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INSTITUTE OF METALLURGY
AND MATERIALS SCIENCE
POLISH ACADAMY OF SCIENCES

European Union
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Characterization of material structure by the X-ray diffraction
II
X-ray diffraction phenomenon.
Part I

Project WND-POWR.03.02.00-00-I043/16

International interdisciplinary PhD Studies in Materials Science with English as the language of instruction

Project co-financed by the European Union within the European Social Funds

Diffraction theories of X-ray on condensed matter

geometrical → describes **only directions**, in which the diffracted rays are observed (no intensity predictions)

kinematical → describes (among others) **intensity** of radiation and is correct in the case of defected and relatively fine-grained materials to fulfil relation: $I_{(scattered)} << I_{(diffracted)}$. No extinction is regarded

dynamical → Describes diffraction on materials with enough large areas of coherent scattering with L dimmension ($\mu L > 0.01$)

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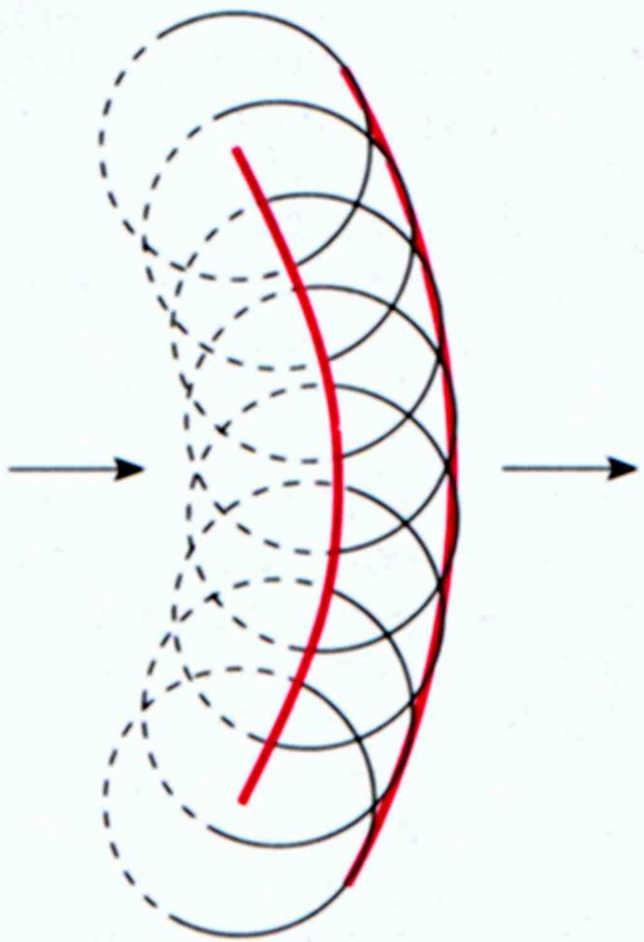
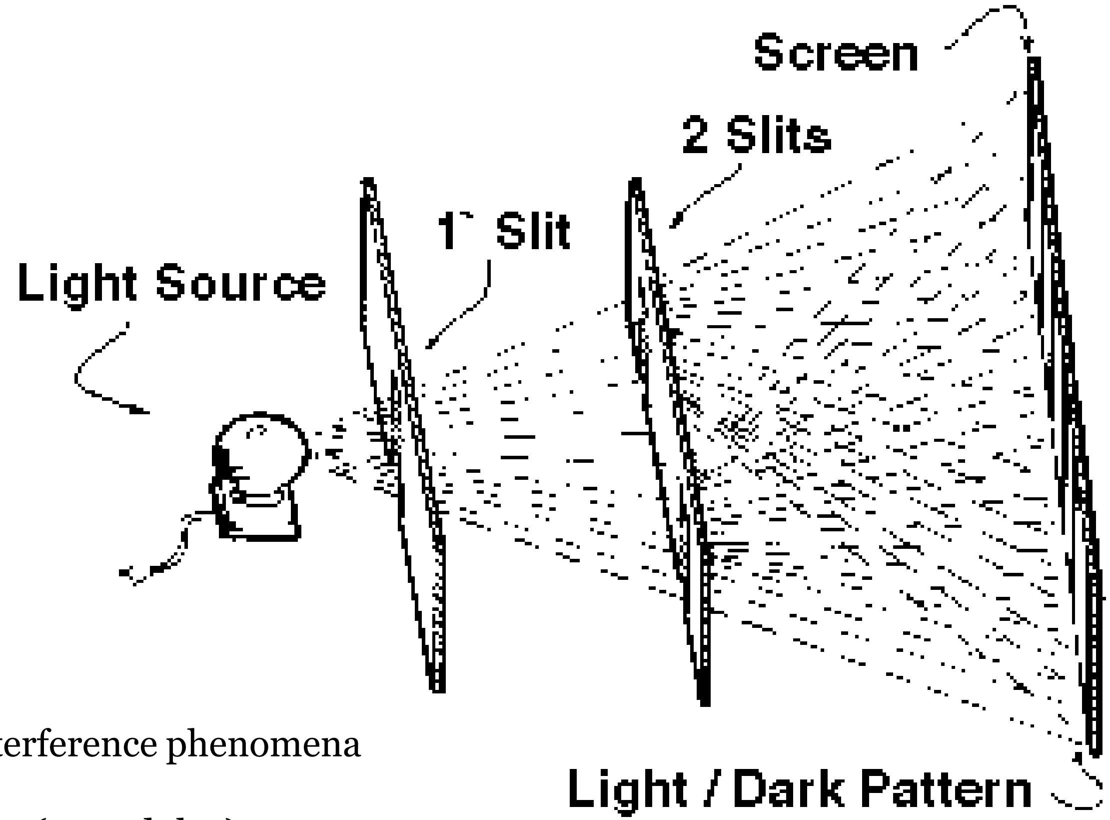


Powstawanie nowej powierzchni falowej jako obwiedni fal cząstkowych

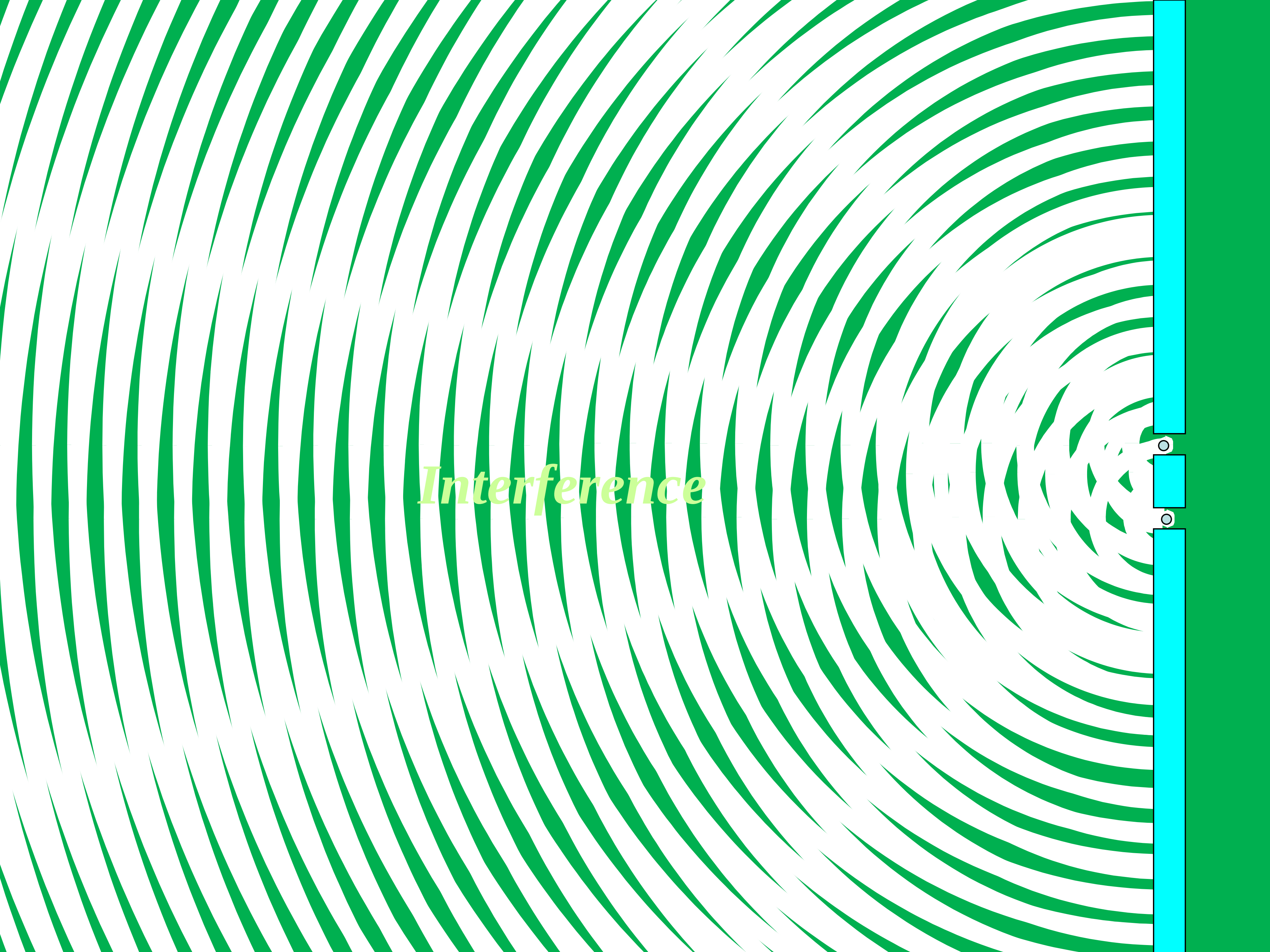
Christian **HUYGENS**
(1629-1695),
1678: outline of light theory

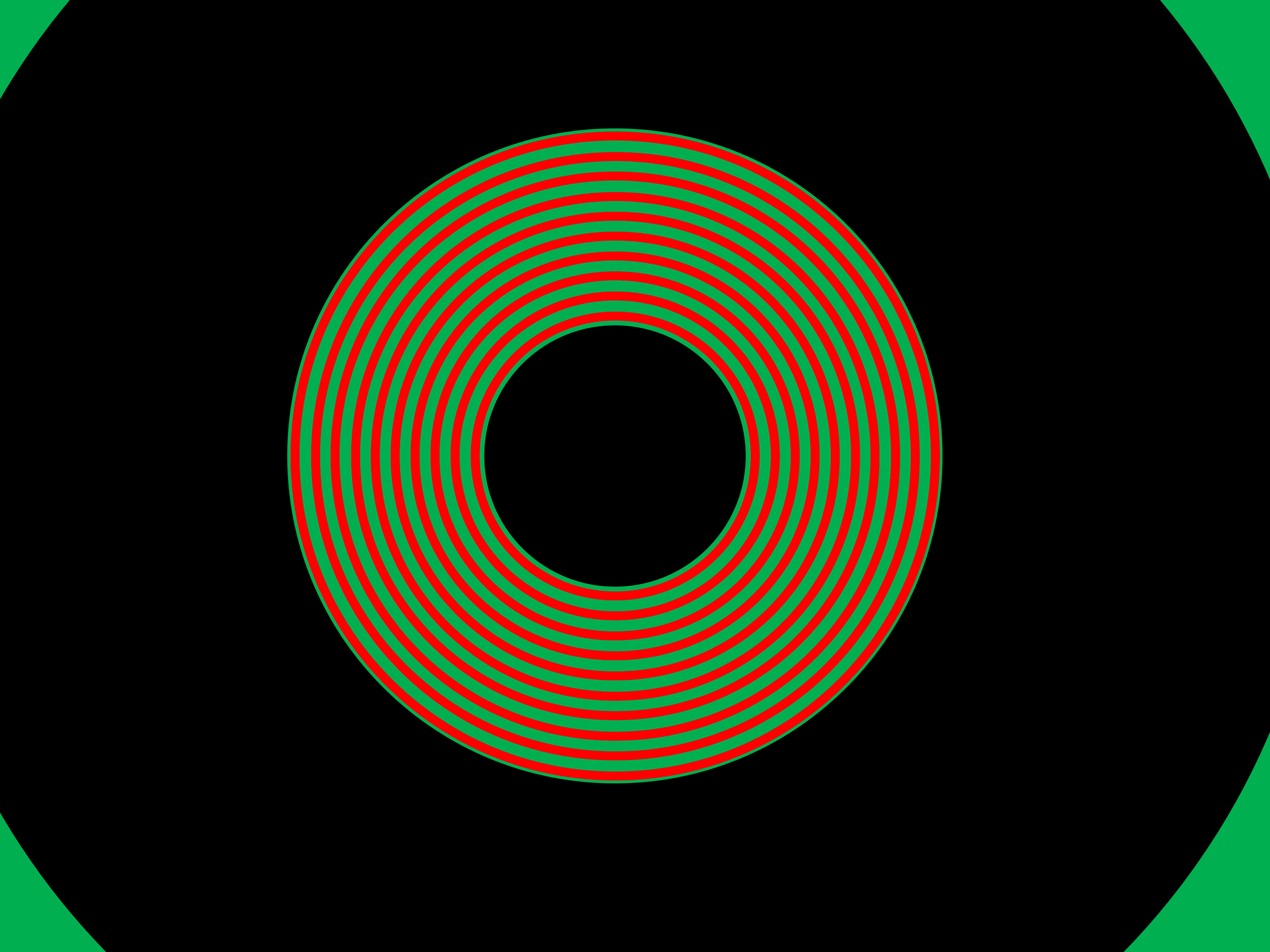
HUYGENS explained mechanizm of waves propagation

FRESNEL
1818: perturbation in any point is a result of interference of elementary waves regarding its amplitude and phase



Thomas **YOUNG** (1773-1829),
1802 carried out and explained the interference phenomena
Estimated wavelength.
Other interests: elasticity of solid bodies (E modulus)
- for steel E = 2.0 x 100 000 MPa (obecnie ≈ 210 Gpa)
- for bronze E = 1.0 x 100 000 MPa
- for glass E = 0.6 x 100 000 MPa


Interference



Obstacle size → scatterind → diffraction

Objec of scattering (size)	**Radiation** (typical wavelength)
Print-paint dot in newspaper (0.1 mm)	Thermal radiation (0.1 nm, typical)
Rain drops (10 mm)	Visible light (520 nm, green) (*prism effect!*)
Row of the parked autos (3 m)	Audible sound wave (1.26 m at 20°C)
Lattice-plane distance (0.5 nm)	X-ray (0.154 nm, CuKa)
Singular atoms in crystal (0.1 nm)	Electron beam (3.7 pm for 100 keV)

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Scattered coherent waves:

Interference constructive **Interference destructive**

Mathematical formulae: von Laue* (1912)

Max von **LAUE** *(1879–1960), physiker, prof. univ. Zurich and Berlin,*

Discoverer of X-ray diffraction*, Nobel Prize, 1914*

Diffraction = scattering + interference

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- in Russian literature → *Br*

William Henry **BRAGG** *(1*
Univ. of London, member
1915 *(along with son W.L. I*

By

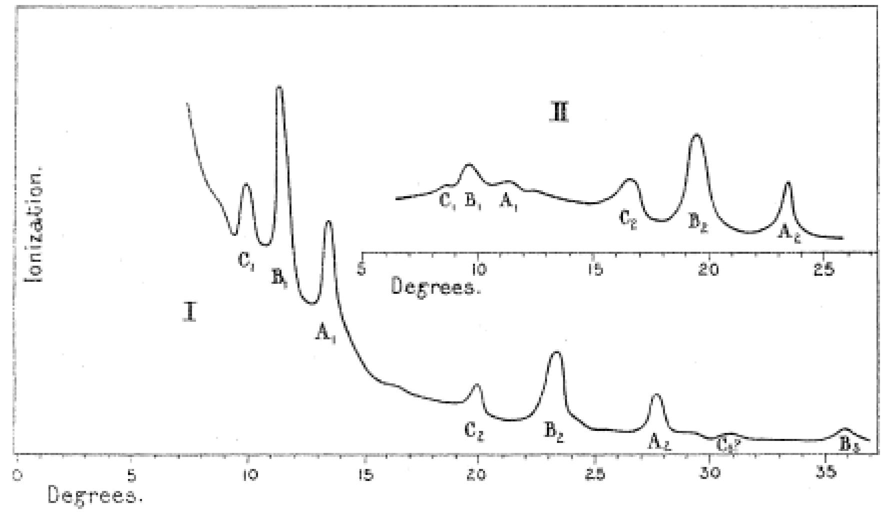


FIG. 3.—Reflection (I) from face (100) and (II) from face (111) of rock-salt. The curves show the variation of strength of reflected beam with angle of incidence.

may conveniently be interpreted as due to the reflection of X-rays in such planes within the crystal as are rich in atoms. This leads at once to the attempt to use cleavage planes as mirrors, and it has been found that mica gives a reflected pencil from its cleavage plane strong enough to make a visible impression on a photographic plate in a few minutes' exposure. It ...hat the reflected pencil can be detected by the

...amining more closely the reflection of X-rays in ...an apparatus resembling a spectrometer in form, ...ing the place of the telescope. The collimator is ...pierced by a hole which can be stopped down to ... The revolving table in the centre carries the ...chamber is tubular, 15 cm. long and 5 cm. in ...ted about the axis of the instrument, to which its ...r. It is filled with sulphur dioxide in order to ...rrent: both air and methyl iodide have also been ...sure that no special characteristics of the gas in

'Proc. Camb. Phil. Soc.,' vol. 17, Part I, p. 43.
'Nature,' Jan. 23, 1913.

It is of great interest to attempt to find the exact wave-length of the rays to which these peaks correspond. On considering Curve I, fig. 3, it seems evident that the peaks $A_1 B_1 C_1$, $A_2 B_2 C_2$ are analogous to spectra of the first and second orders, because of the absence of intervening sets of peaks. The value of n in the equation

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

seems clear. The difficulty of assigning a definite wave-length to the rays arises when we attempt to determine the value of d, the distance of plane from plane.

* We learn that Messrs. Moseley and Darwin have lately been making experiments similar to some of those recorded here. Their results, which have not been published, agree with ours.

Bragg

$$n\lambda = 2d_{hkl} \sin\theta_B$$

[Proceedings of the Royal Society, 1913, 88, 428]

Adnotation at the end of the work of H.W & W.L. Braggs from 1913: „Received April 7, 1913"

Gieorgij W. **Wulf** – two his works from beginning 1913 in Russian [Fizika, 1913, zesz. 1, s. 10 and Priroda, 1913, s. 27] concerned to interference of X-rays and its behaviour in passing through the crystals. *He known the earlier works of W.L. Bragg from 1912r.*

....by ***Wulf:***

$$\frac{\lambda}{2} = \frac{\delta\varepsilon}{m}$$

„Ueber die Kristallroentgenogramme" [Physikalishe Zeitschtrift, **1913**, z. 6, s. 217]

where $\delta = d_{hkl}$, $\varepsilon = \cos\psi$ (ψ – angle between incident beam and normal to diffracting lattice plane), m – order of reflection)

$$m\lambda = 2d_{hkl} \cos\psi$$

Adnotation at the end of the work of G.W. Wulf (sent from Russia) from 1913: „Eingegangen 3 Februar 1913"

Base law (equation) of diffraction theory:

$$n\lambda = 2d_{hkl} \sin\theta_B$$

$$\frac{\lambda}{2} = \frac{\delta\varepsilon}{m}$$

$$m\lambda = 2d_{hkl} \cos\psi$$

Bragg *law (equation)*

Braggs *law (equation)*

Wulf *law (equation)*

Braggs – Wulf *law (equation)*

Wulf – Braggs *law (equation)*

Analysis of crystal structure by diffraction techniques

The crystal structure can be analyzed by X-ray diffraction (XRD from x-ray diffraction) and electron diffraction.

Max von Laue (1879-1960),

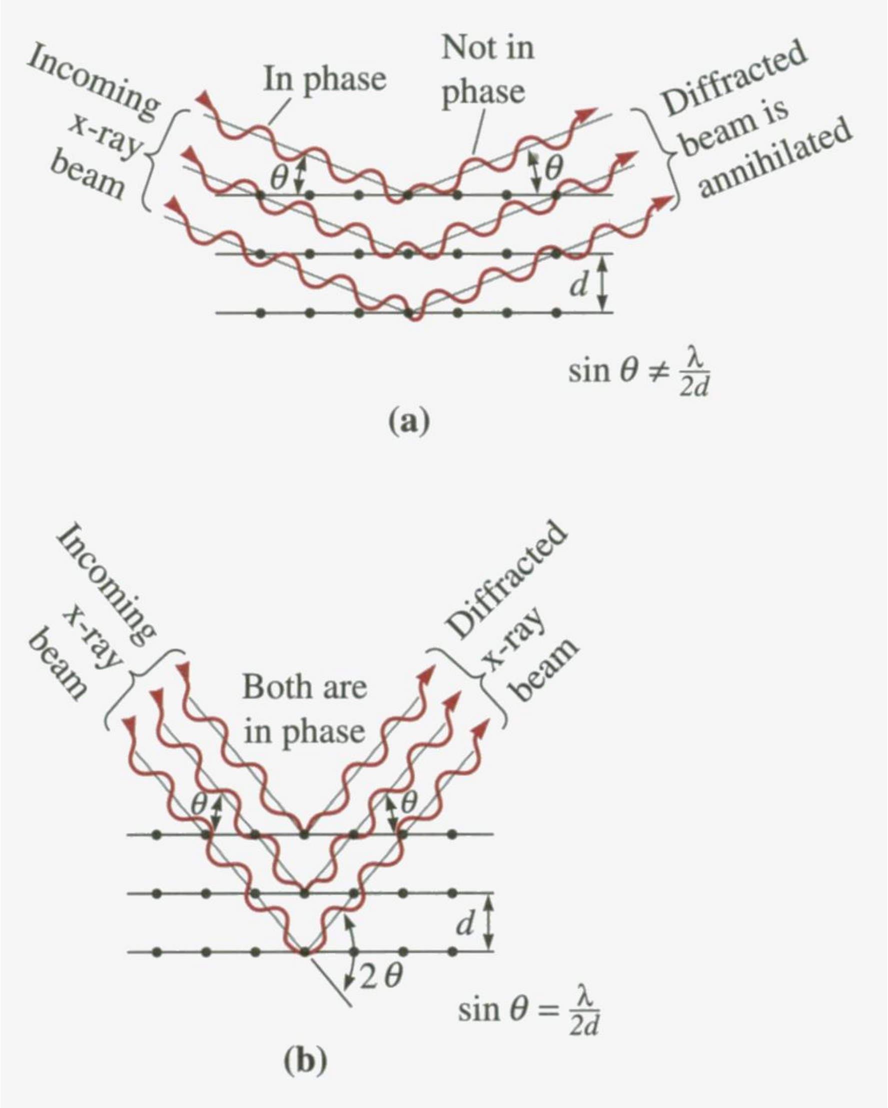
Wiliam Henry Bragg (1862 - 1942) and Wiliam Lawrence Bragg (1890 - 1971) Max von Laue (1879 – 1960),

Diffraction - when an X-ray beam with a wavelength comparable to that between atoms falls on a material, the X-ray beams are scattered in all directions. Most of the radiation scattered by one atom is extinguished by radiation scattered by other atoms. However, when radiation falls on certain crystallographic planes at specific angles, it is amplified and not weakened.

„SURFACE ENGINEERING FOR CORROSION AND WEAR RESISTANCE” Editet by J.R. Davis, Davis & Associates, 2001.

„INŻYNIERIA WARSTWY WIERZCHNIEJ” Piotr Kula, Wydawnictwo Politechniki Łódzkiej, 2000.

Analysis of crystal structure by diffraction techniques



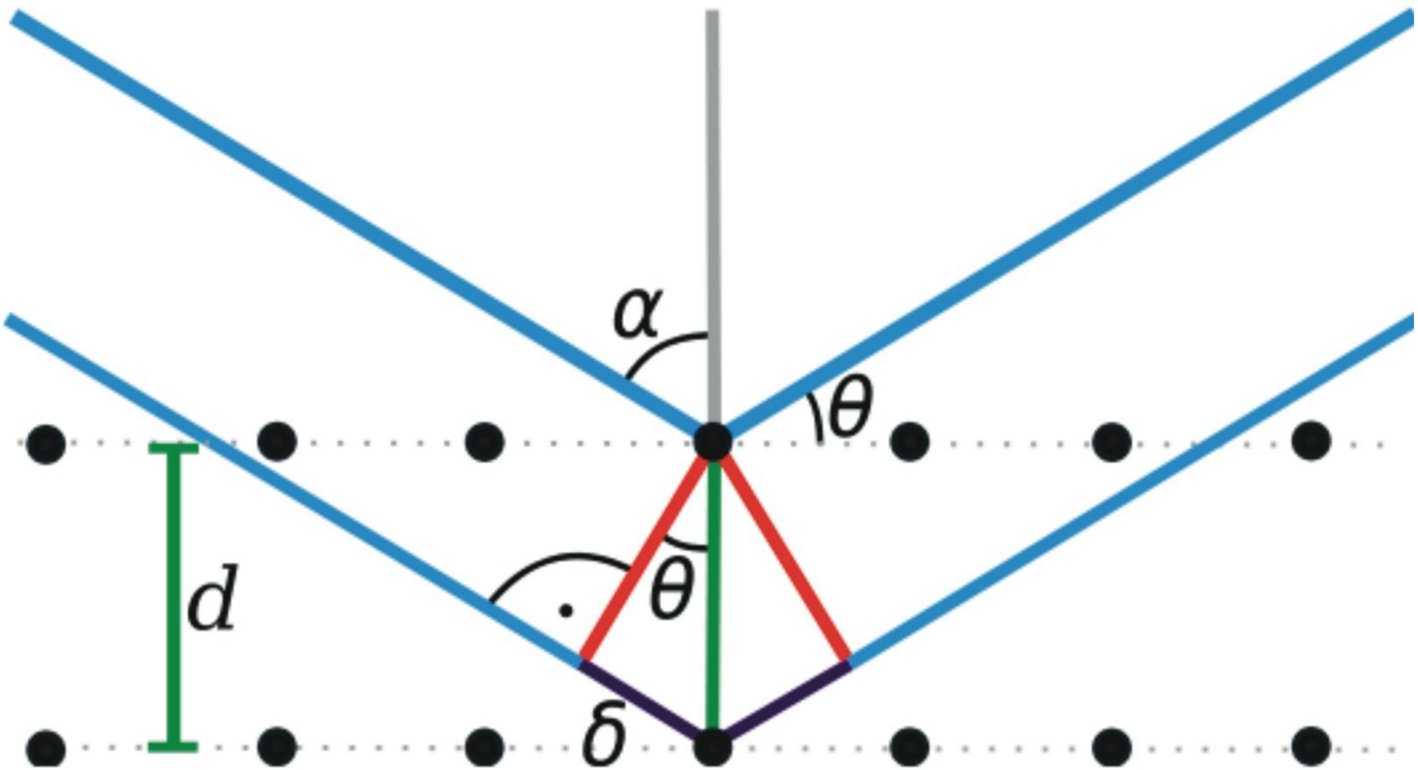
Weakening (a) and strengthening (b) of the interaction between X-rays and crystalline material.

The amplification shall be provided at a raading angle θ corresponding to Bragg's equation → sin θ=λ/2dhkl

Donald R. Askeland, Pradeep P. Phulé „The science and engineering of materials", Thomson 2006.

Analysis of crystal structure by diffraction techniques

The amplification shall be provided at an angle of incidence θ corresponding to Bragg's equation → $\sin \theta = n\lambda / 2d_{hkl}$



Donald R. Askeland, Pradeep P. Phulé „The science and engineering of materials", Thomson 2006.

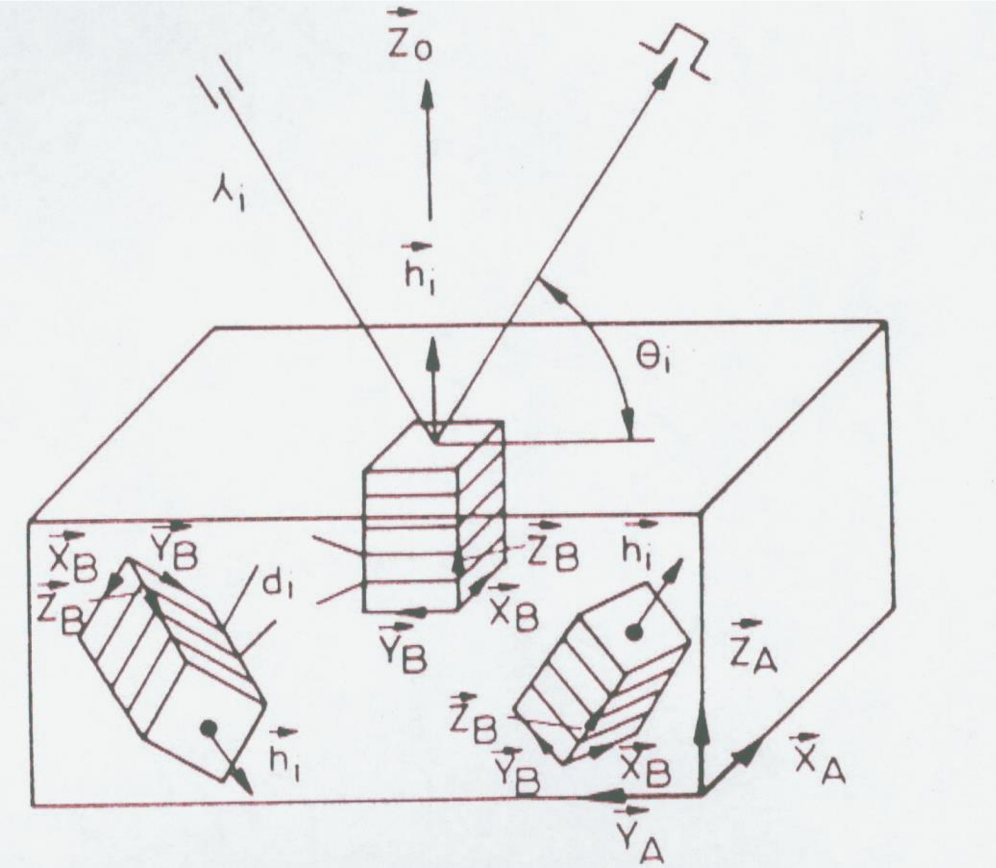
Analysis of crystal structure by diffraction techniques

In the practical description of the interaction of radiation with the crystal, its structure is treated as a periodic system of atomic planes behaving as mirrors. Reinforcement shall be provided at an incidence angle θ corresponding to Bragg's equation → $\sin \theta = n\lambda/2d_{hkl}$
where: n is the total number (designating the row of scattering), λ - the wavelength of the radiation (for particle streams, the wavelength shall be determined from de Broglie: $\lambda = h/p$ where: h - Planck constant and p - particle momentum), d - distance between atomic planes in the crystal, θ - angle between the beam of incident radiation and the plane of reflection of the beam (angle of deflection at which the maximum intensity of deflected radiation is observed).

Donald R. Askeland, Pradeep P. Phulé „The science and engineering of materials", Thomson 2006.

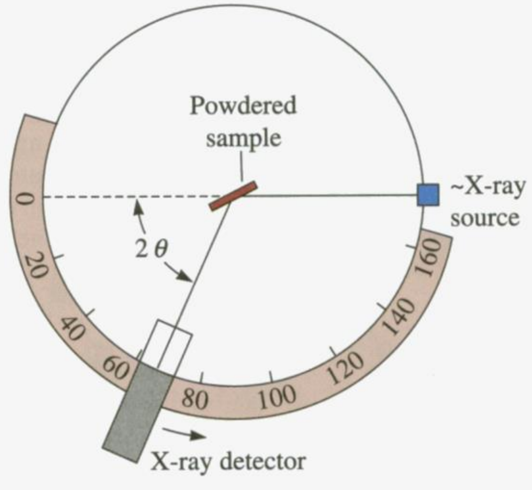
Analysis of crystal structure by diffraction techniques

Powder sample

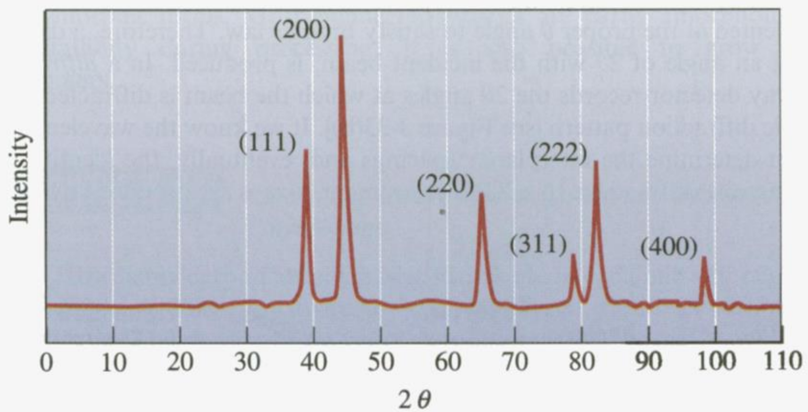


In the powder sample always some part of the powder particles (microcrystals) have so oriented certain planes (hkl), they meet the Bragg condition.

Analysis of crystal structure by diffraction techniques



(a)

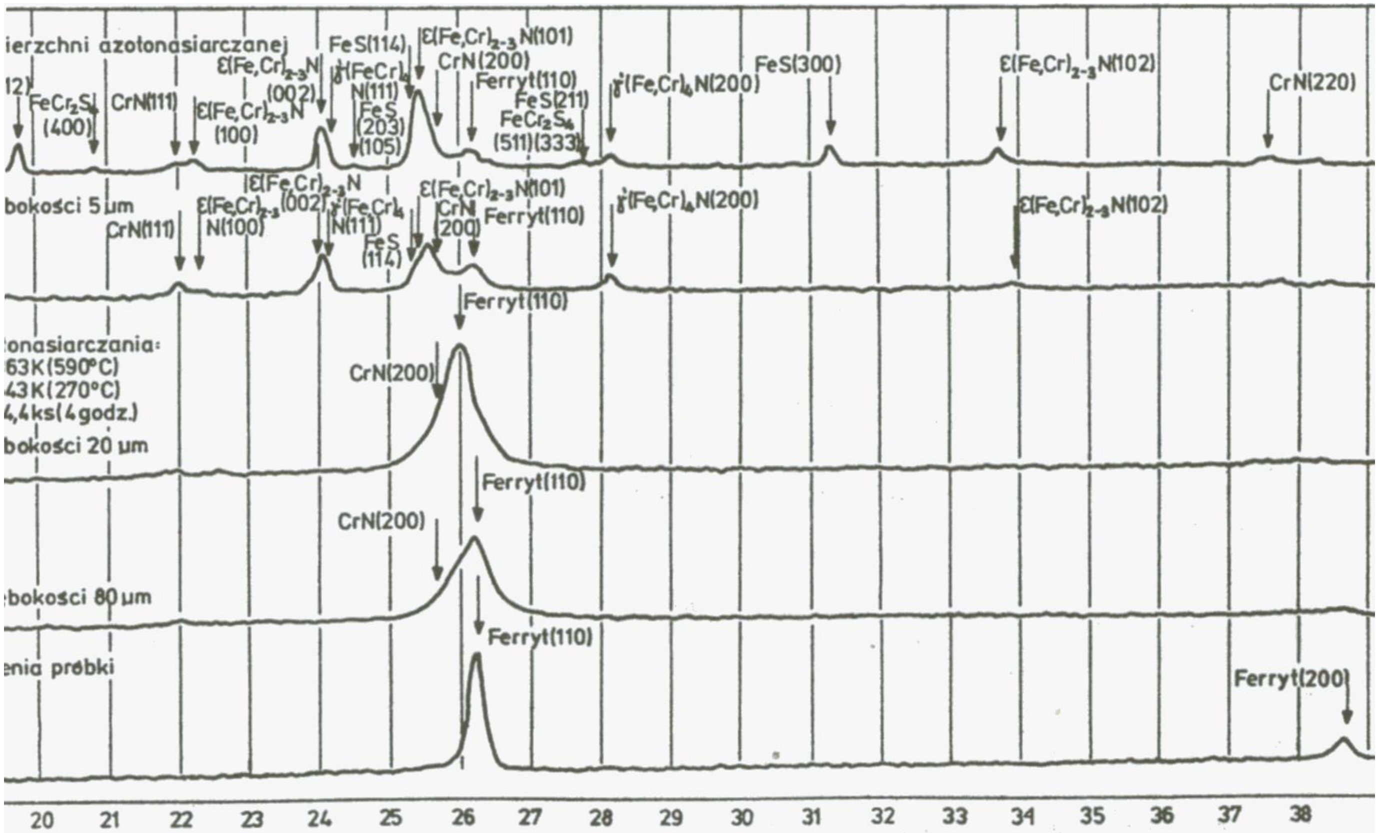


a) Scheme of diffractometer,
b) Diffractogram obtained from a gold powder sample.

If we know the wavelength of X-rays (λ), we can determine the distances between the planes (and identify the reflective crystallographic planes).

Donald R. Askeland, Pradeep P. Phulé „The science and engineering of materials", Thomson 2006.

Listing of diffractograms recorded after removal of subsequent surface zones of the 4H13 steel nitrate sulphate layer → structural layer analysis.



„SURFACE ENGINEERING FOR CORROSION AND WEAR RESISTANCE” Editet by J.R. Davis, Davis & Associates, 2001.
„INŻYNIERIA WARSTWY WIERZCHNIEJ” Piotr Kula, Wydawnictwo Politechniki Łódzkiej, 2000.

Distance between crystallographic planes {hkl}:

$$d_{hkl} = \frac{a_0}{\sqrt{h^2 + k^2 + l^2}}$$

$$\sin^2 \Theta = \frac{\lambda^2}{4a_0^2}(h^2 + k^2 + l^2)$$

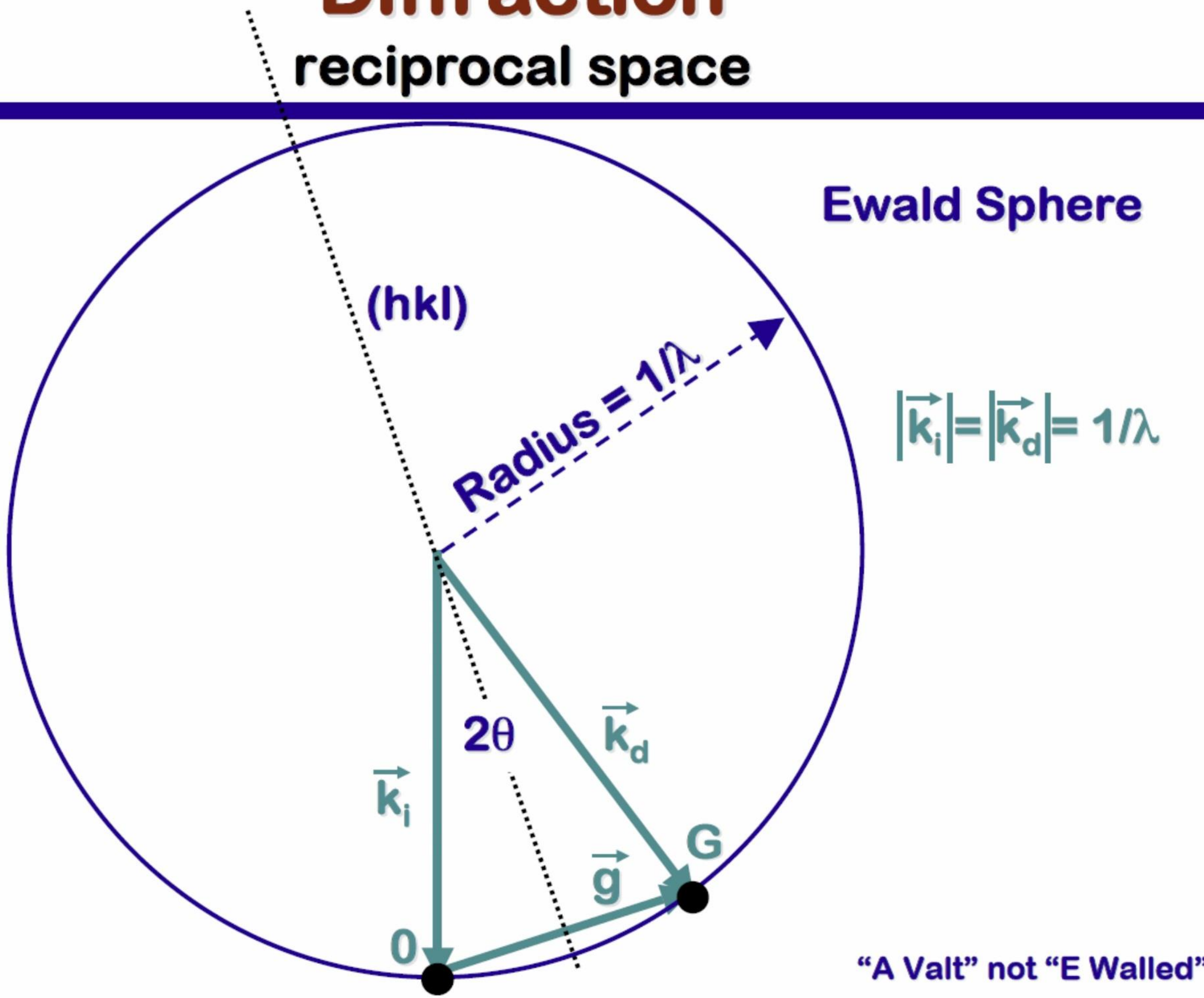
Cubic primitive cell : $h^2+k^2+l^2= 1, 2, 3, 4, 5, 6, 8, \ldots$

Cubic body centred cell : $h^2+k^2+l^2= 2, 4, 6, 8, 10, 12, 14, 16, \ldots$

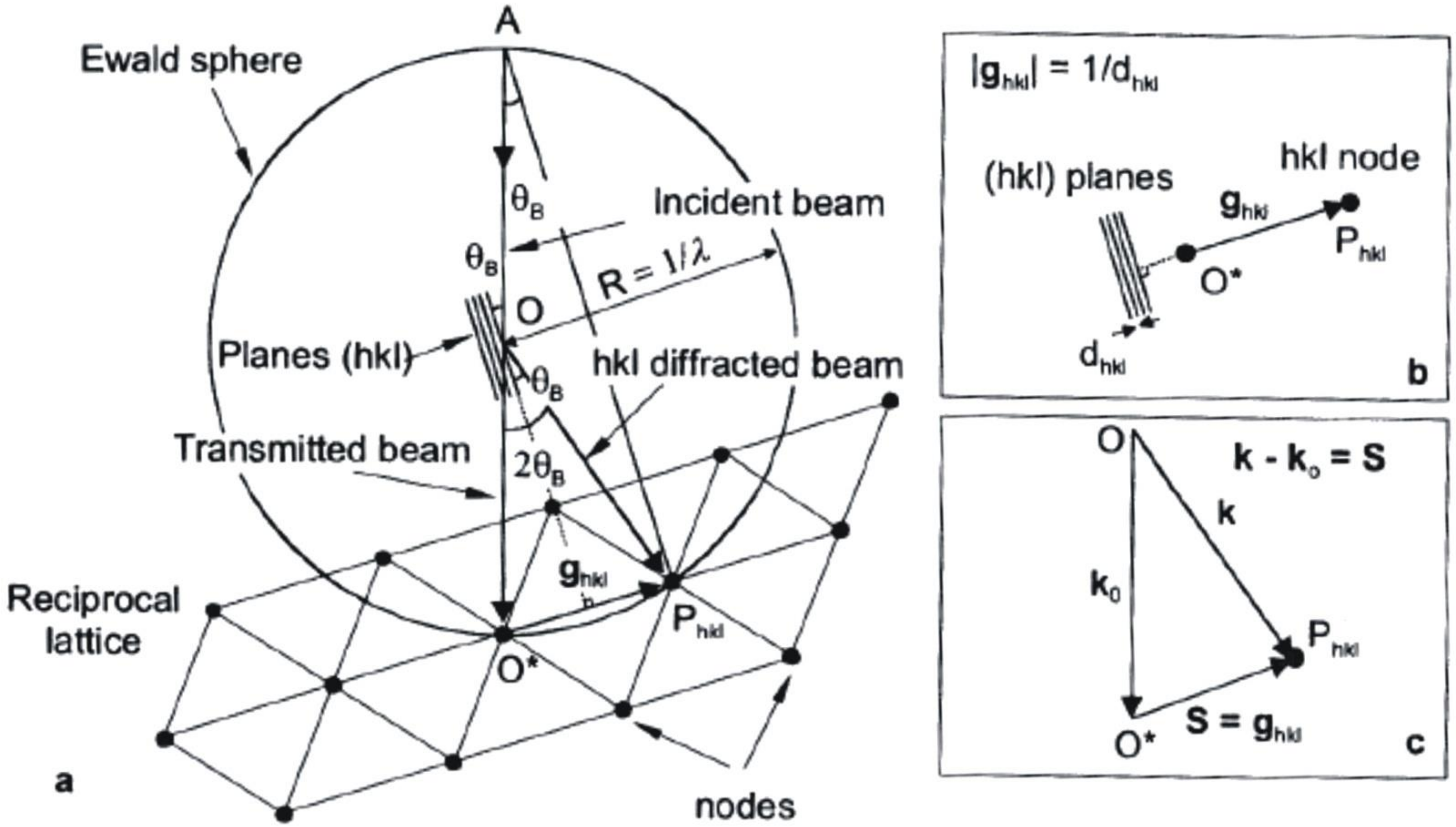
Cubic face centred cell : $h^2+k^2+l^2= 3, 4, 8, 11, 12, 16, \ldots$

Diffraction

reciprocal space



Ewald sphere construction. General Case.



a) A diffracted beam is produced if a hkl node of the reciprocal lattice is located exactly on the Ewald sphere. This situation occurs for the node P_{hkl}.

b) Relationship between a set of (hkl) lattice planes and its corresponding reciprocal lattice vector g_{hkl}. This vector is perpendicular to the (hkl) lattice planes and its modulus g_{hkl} is equal to $1/d_{hkl}$.

c) Vector description of Bragg's law. Bragg's law is satisfied when the scattering vector **S** is equal to the reciprocal lattice vector $\mathbf{g}_{hkl}$.

The principle of Laue Equation
Reciprocal space

All the reciprocal lattice points can be described by a linear combination of multiples of three basis vectors: $\vec{b}_1, \vec{b}_2, \vec{b}_3$. Its definition is equivalent to the following relations:

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

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

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

An interesting property of the reciprocal lattice vector is that the relations are still valid if we replace lattice vectors by reciprocal lattice vectors and inversely reciprocal lattice vectors by lattice vectors. If V* is the volume of the reciprocal unit cell, the reader can show that the expression VV* = 1 is also valid.

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Now a reciprocal lattice vector $\vec{h}$ can be define by a linear combination of integer multiples of the three reciprocal lattice vectors:

$$\vec{h} = h\overrightarrow{b_1} + k\overrightarrow{b_2} + l\overrightarrow{b_3}$$

The reciprocal vectors play an important role in diffraction.

Miller indices

By construction, every reciprocal lattice vector is normal to a series of lattice planes. We know also that the faces of a crystal are parallel to lattice planes and therefore normal to the reciprocal vectors. We can therefore uniquely characterise each face of a crystal by the integer components of a reciprocal vector with one important subtlety. A face normal to vector $\vec{h}$ cannot be distinguished from a normal to vector $n\vec{h}$. Therefore, we shall characterise each face of a crystal by three integer components but without any common denominator. The triplet **(h,k,l)** satisfying this condition is called the Miller indices of the face. With this specification, we realise that Miller indices are only a subset of the possible reciprocal lattice vectors.

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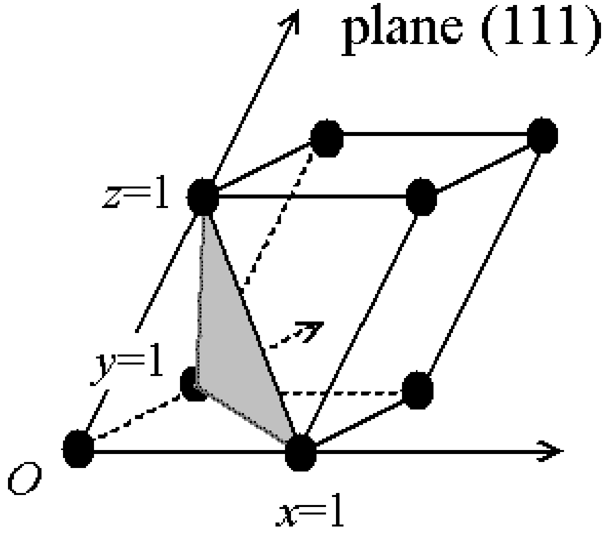
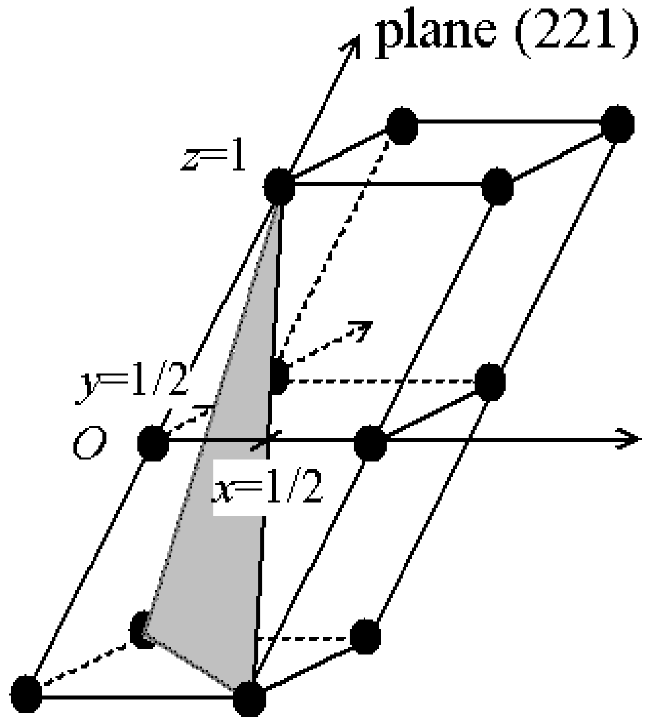
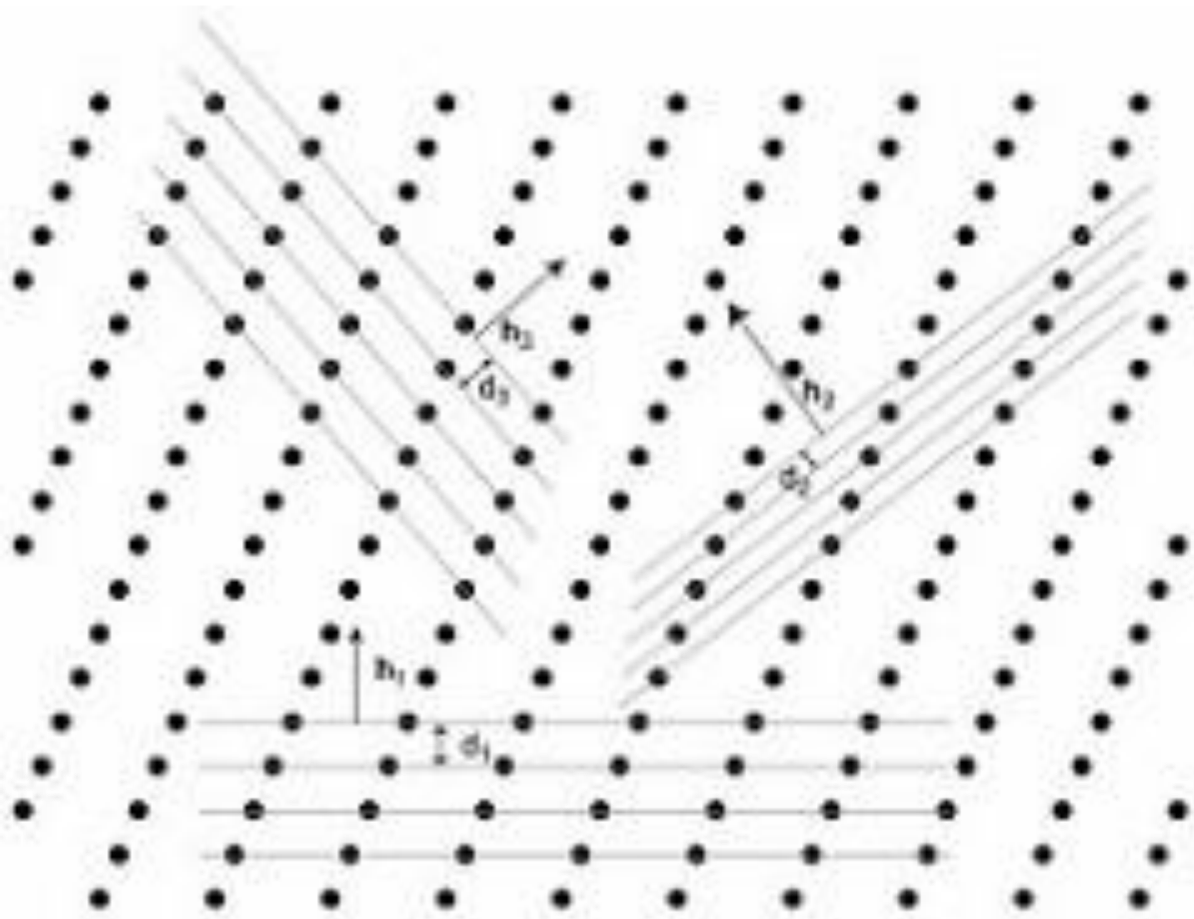
Miller indicators

The plane intersects the axes of the crystal at certain points, cutting off segments of a certain length. The ratio of the net constant to the length of these sections, multiplied by the constant, gives Miller indicators of this plane. The constant must be chosen so that the indicators are as low as possible in absolute terms. Where the plane is parallel to either axis, the intersection is infinite, giving a Miller Index of 0.



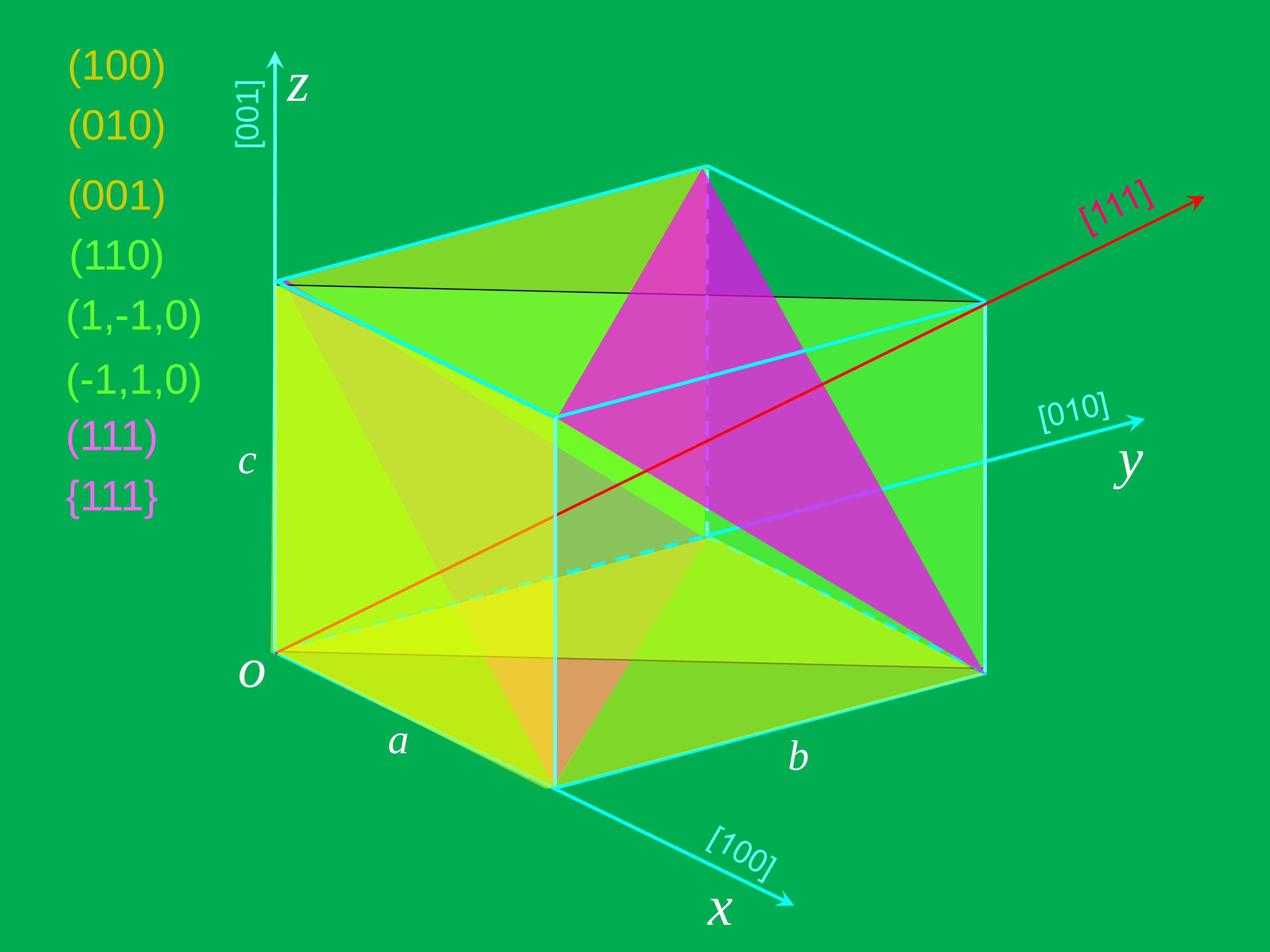


An abstraction of a crystalline structure where only the nodes of the lattice are given. We have also reported a series of lattice planes with distances d_i and the corresponding normal $\vec{h_i}$ to the series of planes.



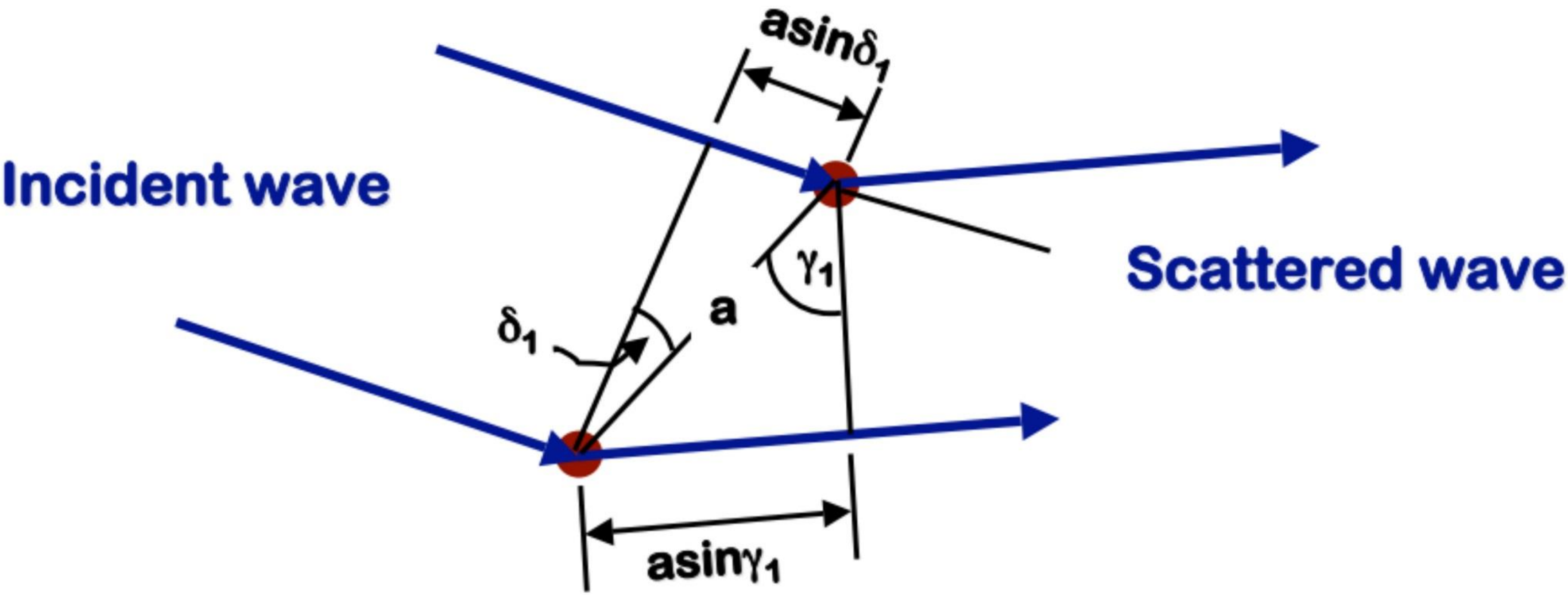
An important relation between the distances d and the reciprocal lattice vector $\vec{h}$ normal to the series of equidistant planes :

$$d = \frac{1}{|\vec{h}|}$$



(100)
(010)
(001)
(110)
(1,-1,0)
(-1,1,0)
(111)
{111}
z
[001]
[111]
[010]
y
c
O
a
b
[100]
x

Laue Equations



Constructive interference when:

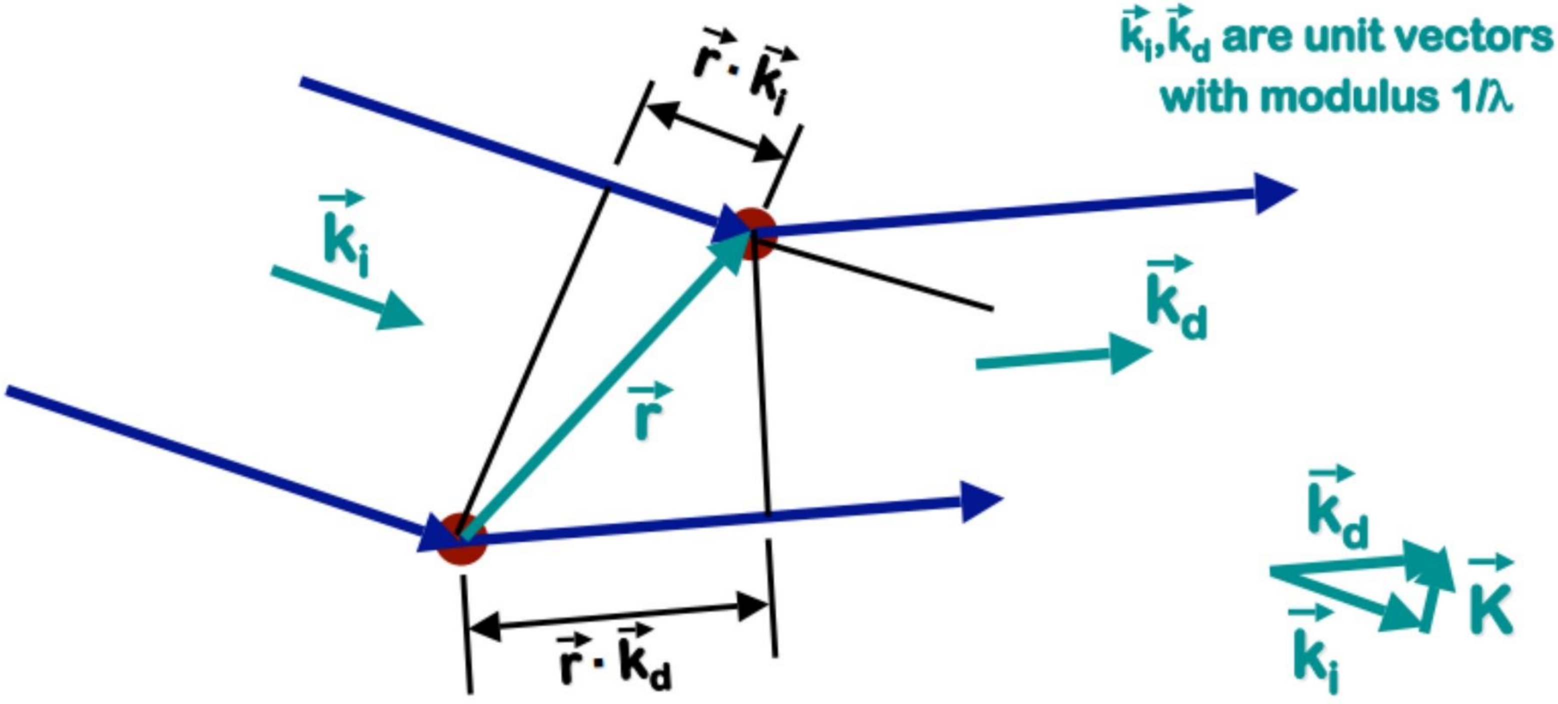
$$a(\sin\gamma_1 - \sin\delta_1) = h\lambda$$

$$b(\sin\gamma_2 - \sin\delta_2) = k\lambda$$

$$c(\sin\gamma_3 - \sin\delta_3) = l\lambda$$

h,k,l = integers

Laue Equations



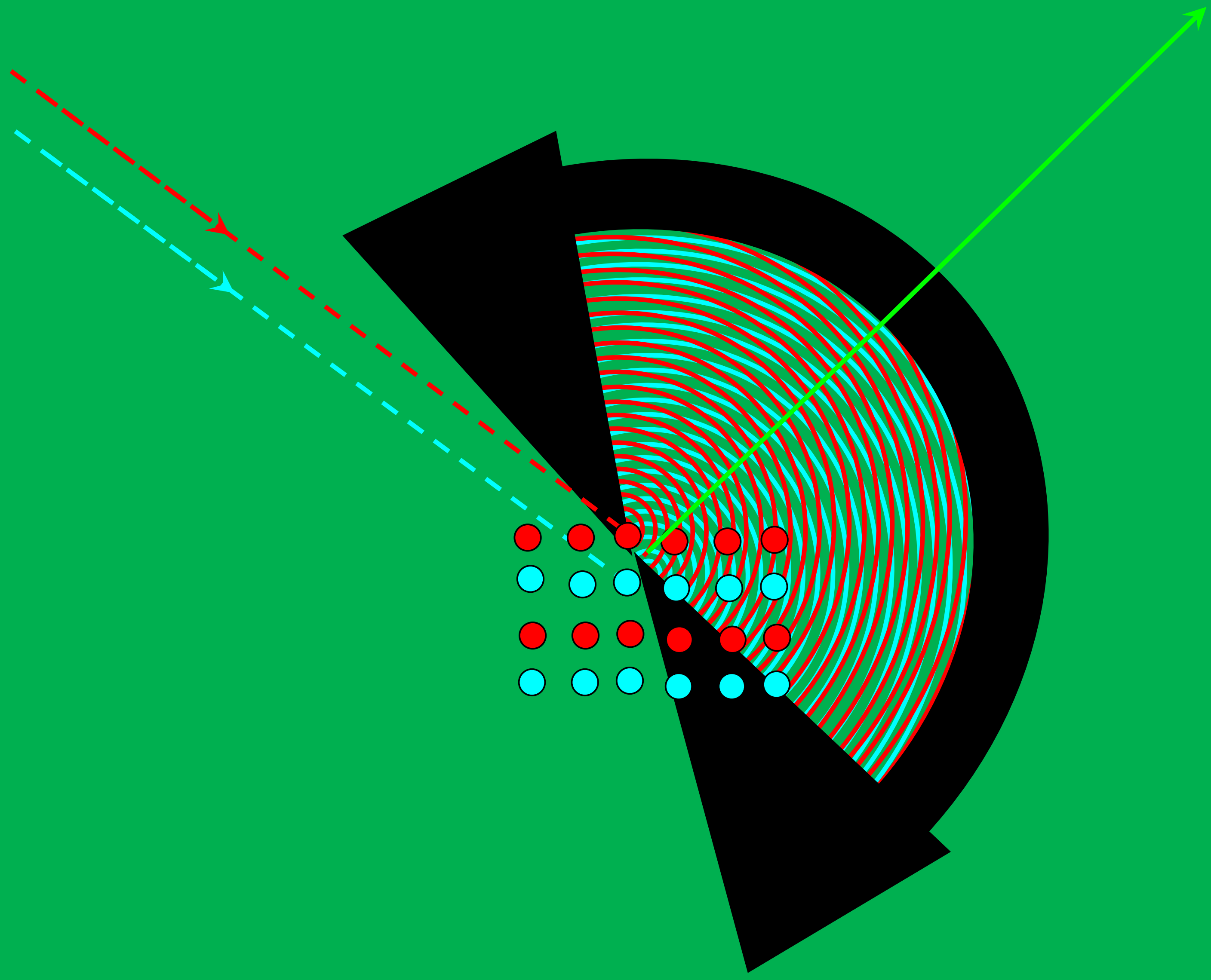
$$\vec{r}\cdot\left(\vec{k}_d-\vec{k}_i\right)=\vec{r}\cdot\vec{K}=m \quad \text{with } m=\text{integer}$$

Resolve onto lattice unit vectors

$$\vec{K}\cdot\vec{a}=h$$
$$\vec{K}\cdot\vec{b}=k$$
$$\vec{K}\cdot\vec{c}=l$$

with h,k,l = integers

Scattering on many atomic layers in crystalline materials



Reciprocal lattice

proofs

Prove: $\vec{g} \perp (hkl)$

1.) $\frac{\vec{a}}{h} + \overrightarrow{AB} = \frac{\vec{b}}{k}$

$\overrightarrow{AB} = \frac{\vec{b}}{k} - \frac{\vec{a}}{h}$

2.) Is $\vec{g} \perp \overrightarrow{AB}$?

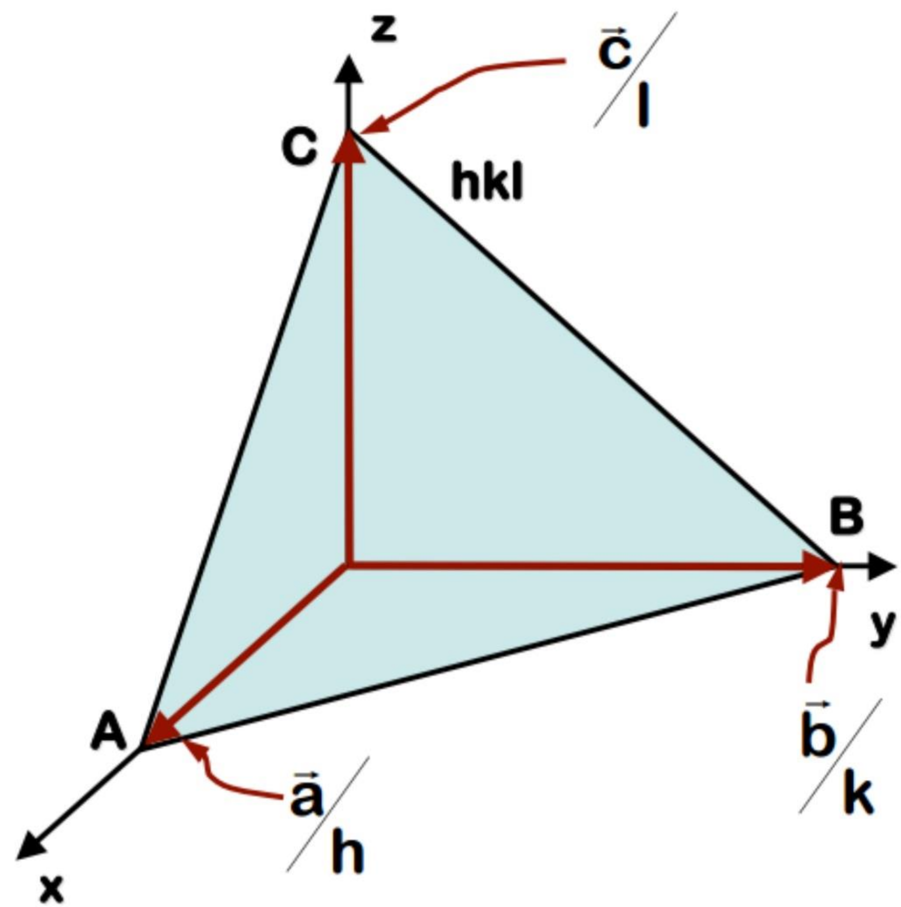
$\vec{g} \cdot \overrightarrow{AB} = 0$

$\left(ha^* + kb^* + lc^*\right) \cdot \left(\frac{\vec{b}}{k} - \frac{\vec{a}}{h}\right) = 0$

3.) Can repeat to show:

$\vec{g} \perp \overrightarrow{AC}$

4.) $\vec{g} \perp (hkl)$



$$\vec{a}^* \cdot \vec{b} = \vec{a}^* \cdot \vec{c} = \vec{b}^* \cdot \vec{c} = \vec{b}^* \cdot \vec{a} = \vec{c}^* \cdot \vec{a} = \vec{c} \cdot \vec{b} = 0$$

$$\vec{a}^* \cdot \vec{a} = \vec{b}^* \cdot \vec{b} = \vec{c}^* \cdot \vec{c} = 1$$

Reciprocal lattice

proofs

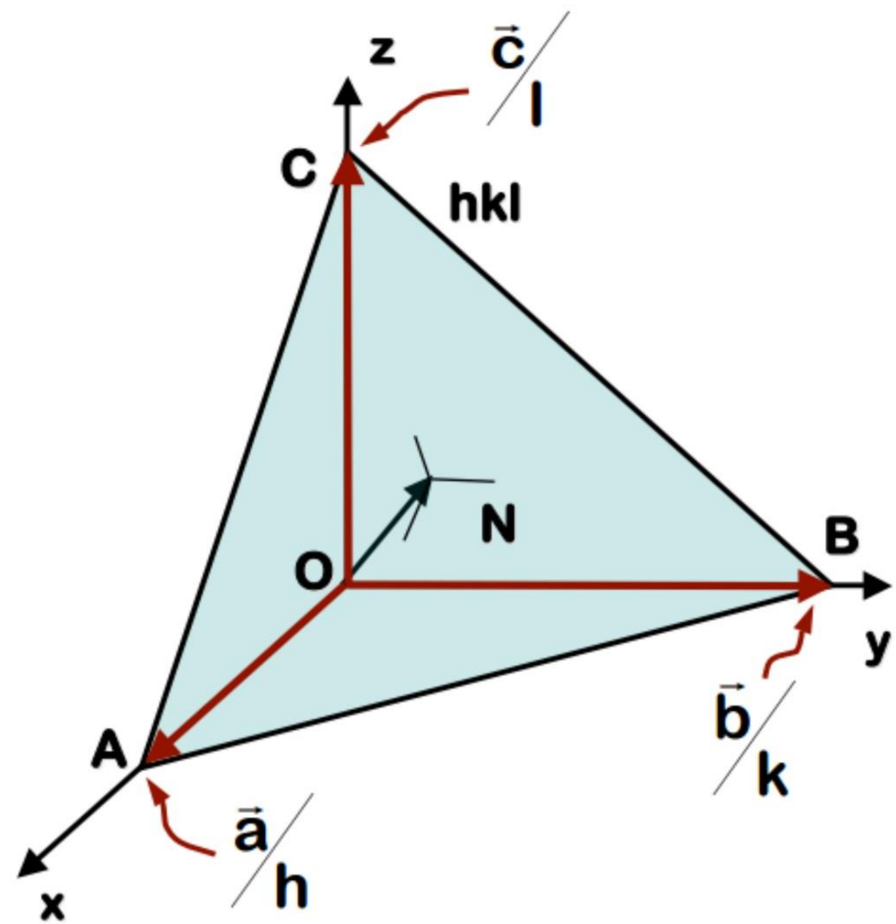
Prove: $\left|\vec{g}\right| = \frac{1}{d_{hkl}}$

Shortest distance must be projection of real lattice vector on to a unit vector in direction $\vec{g}$ (define as $\vec{n}$)

$$d_{hkl} = ON = \frac{\vec{a}}{h}\cdot\vec{n} = \frac{\vec{a}}{h}\cdot\frac{\vec{g}}{\left|\vec{g}\right|}$$

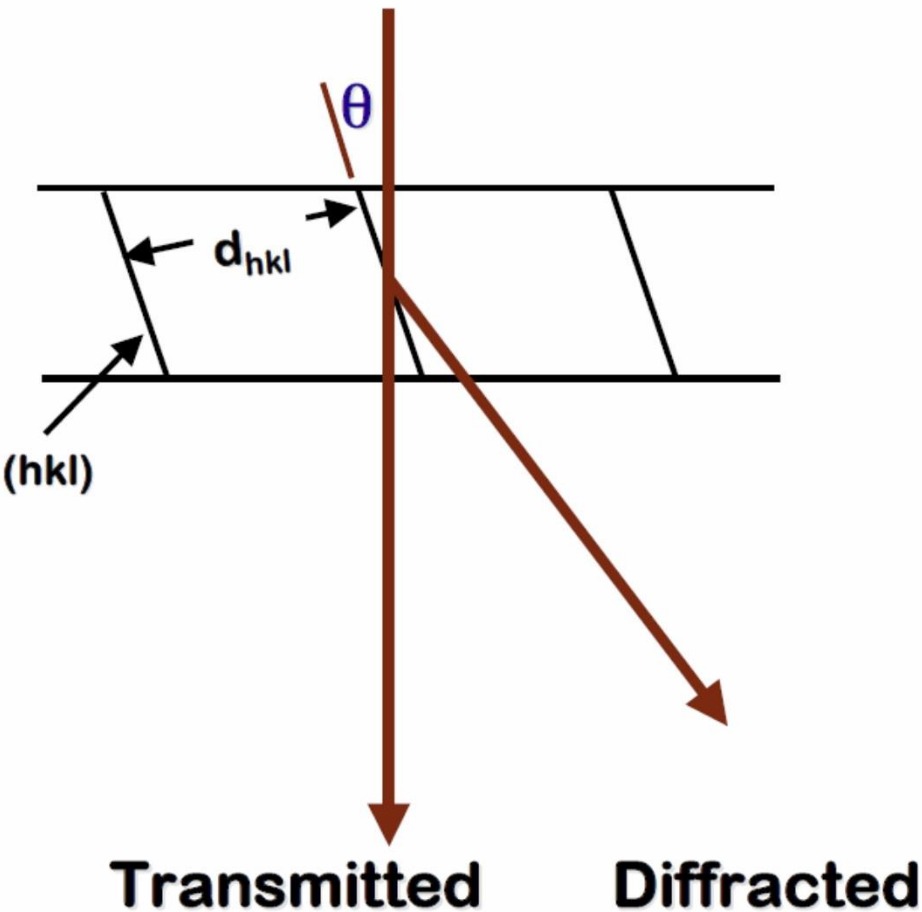
$$d_{hkl} = \frac{\vec{a}}{h}\cdot\frac{h\vec{a}^{*}+k\vec{b}^{*}+l\vec{c}^{*}}{\left|\vec{g}\right|} = \frac{1}{\left|\vec{g}\right|}$$

$$\left|\vec{g}\right| = \frac{1}{d_{hkl}}$$

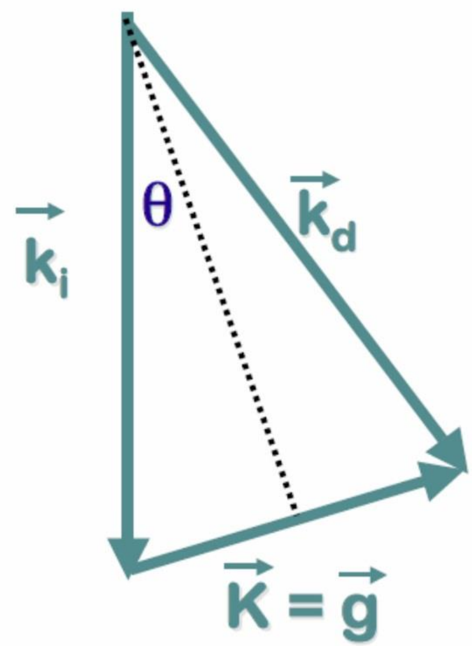


Diffraction

real space vs. reciprocal space

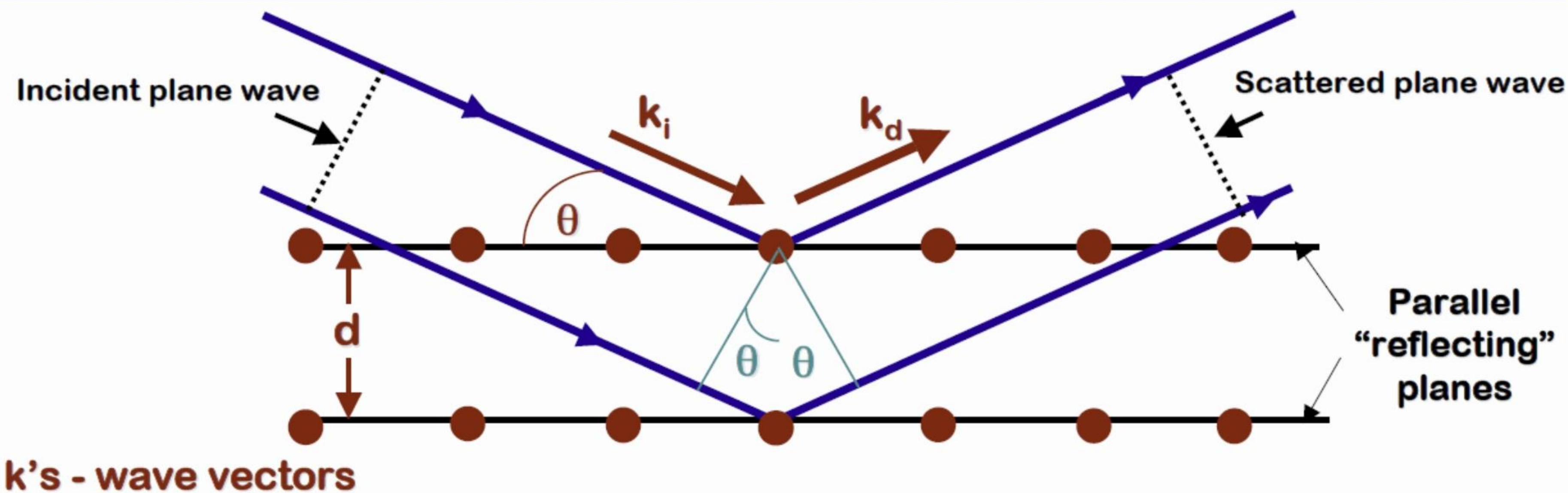


Real space

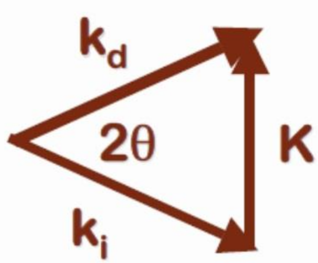


Reciprocal space

Bragg's Law



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



$$\vec{k}_d - \vec{k}_i = \vec{K}$$

$$|\vec{K}| = \frac{2\sin\theta}{\lambda} = \frac{n}{d}$$

$$\vec{K} = \vec{g}$$

$$|\vec{K}| \propto \frac{1}{\lambda} \quad \& \quad |\vec{K}| \propto \frac{1}{d}$$

Laue Equations & Bragg's Law

Laue Equations have sol^n:

$$\vec{K} = h\vec{a}^* + k\vec{b}^* + l\vec{c}^* = \vec{g}$$

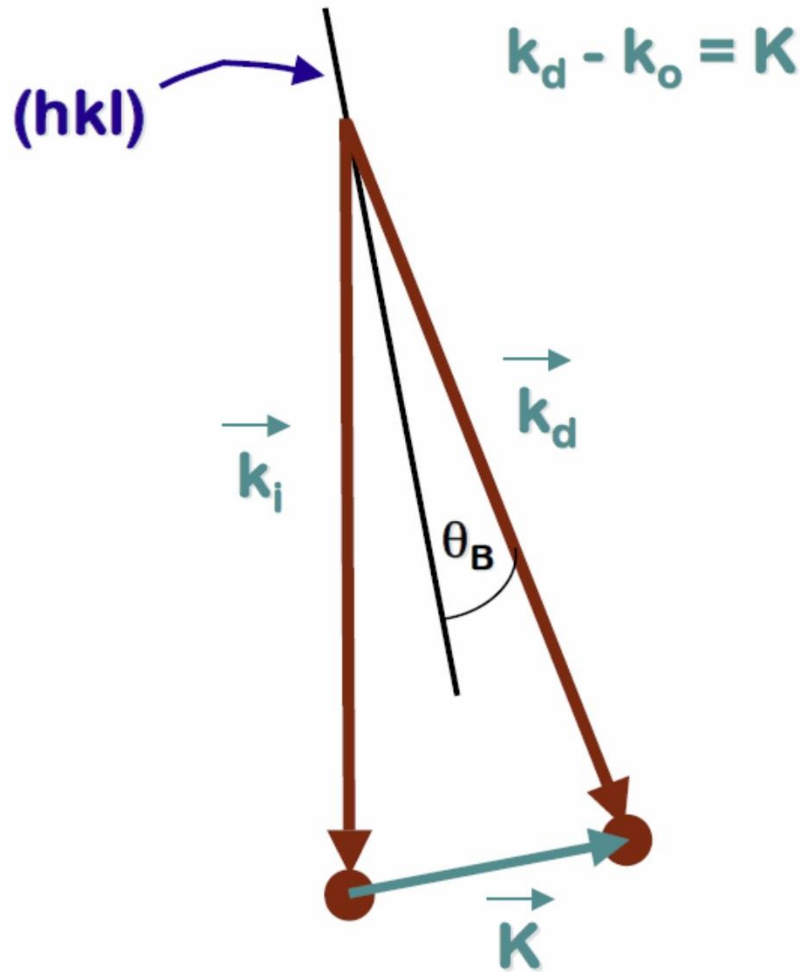
We have shown that:

$$\left|\vec{K}\right| = \frac{2\sin\theta_B}{\lambda} \quad \& \quad \left|\vec{g}\right| = \frac{1}{d_{hkl}}$$

We recover Bragg's Law:

$$\frac{2\sin\theta_B}{\lambda} = \frac{1}{d_{hkl}}$$

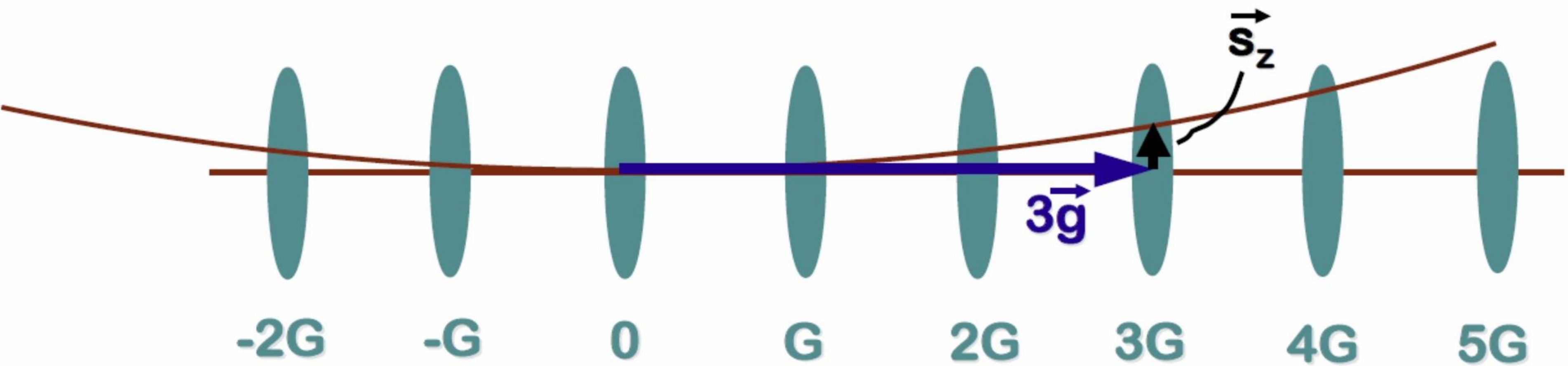
$$2d_{hkl}\sin\theta_B = \lambda$$

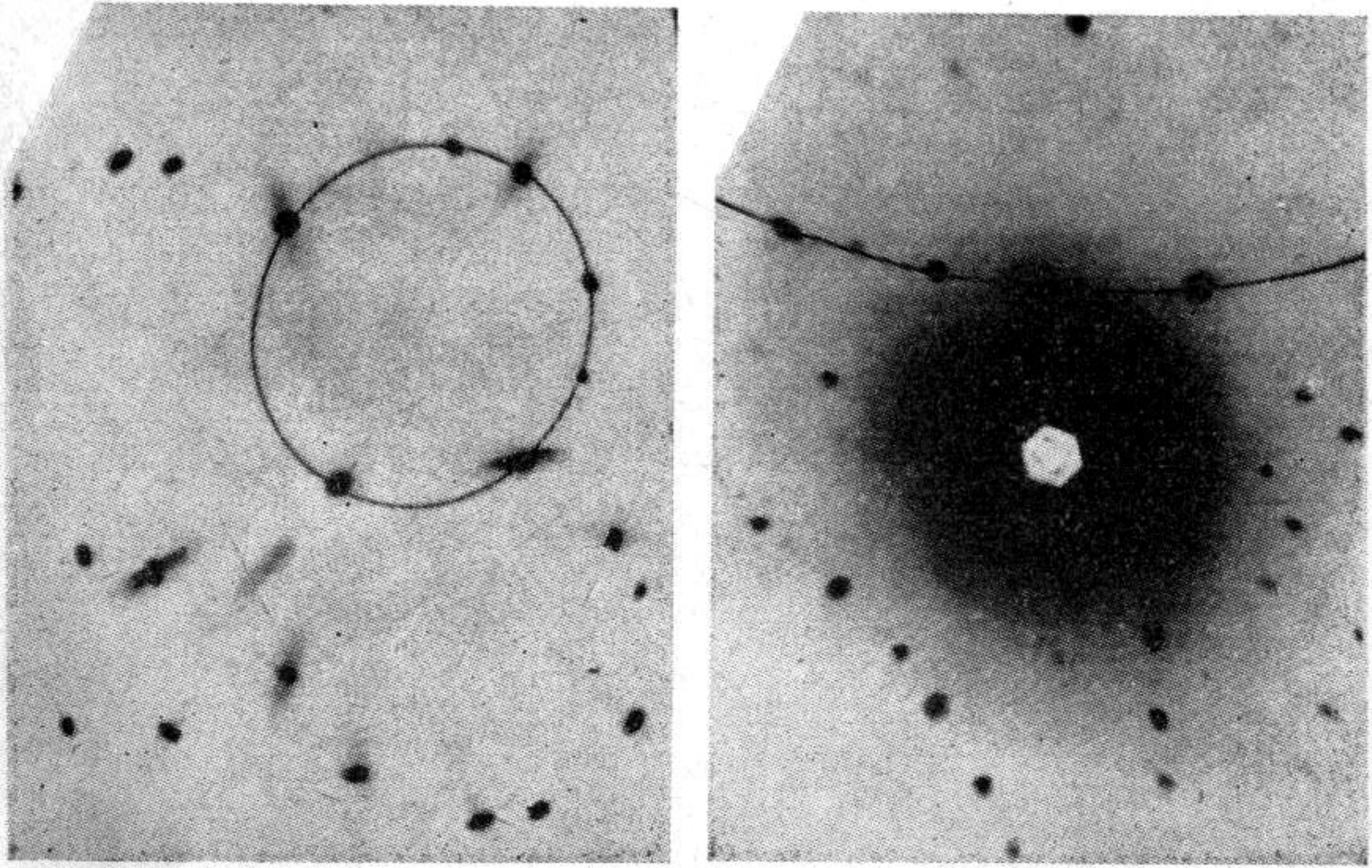


Ewald Sphere and Rel-rods

Presence of rel-rods “relaxes” diffraction requirements

New vector - $\vec{s}$ - called “deviation parameter”

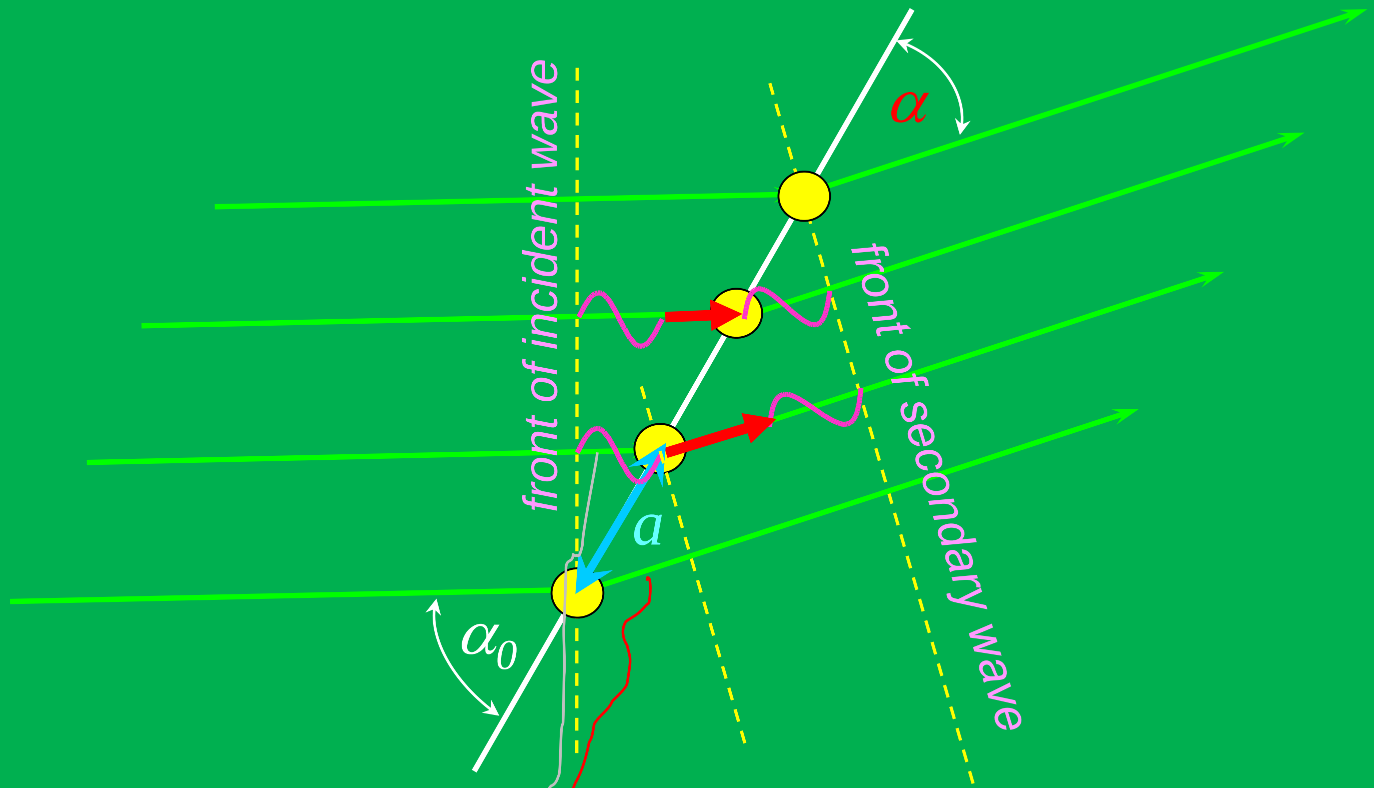




a) b)

Rys. 3.6. Lauegramy wykonane metodą: a) promieni przechodzących i b) promieni zwrotnych. Promieniowanie anody wolframowej 30 kV, 19 mA

Scattering on many atom layers in crystalline materials



Condition of X-ray diffraction on a lattice axis: $\Delta S = a(\cos\alpha - \cos\alpha_0) = H\lambda$

$$a(\cos\alpha - \cos\alpha_0) = H\lambda$$
$$b(\cos\beta - \cos\beta_0) = K\lambda$$
$$c(\cos\gamma - \cos\gamma_0) = L\lambda$$

LAUE's equations (condition of X-ray diffraction on a space lattice of crystal)

Thank you

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