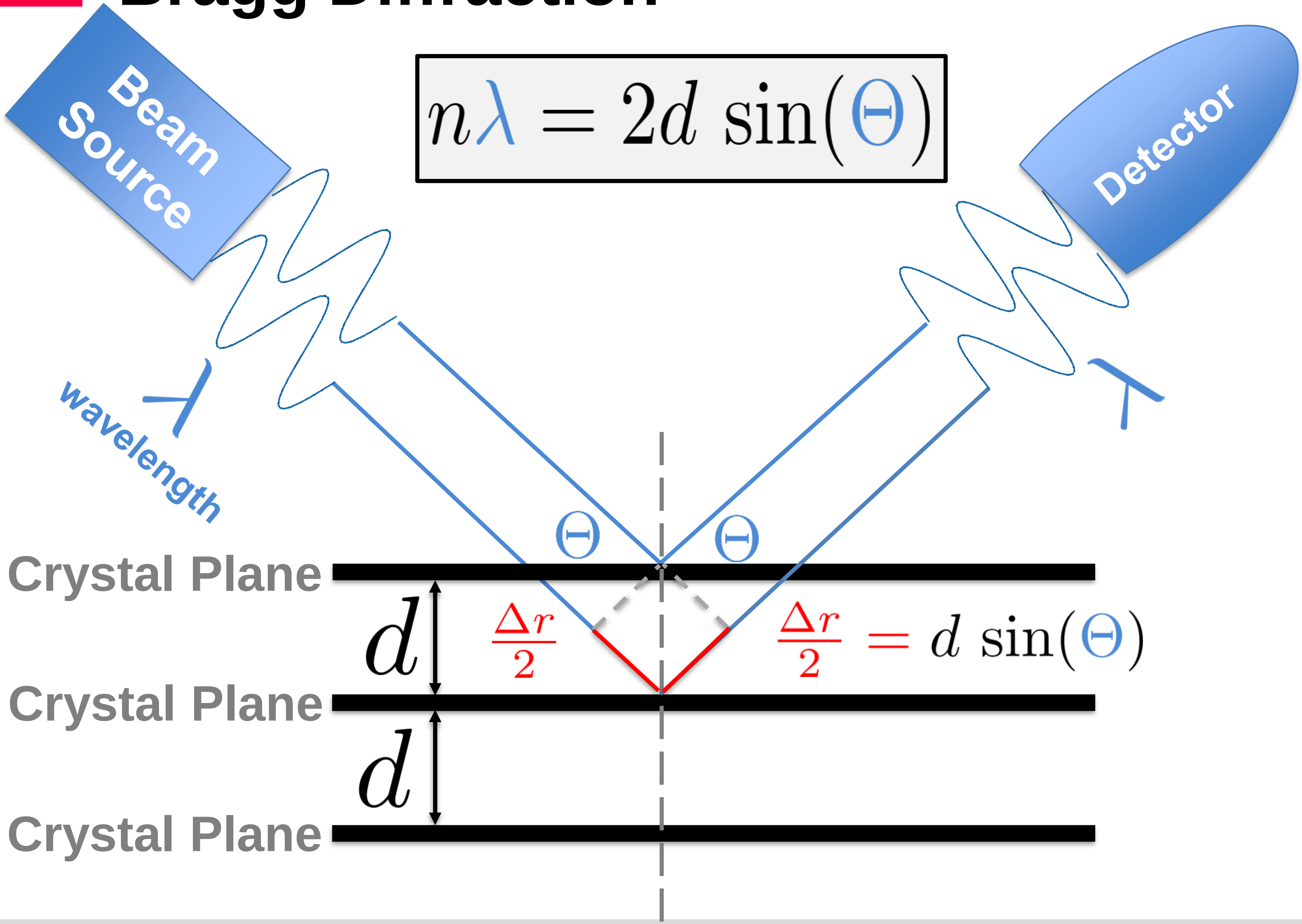
Basic Concept: Interference

$$E = E_0 \times \left(e^{i\vec{k}\vec{r}} + e^{i\vec{k}(\vec{r}+\Delta\vec{r})} \right)$$



Bragg Diffraction

$$n\lambda = 2d\,\sin(\Theta)$$



Implications of the Bragg-Picture

- **Wavelength: λ < *2d***

$$n\lambda = 2d \sin(\Theta)$$

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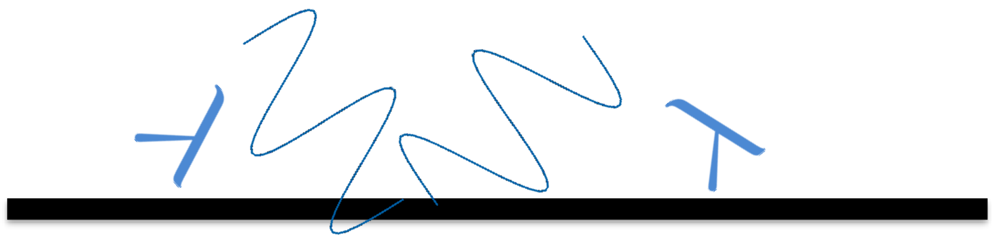
- **Scattering is coherent and elastic**

Crystal Plane



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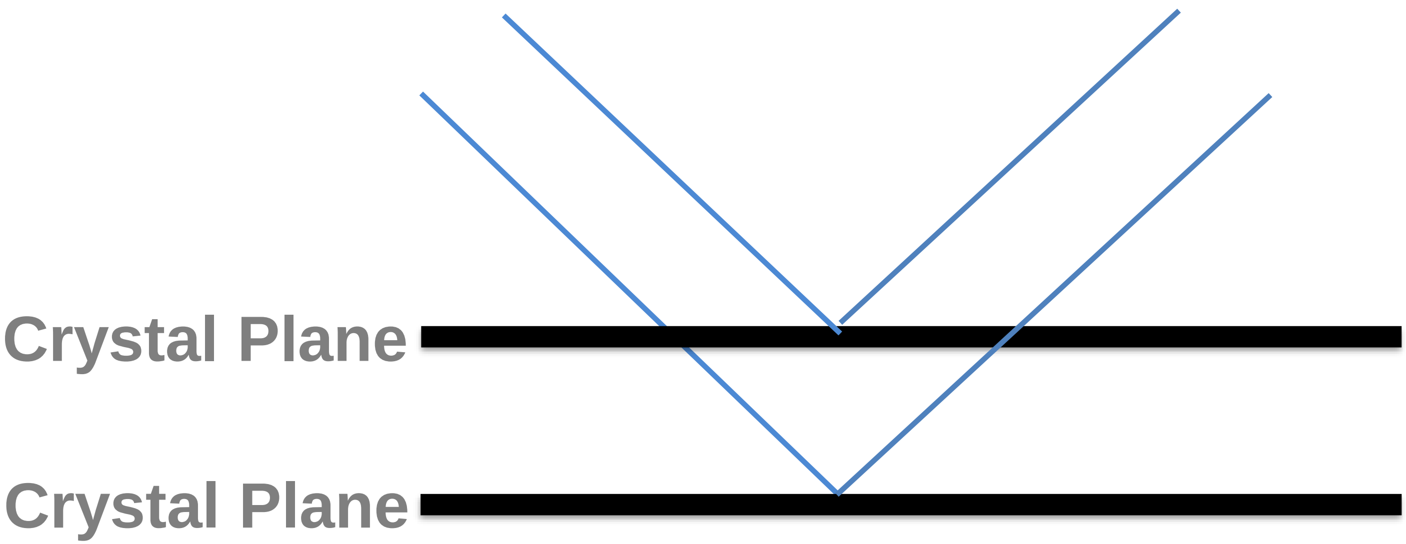

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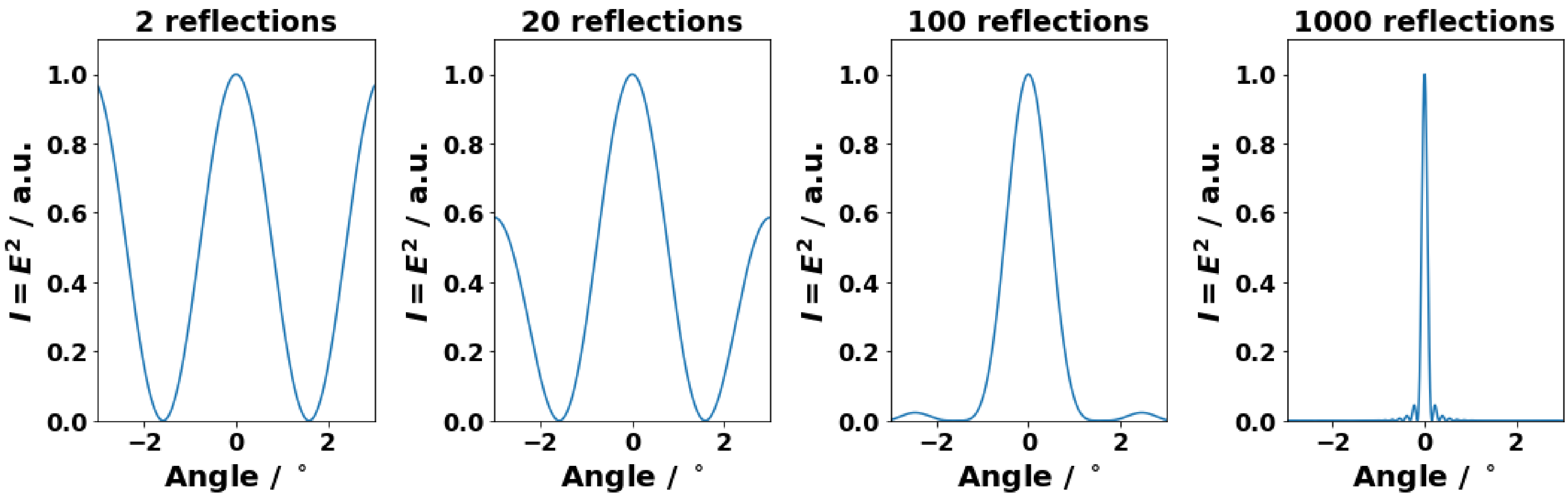


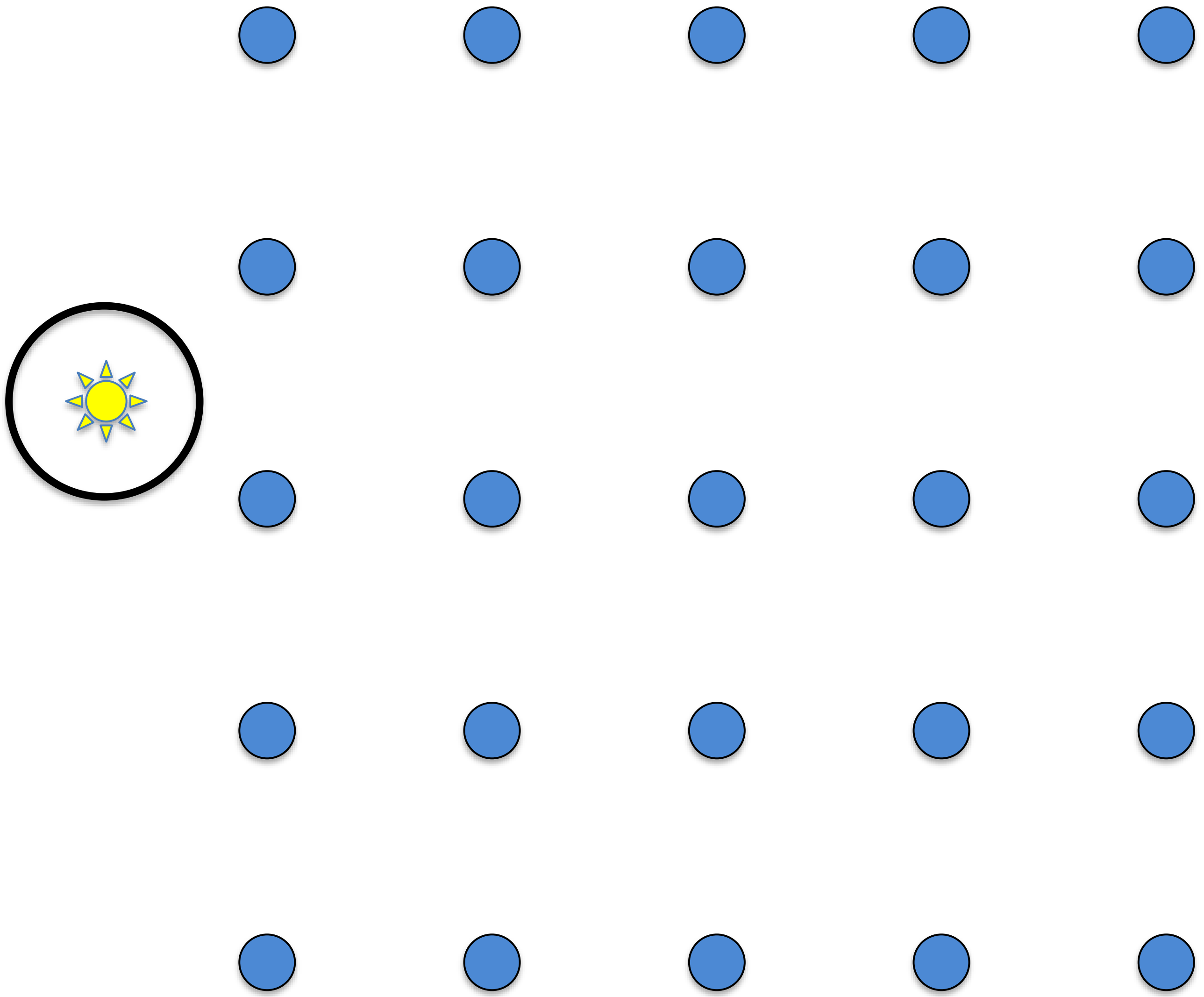
Implications of the Bragg-Picture

$$n\lambda = 2d\,\sin(\Theta)$$

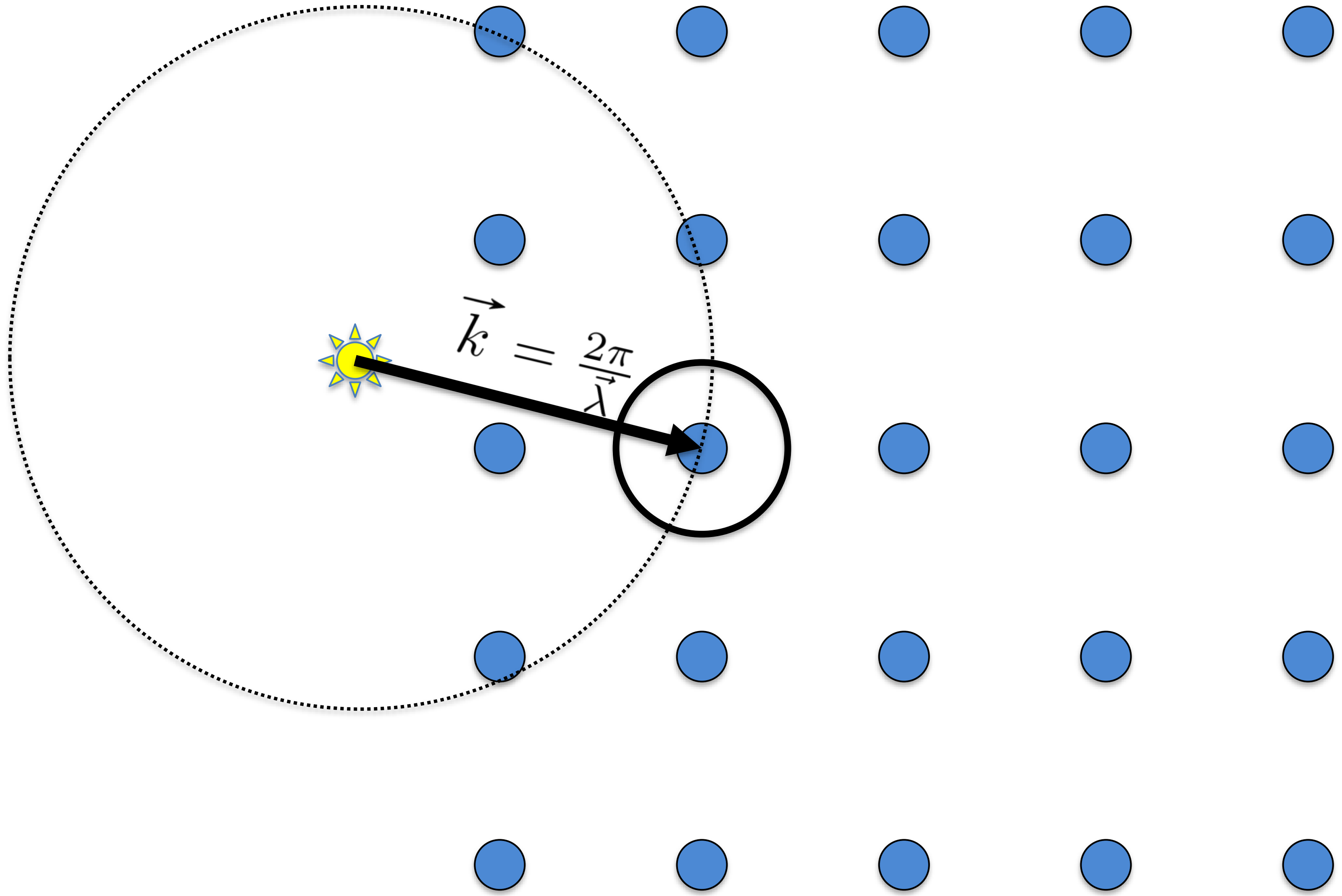
- **Wavelength: λ < *2d***
- **Scattering is coherent and elastic**
- **No multiple scattering**
- **Many repeat units required, pentration probability**
- **Needs to be performed for all lattice planes**

Solve in reciprocal space

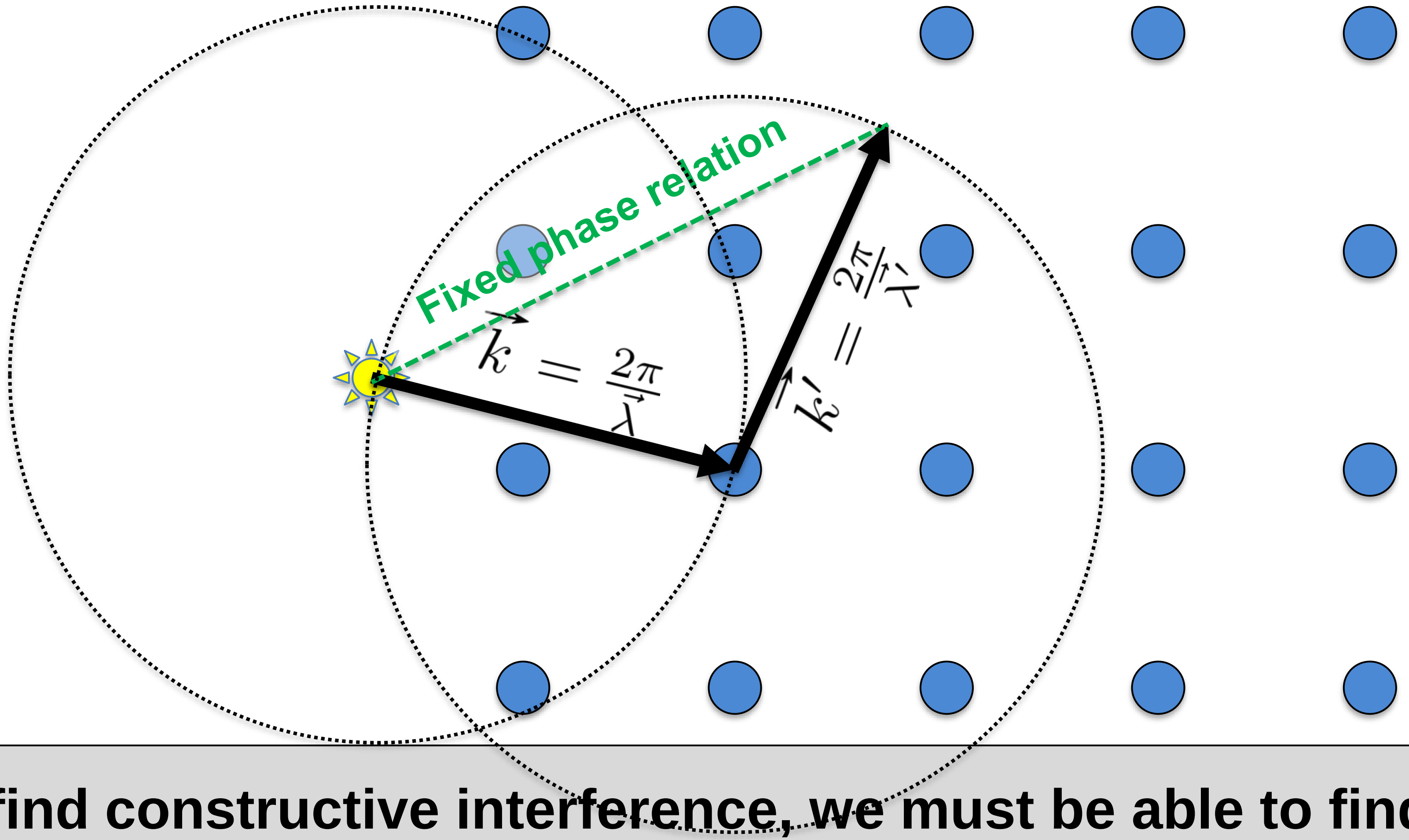
Diffraction in Reciprocal Space



Diffraction in Reciprocal Space

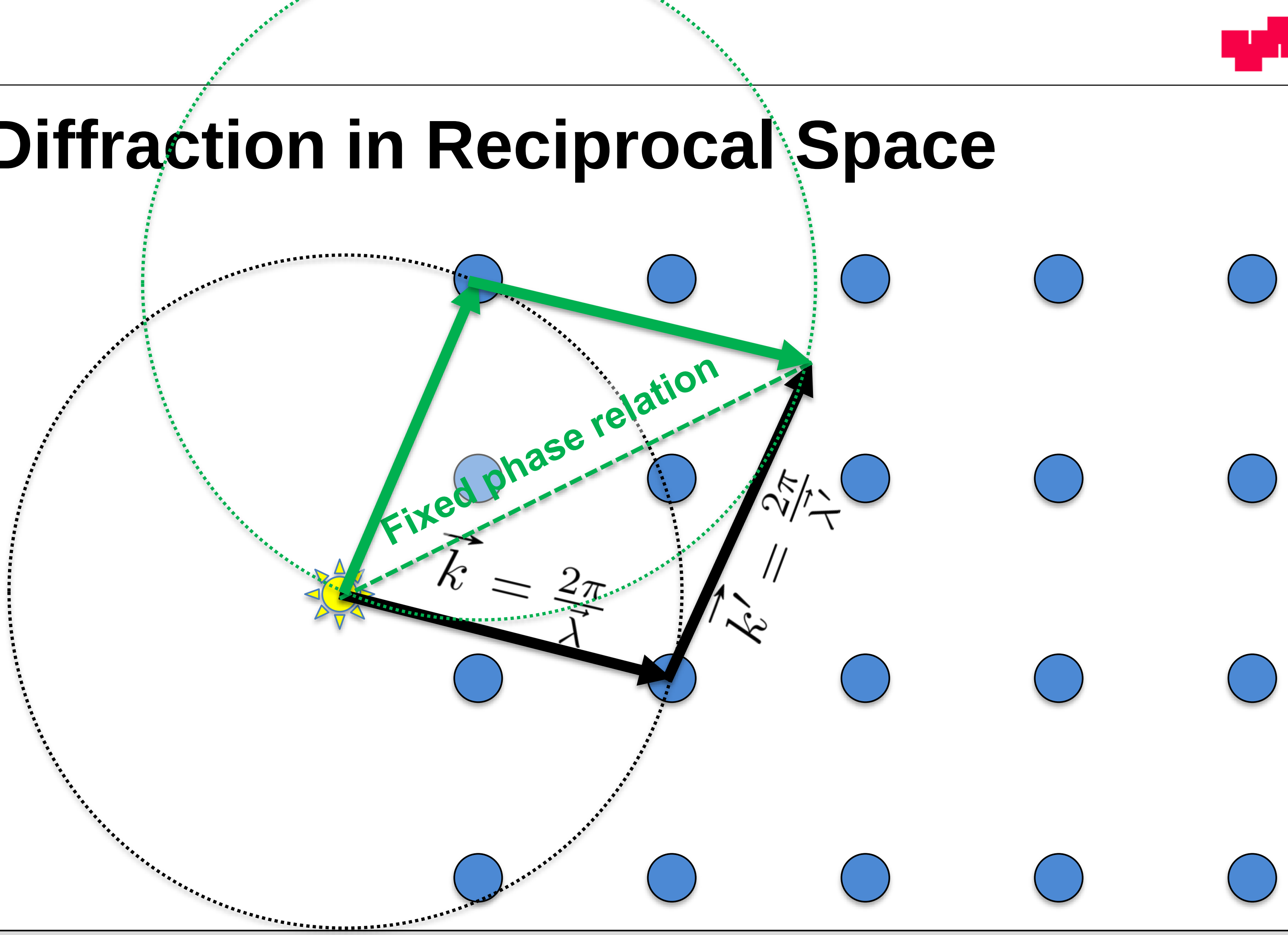


Diffraction in Reciprocal Space



To find constructive interference, we must be able to find a different path with the same phase relation

Diffraction in Reciprocal Space



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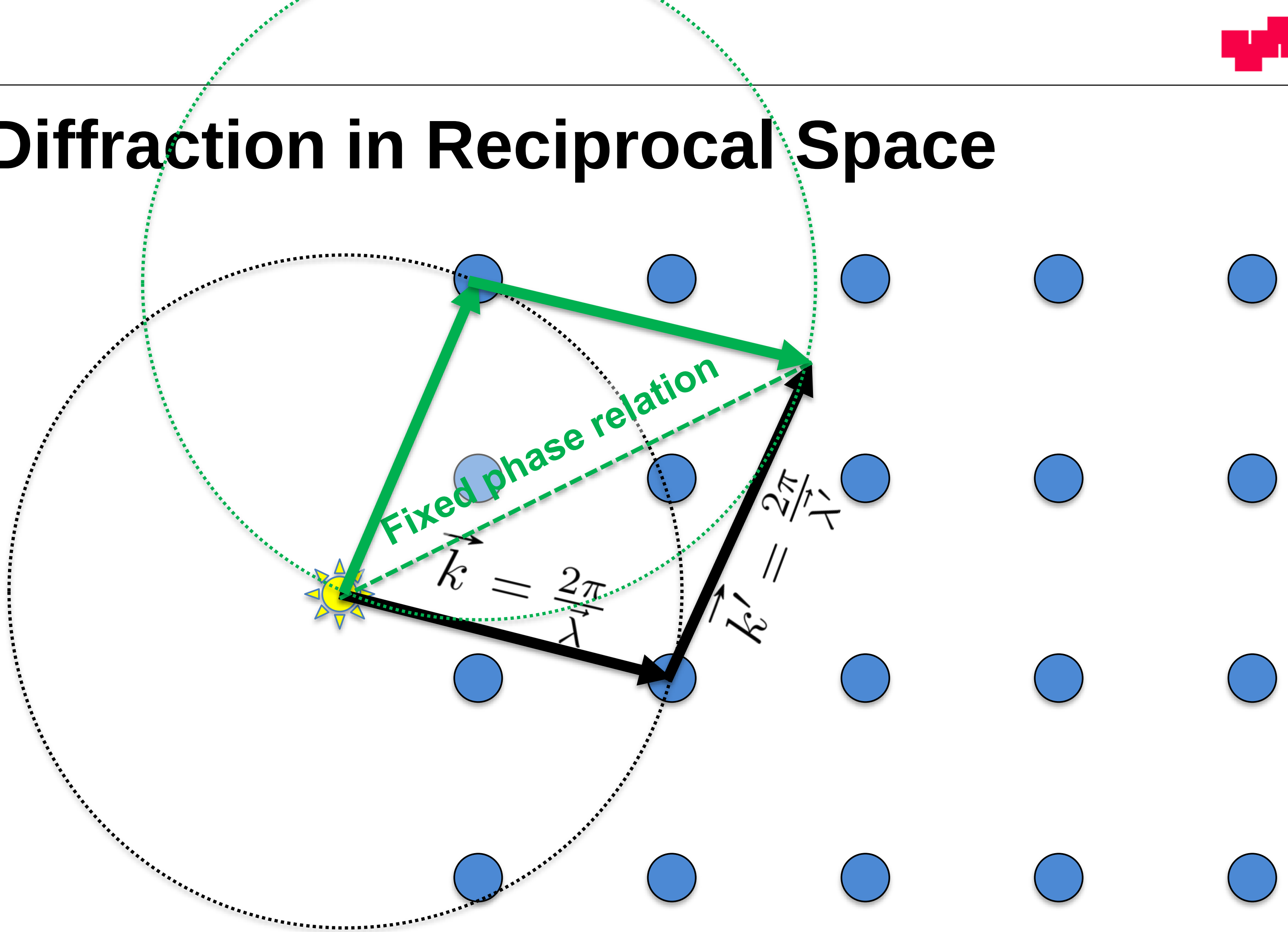
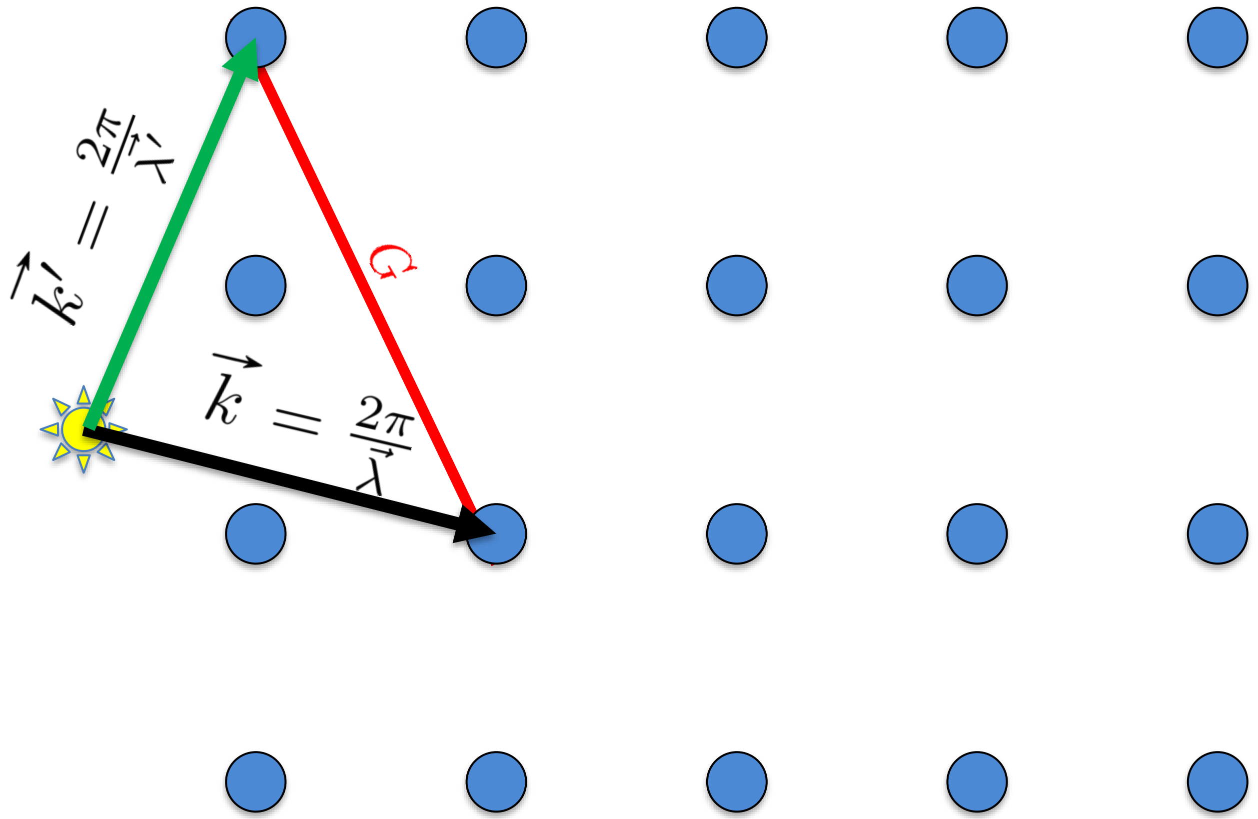
Diffraction in Reciprocal Space



Constructive interference if: $\vec{k'} - \vec{k} = \Delta \vec{k} = \vec{G}$

Diffraction in Reciprocal Space



Laue Condition

Constructive interference if: $\vec{k}' - \vec{k} = \Delta\vec{k} = \vec{G}$

Sanity check: Example

Bragg

$$n\lambda = 2dsin(\Theta)$$

Laue

$$\Delta k = G$$

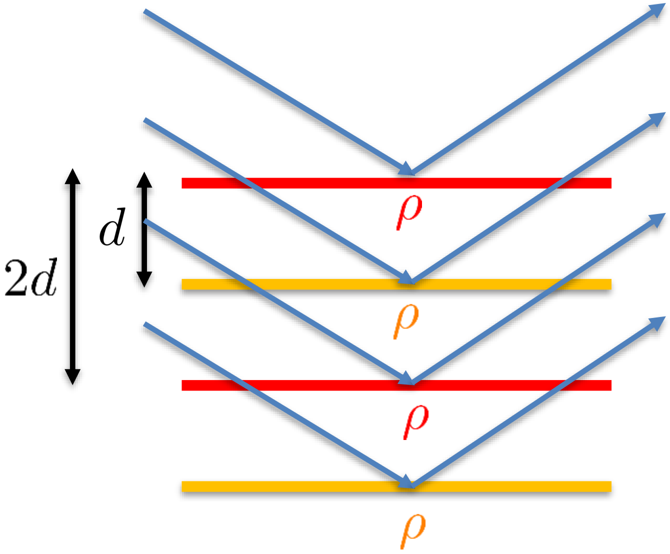
Measuring a simple cubic system with

- **Wavelength l = 4.67Å.**
- **Reflection observed under Θ = 45°**

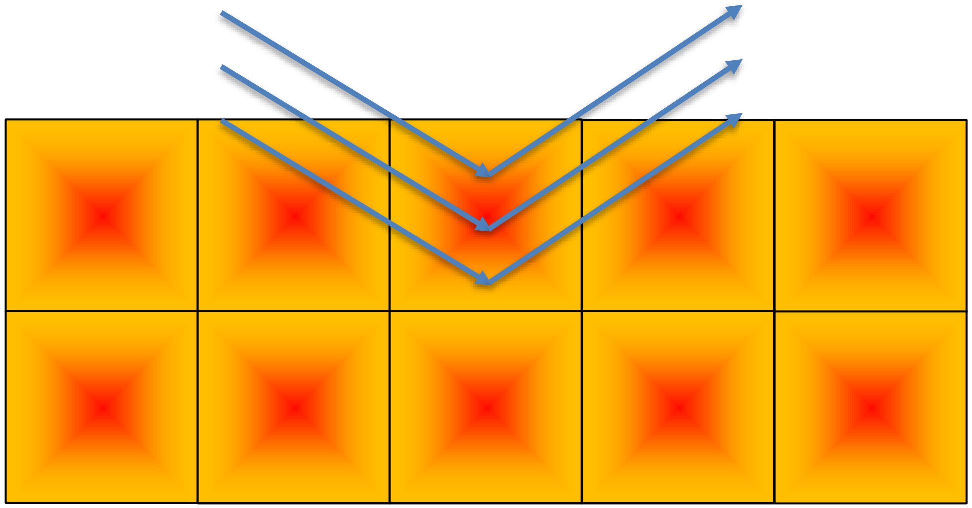
What is the lattice constant of the system?

General Diffraction

Scattering on planes



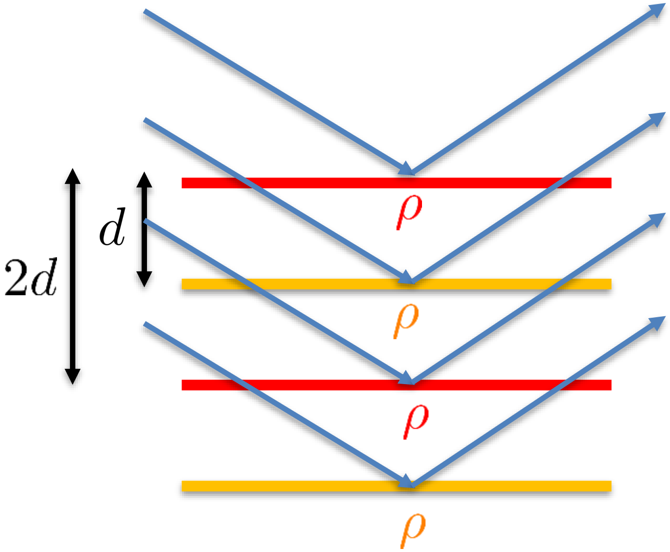
Continous Scattering



Ray is scattered with a <u>scattering probability density *ρ(r)*</u>

General Diffraction

Scattering on planes



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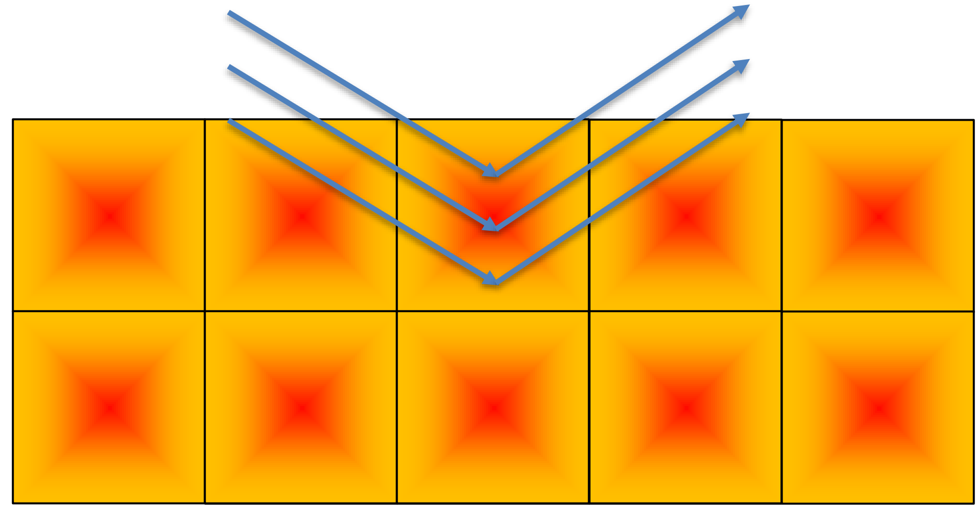


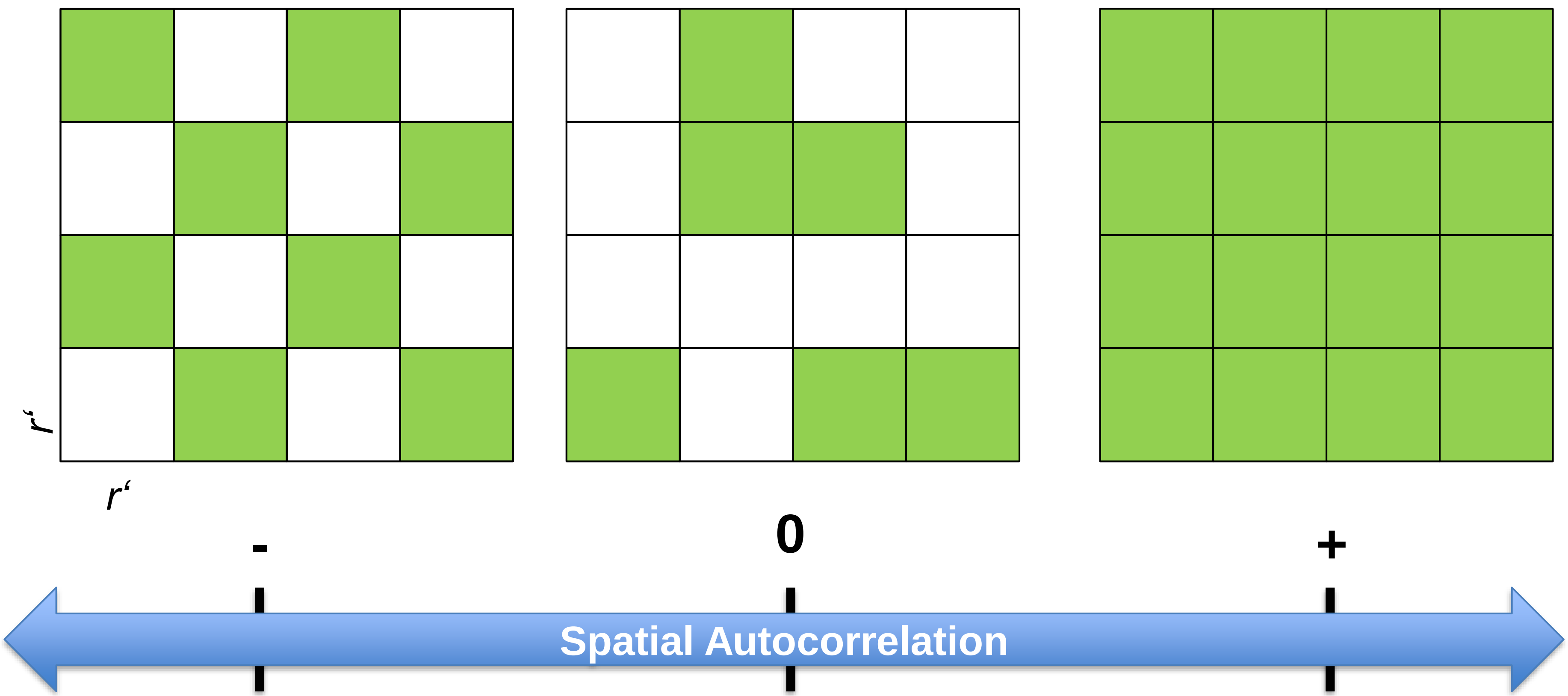
Autocorrelation Function

$$I(\Delta k) \propto \int \underbrace{\int \rho(r')\rho(r+r')d^3r'}_{\text{Autocorrelation Function}} e^{i\Delta k r} d^3r$$

Autocorrelation Explained (Roughly)

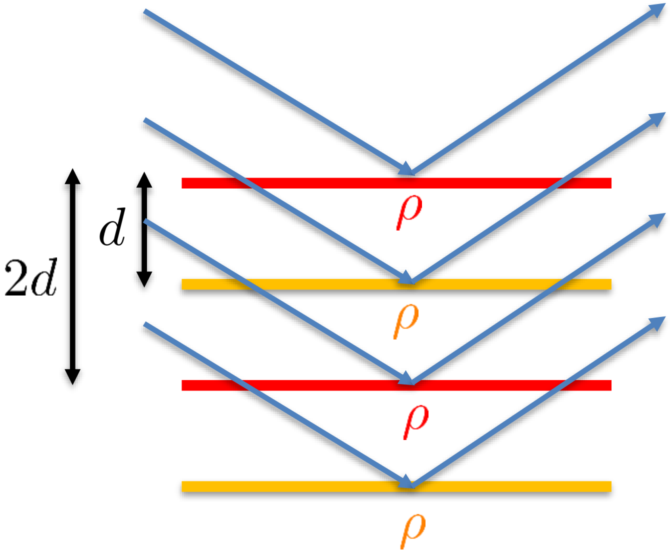
„Everything is related to everything else“

$$\int \rho(r')\rho(r+r')d^3r'$$



General Diffraction

Scattering on planes



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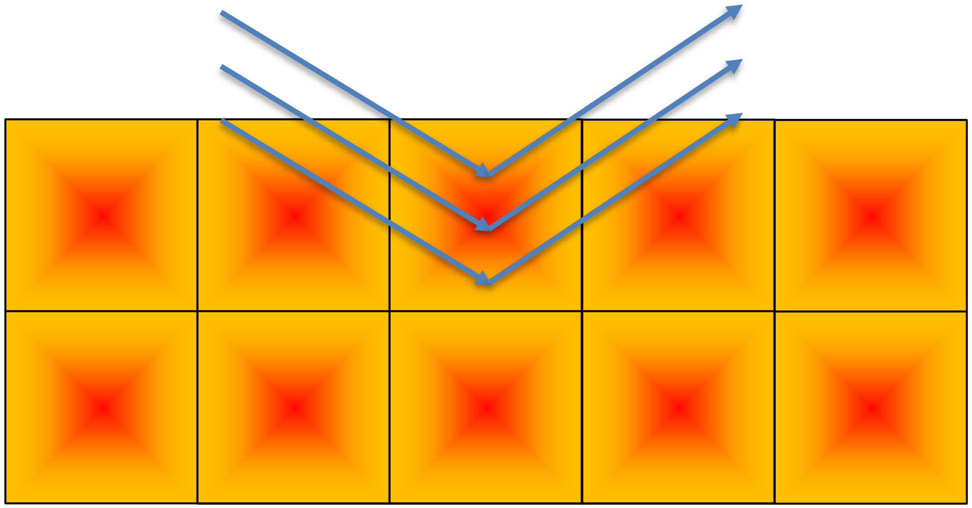
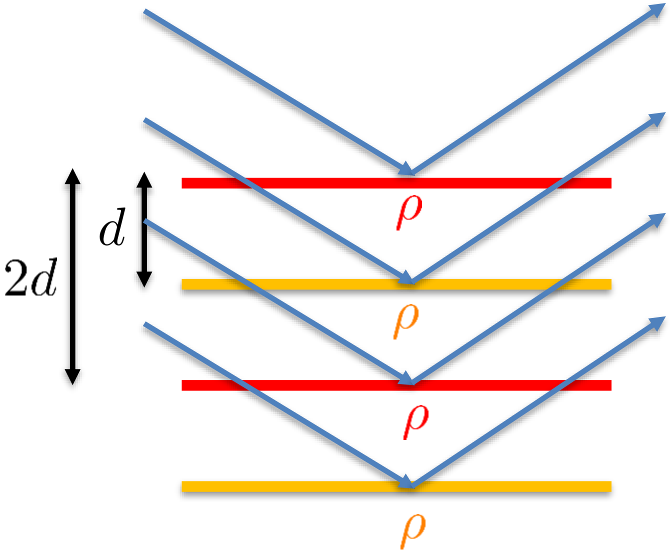


Autocorrelation function → square of Fourier transform

$$I(\Delta k) \propto |FT(\rho(r))|^2$$

General Diffraction

Scattering on planes



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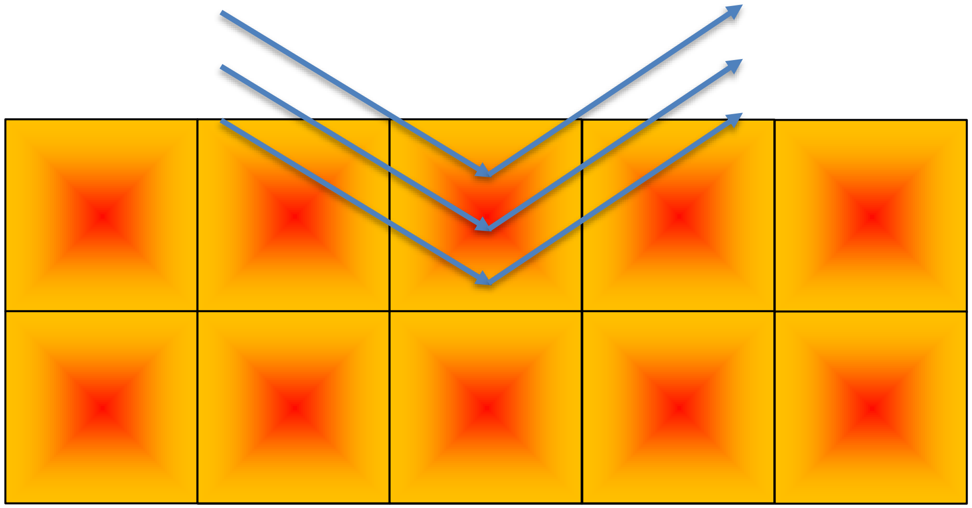
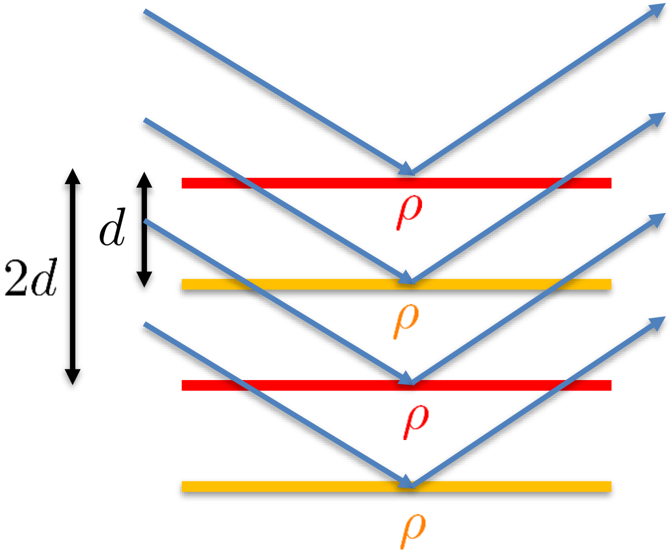


ρ is a lattice periodic function of basis and lattice

$$I(\Delta k) \propto |FT(lattice \otimes basis)|^2$$

General Diffraction

Scattering on planes



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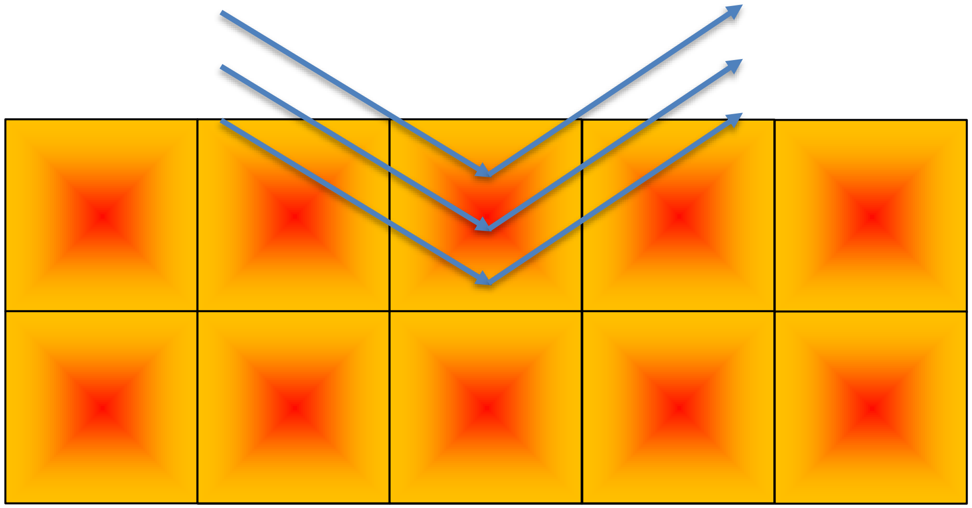

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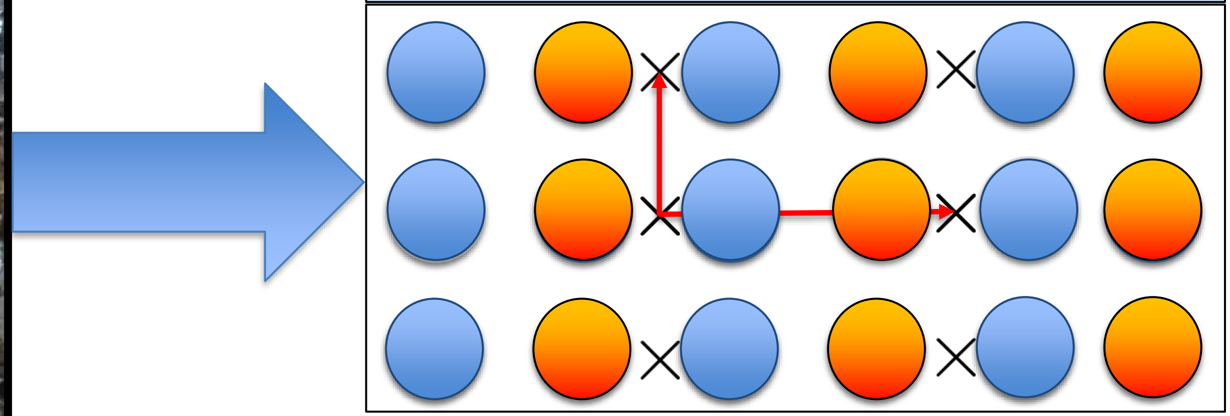
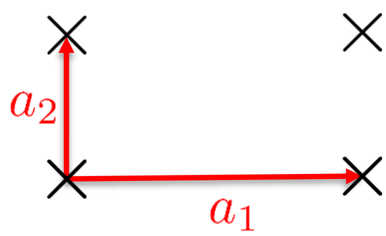
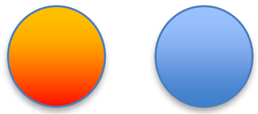
$$I(\Delta k) \propto |FT(lattice) \cdot FT(basis)|^2$$

General Diffraction

Periodic building blocks



Periodicity: Lattice	Building blocks: Basis
	

$$I(\Delta k) \propto \left|FT(lattice) \cdot FT(basis)\right|^2$$

General Diffraction

$$\mathrm{FT}(\mathrm{lattice}) = \sum e^{i(\Delta k - G)r}$$

$0 \text{ for } \Delta k \neq G$

Laue condition

$$\mathrm{FT}(\mathrm{basis}) = \sum \int_{UC} \rho(r) e^{-iGr} d^3 r$$

Structure factor S_G

$|S_G|^2$ determines peak intensity

corresponds to position of basis

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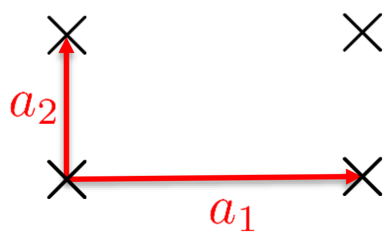	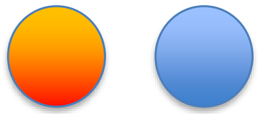
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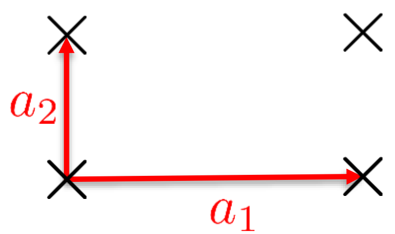	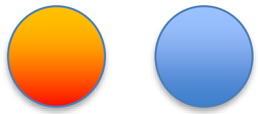

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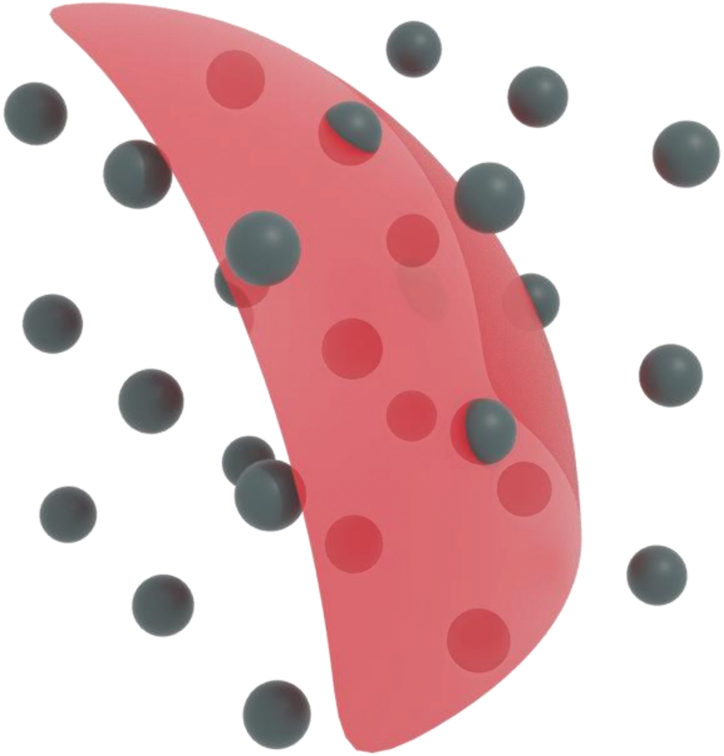
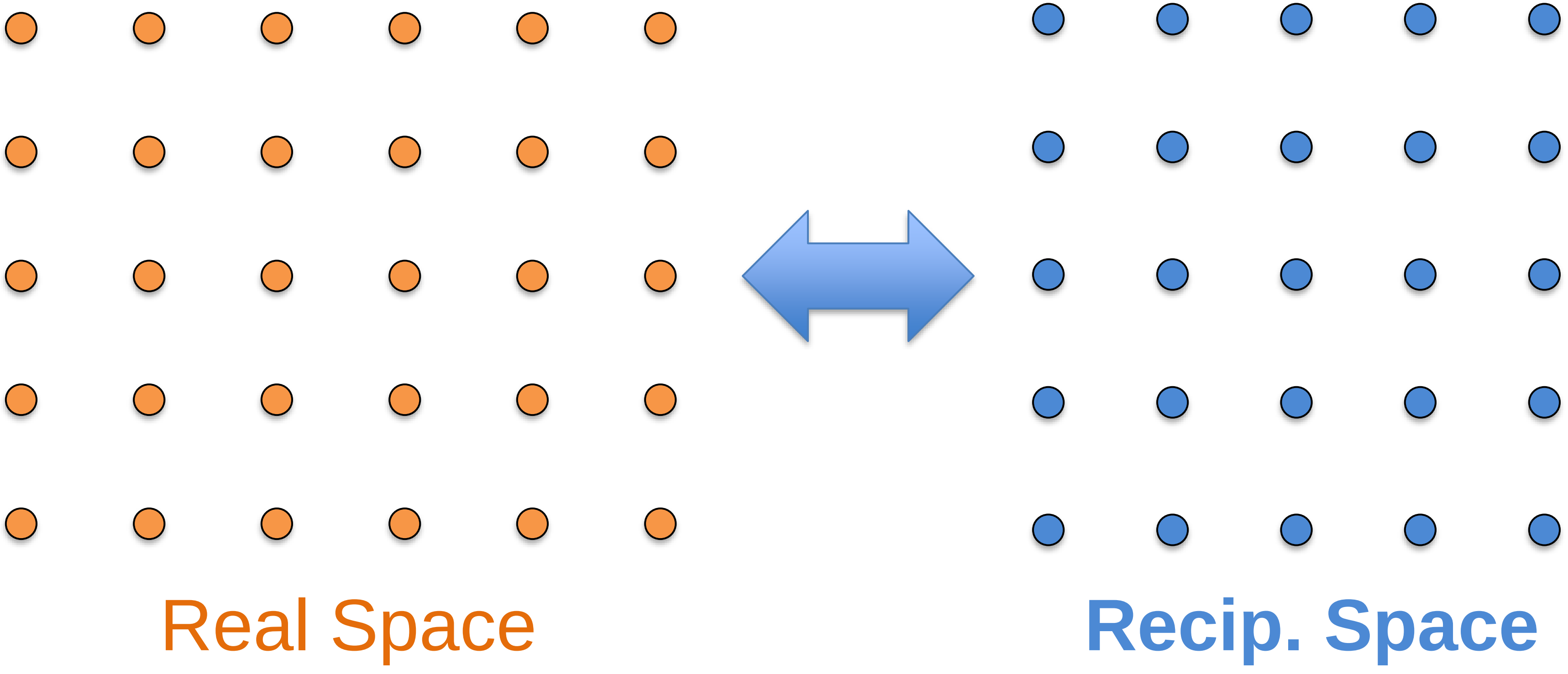
Ewald Construction
a.k.a.
„When we will see a peak?“



Ewald Construction

1) Setup reciprocal lattice
2) define 0,0 (on lattice point, arbitrary)



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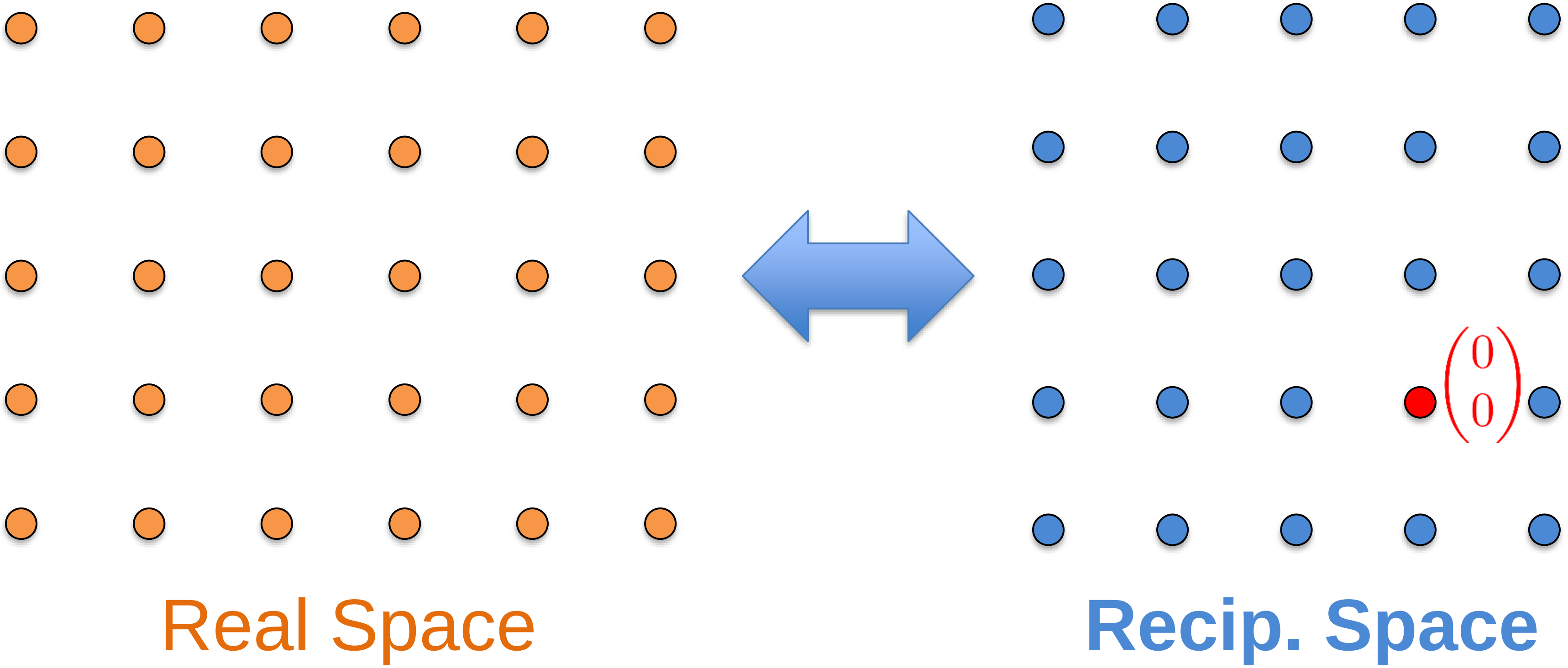

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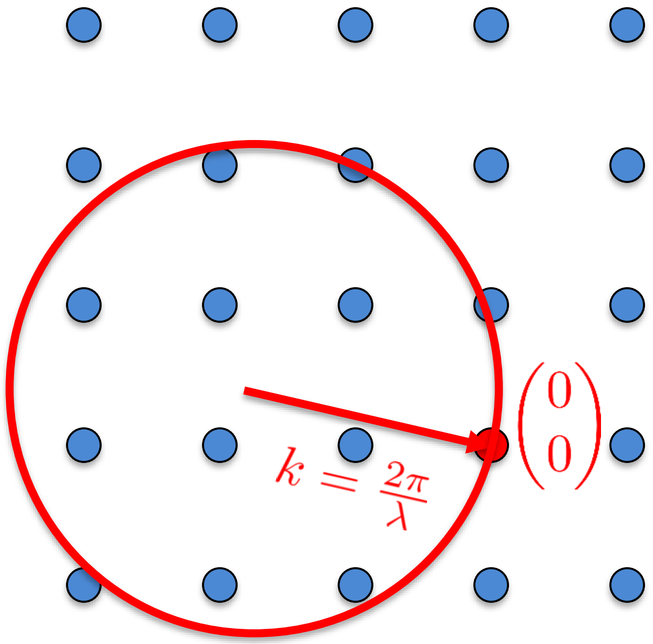
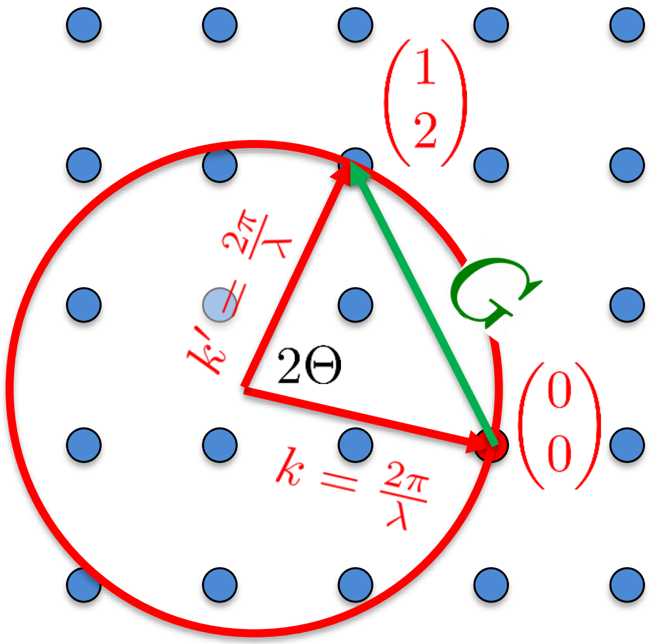
3) Incoming wave *k* (direction & length)
4) |*k*'| = |*k*| → sphere (circle in 2D)



Recip. Space

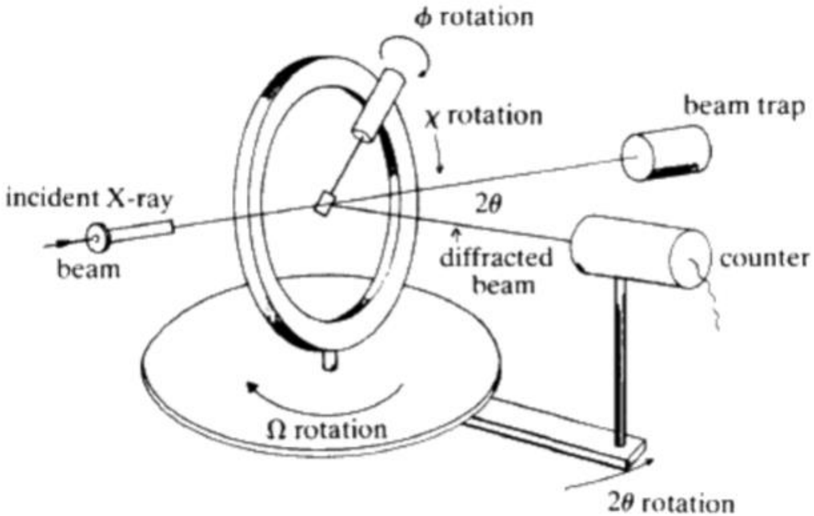
Ewald Construction

1) Setup reciprocal lattice
2) define 0,0 (on lattice point, arbitrary)
3) Incoming wave *k* (direction & length)
4) |*k*'| = |*k*| → sphere (circle in 2D)
5) Reflection observed if sphere hits point
6) Angle = 2Θ
7) Δ*k* = *G*



Recip. Space

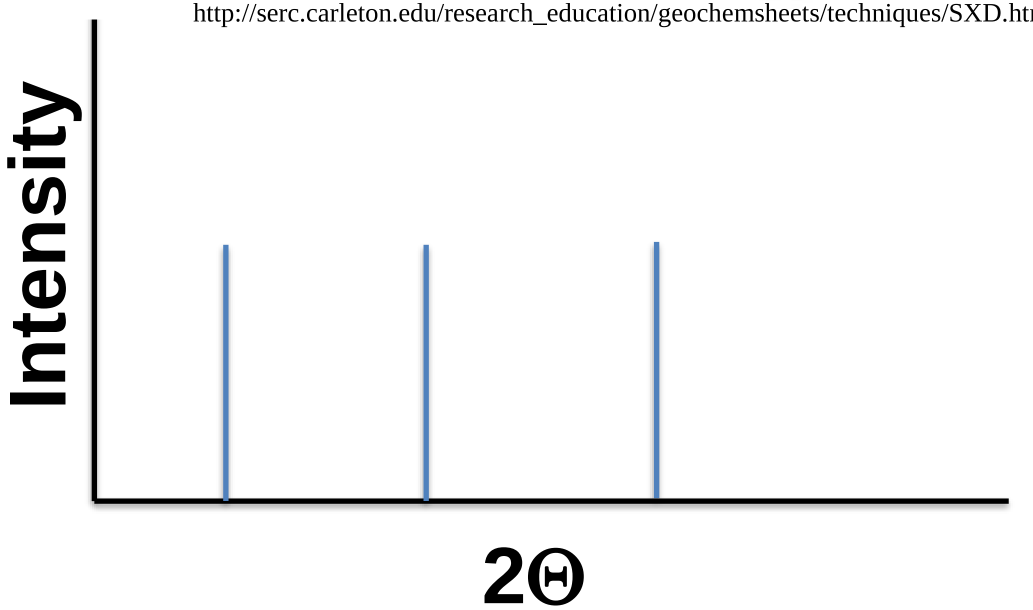
Experimental Setup for Diffraction

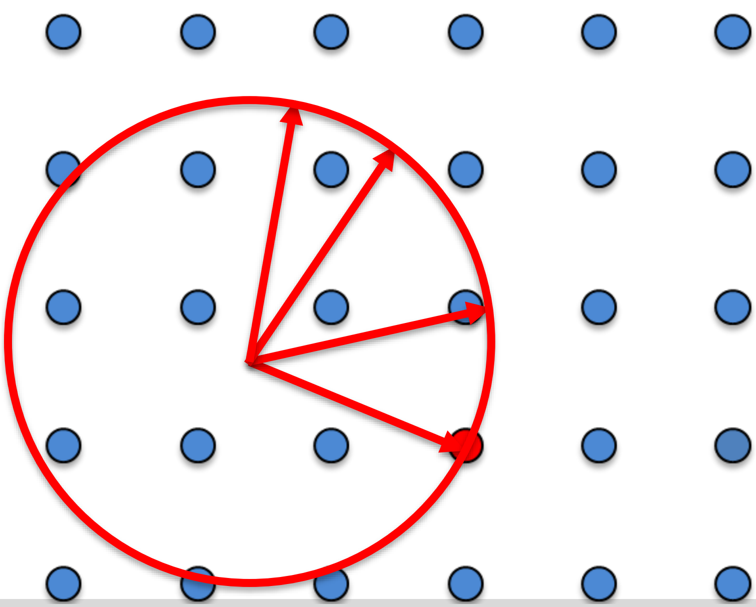


http://serc.carleton.edu/research_education/geochemsheets/techniques/SXD.html

To measure diffraction:

- *Rotate single crystal*
- *Use powders*
- *Change wavelength*





Summary – Today‘s Concepts

- **Bragg Diffraction:** $n\lambda = 2dsin(\Theta)$
- **Laue condition:** $\Delta\vec{k} = \vec{G}$
- **General diffraction:** $I(\Delta k) \propto |FT(lattice) \cdot FT(basis)|^2$
- **Structure factor:** $\int_{UC} \rho(r) e^{-iGr} d^3r = S_G$

Outlook for the Next Lecture:

- **Structure factor**
- **Ambiguity when choosing lattice & basis**
- **Solving diffraction patterns in practise**

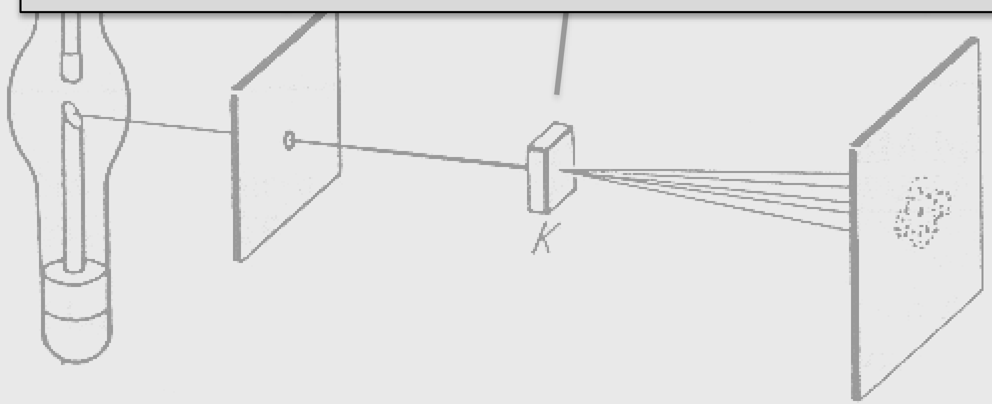
Crystal Diffraction

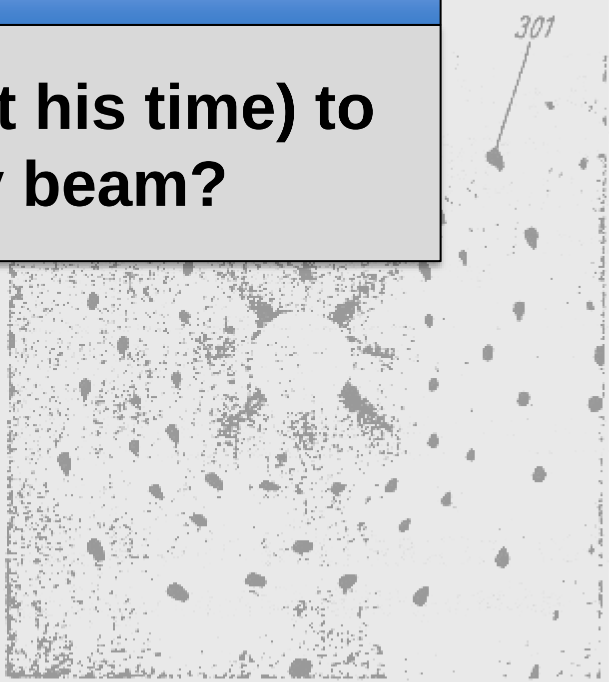
Historical experiment by Max von Laue,
Nobel price 1914

X-ra[y source]

Student Challenge:

What could von Laue have done (at his time) to obtain a monochromatic x-ray beam?



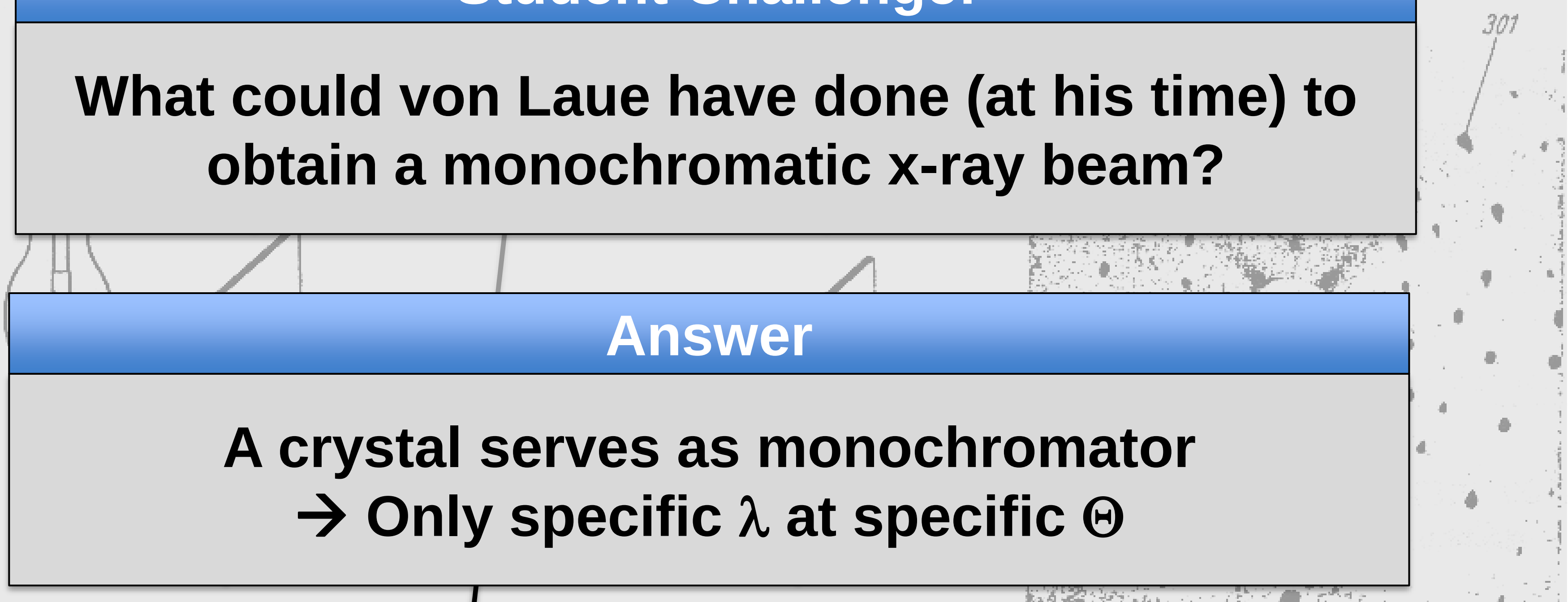


Modified from from: http://www.chemgapedia.de/vsengine/glossary/de/laue_00045verfahren.glos.html

Crystal Diffraction

Historical experiment by Max von Laue, Nobel price 1914

X-ra



Student Challenge:

What could von Laue have done (at his time) to obtain a monochromatic x-ray beam?

Answer

A crystal serves as monochromator
→ Only specific λ at specific Θ

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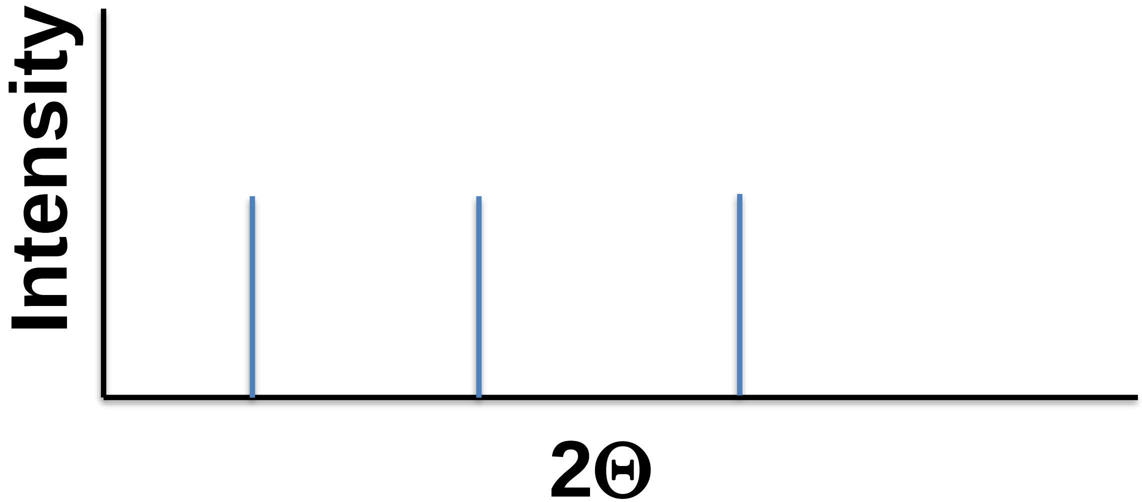
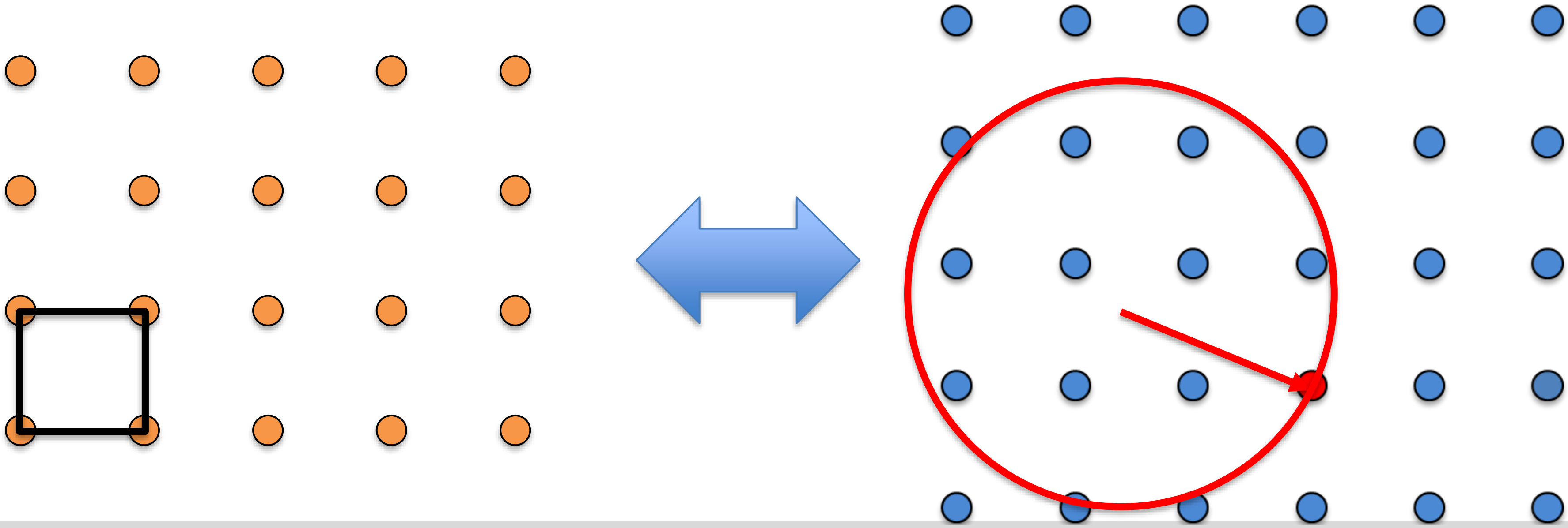
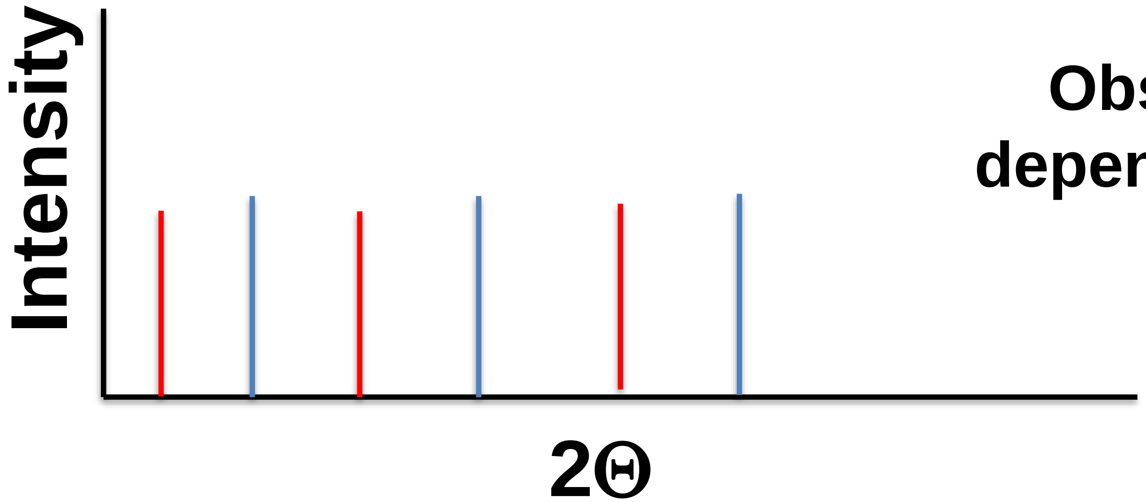
Why Do We Need the Structure Factor?

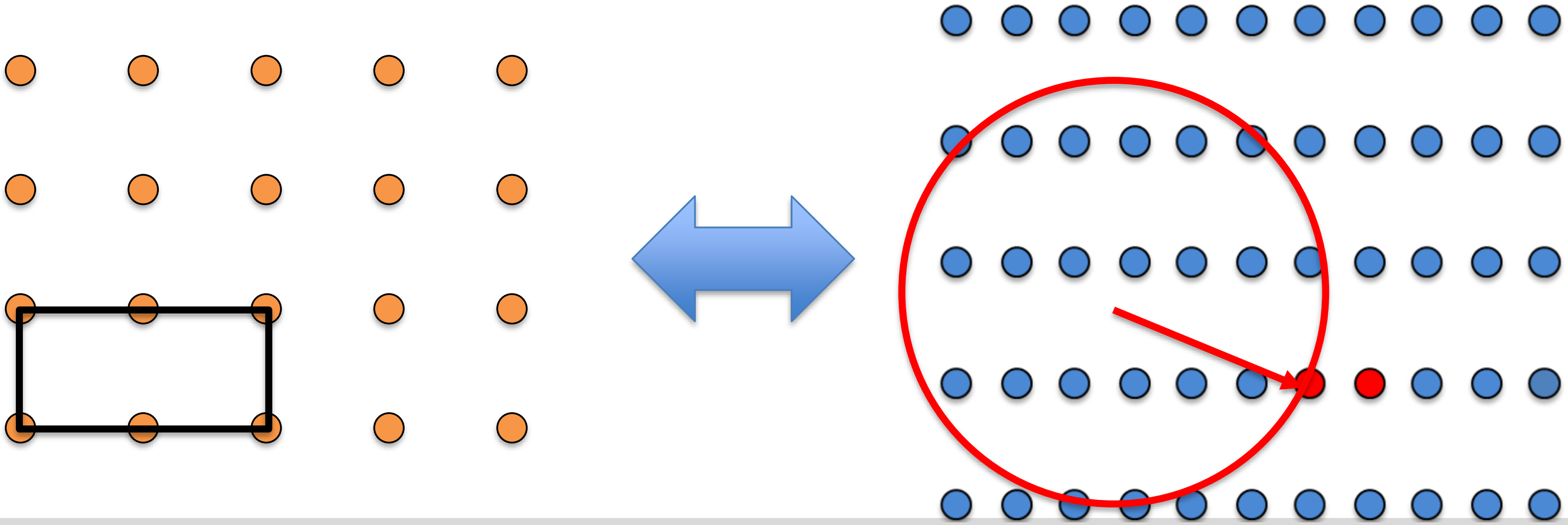




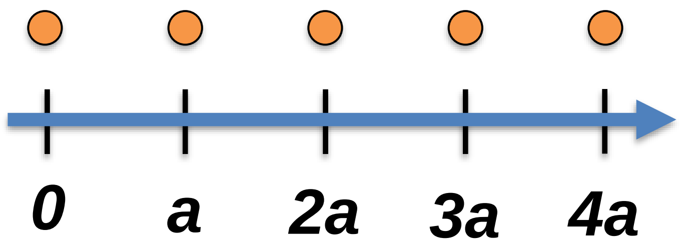
Why Do We Need the Structure Factor?

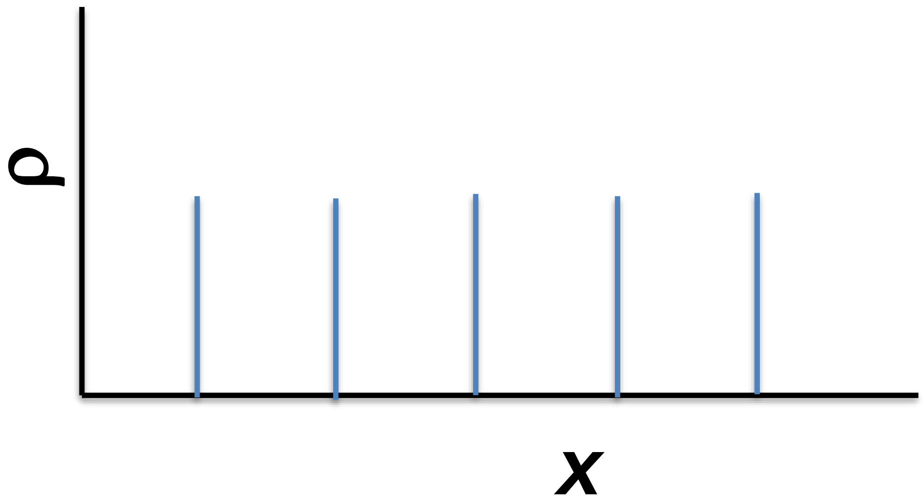


Observables **must not** depend on the <u>definition</u> of the unit cell!



A simplified example – 1D crystal

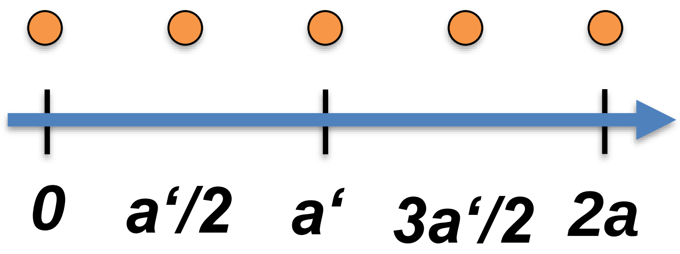


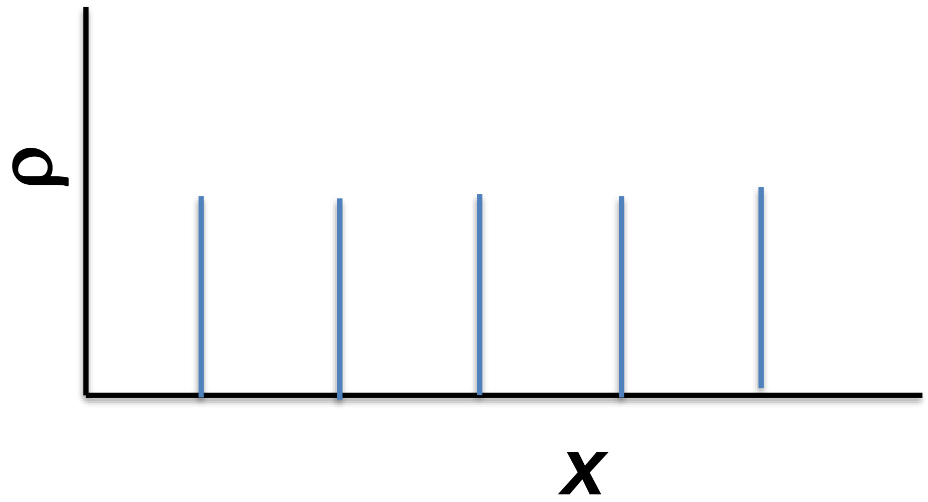


$$S_1 =$$

$$S_2 =$$

A simplified example – 1D crystal



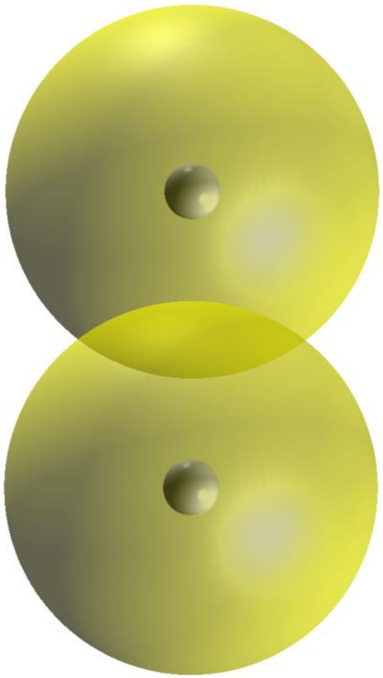


$$S_1 =$$

$$S_2 =$$

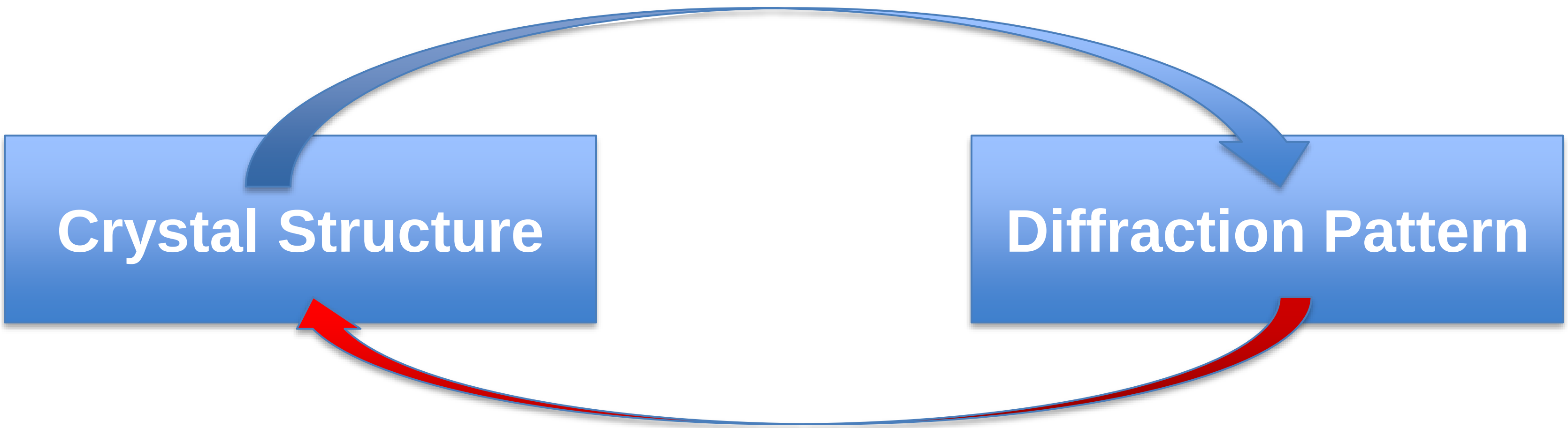
Structure Factor in Practise

- Calculate electron density
- Sum over atoms & form factors:



Solving a Diffraction Pattern

$$I(\Delta k) = \left| \int \rho_{UC}(r) e^{iGr} e^{-i\Delta k r} \right|^2$$



Inverse FT is not possible, because we loose the phase information

To solve a diffraction pattern, crystal structures are proposed and their diffraction pattern is calculated. From there, the structure is iteratively refined

Example

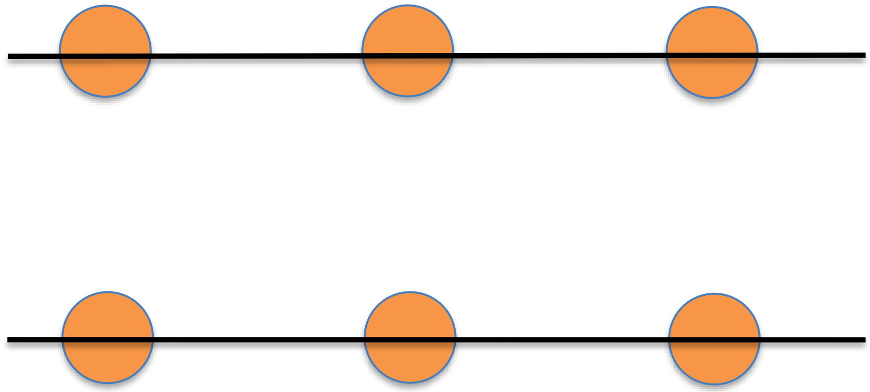
Measuring a simple cubic system with

- **Wavelength λ = 4.67Å.**
- **Reflection observed under θ = 45°**

What is the lattice constant of the crystal?

$$d = \frac{\lambda}{2sin(\theta)}$$

$$d = 3.3\text{Å}$$
$$a = d = 3.3\text{Å}$$

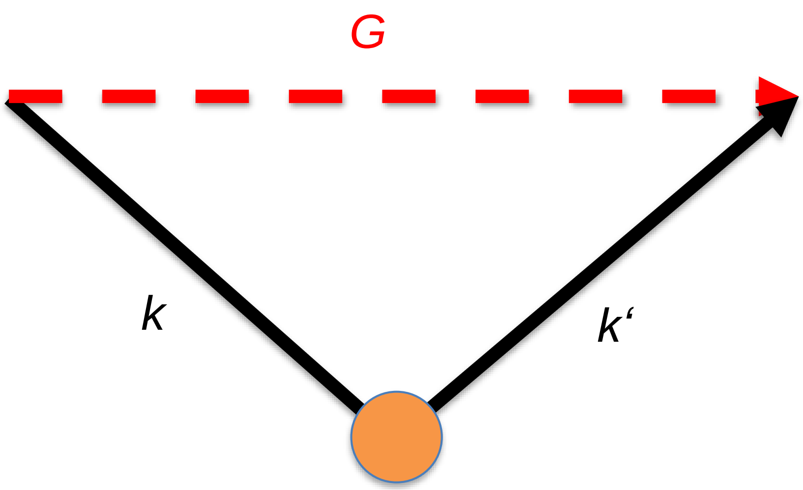


Laue Diffraction - Example

Measuring a simple cubic system with

- **Wavelength λ = 4.67Å.**
- **Reflection observed under $\theta = 45^\circ$**

What is the lattice constant of the crystal?



$$k = \frac{2\pi}{\lambda}\begin{pmatrix}1\\-1\end{pmatrix}\frac{1}{\sqrt{2}}$$

Reciprocal wavelenght	Direction (45 degrees)	Vector normalization

Laue Diffraction - Example

Measuring a simple cubic system with

- **Wavelength λ = 4.67Å.**
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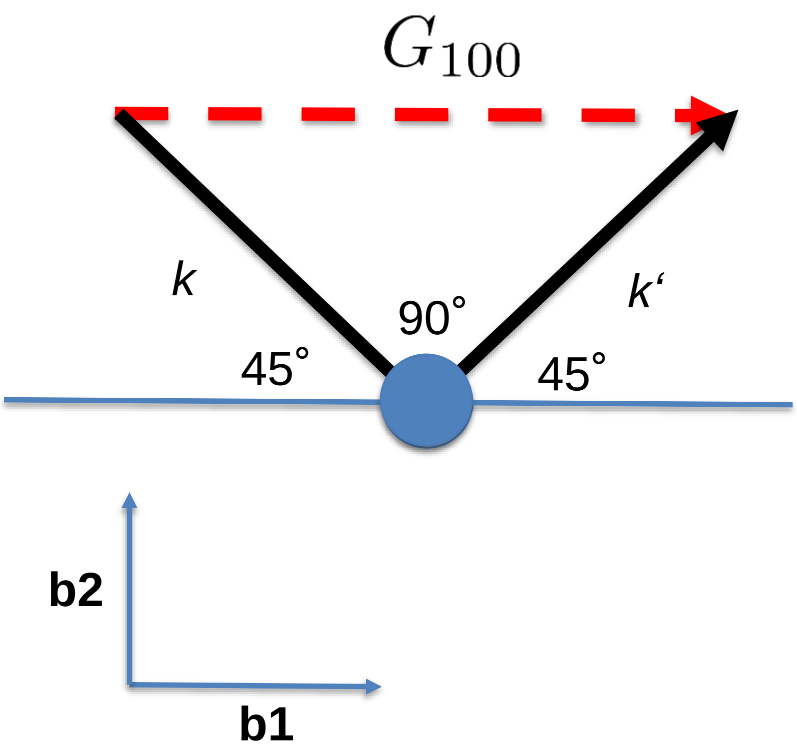
What is the lattice constant of the crystal?



$$k = \frac{2\pi}{\lambda}\begin{pmatrix}1\\-1\end{pmatrix}\frac{1}{\sqrt{2}}$$

Reciprocal wavelenght | **Direction (45 degrees)** | **Vector normalization**

$$k' = \frac{2\pi}{\lambda}\begin{pmatrix}1\\1\end{pmatrix}\frac{1}{\sqrt{2}}$$

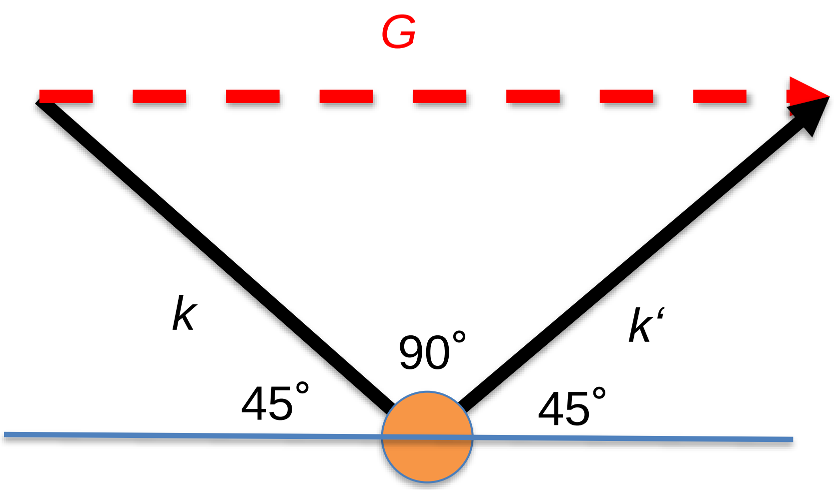
Direction changed by 90°

Laue Diffraction - Example

Measuring a simple cubic system with

- **Wavelength λ = 4.67Å.**
- **Reflection observed under $\theta = 45^\circ$**

What is the lattice constant of the crystal?



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$$k' = \frac{2\pi}{\lambda}\begin{pmatrix}1\\1\end{pmatrix}\frac{1}{\sqrt{2}}$$

$$G_{hkl} = k - k' = \frac{2\pi}{\lambda}\frac{1}{\sqrt{2}}\left[\begin{pmatrix}1\\-1\end{pmatrix} - \begin{pmatrix}1\\1\end{pmatrix}\right]$$

Laue Diffraction - Example

Measuring a simple cubic system with

- **Wavelength λ = 4.67Å.**
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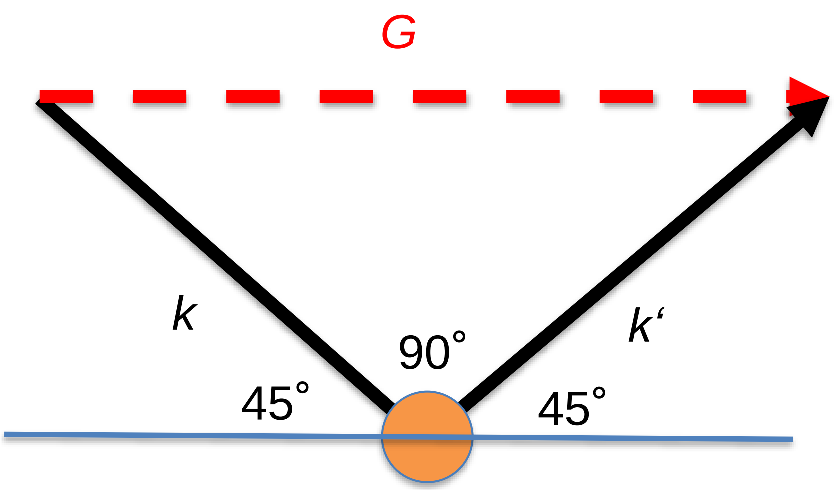
What is the lattice constant of the crystal?



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$$k' = \frac{2\pi}{\lambda}\begin{pmatrix}1\\1\end{pmatrix}\frac{1}{\sqrt{2}}$$

$$G_{hkl} = \frac{2\pi}{\sqrt{2}\lambda}\begin{pmatrix}0\\-2\end{pmatrix}$$

Laue Diffraction - Example

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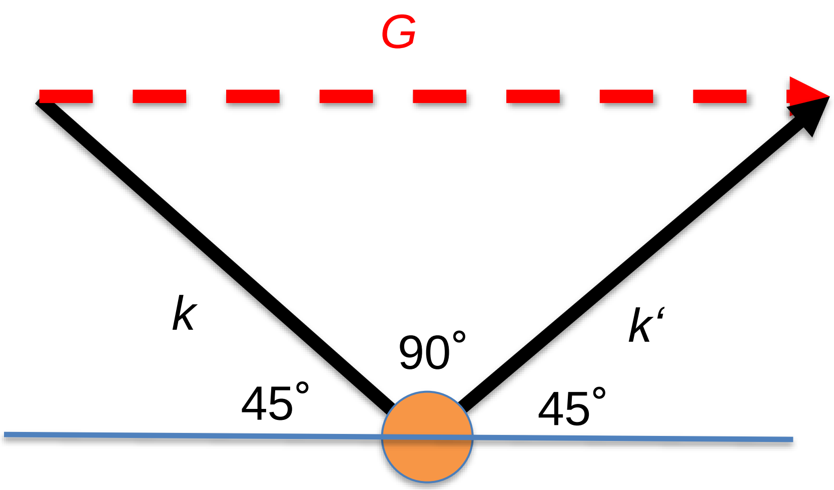

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$$G_{hkl} = \frac{2\pi}{\sqrt{2}\lambda}\begin{pmatrix}0\\-2\end{pmatrix} = \frac{2\pi}{a}\begin{pmatrix}h\\k\end{pmatrix}$$

→ *Definition of G!*

Laue Diffraction - Example

Measuring a simple cubic system with

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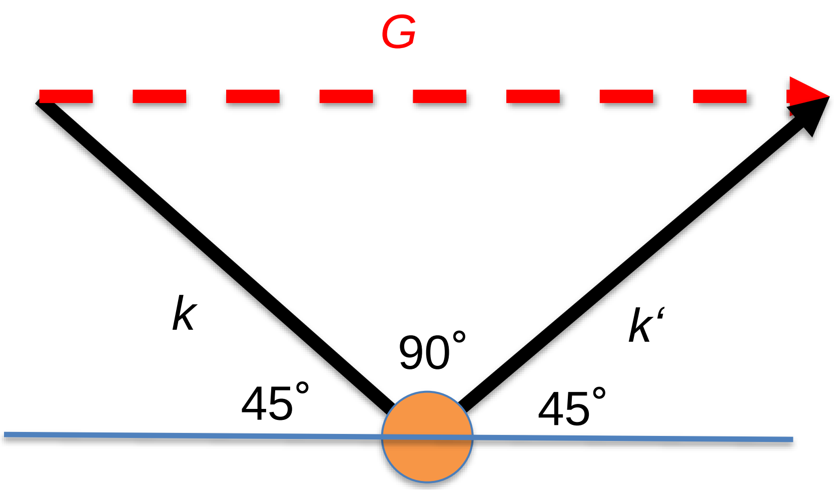

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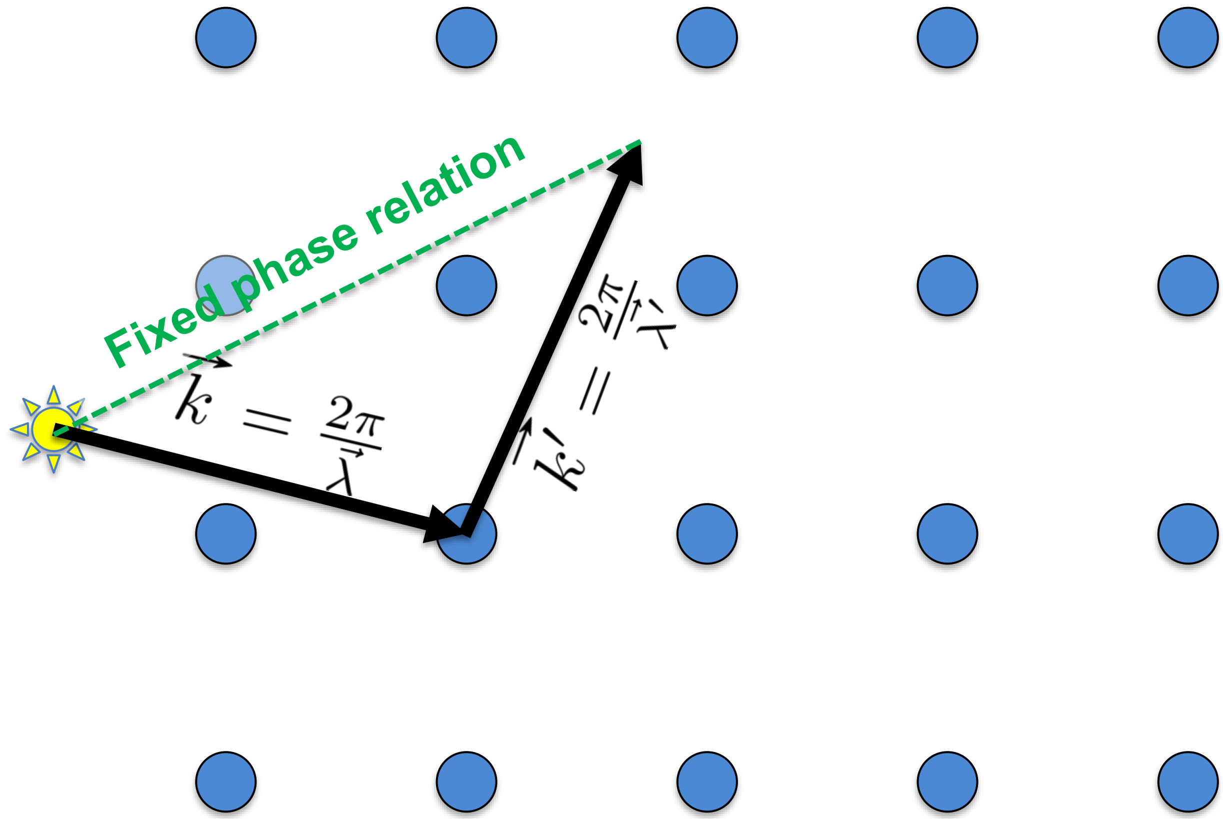
$$G_{hkl} = \frac{2\pi}{\sqrt{2}\lambda}\begin{pmatrix}0\\-2\end{pmatrix} = \frac{2\pi}{a}\begin{pmatrix}h\\k\end{pmatrix}$$

h = 0 (obviously)
k = 1 (index assumed!)

$$a = 3.3\text{Å}$$

Diffraction in Reciprocal Space



To find constructive interference, we must be able to find a different path with the same phase relation