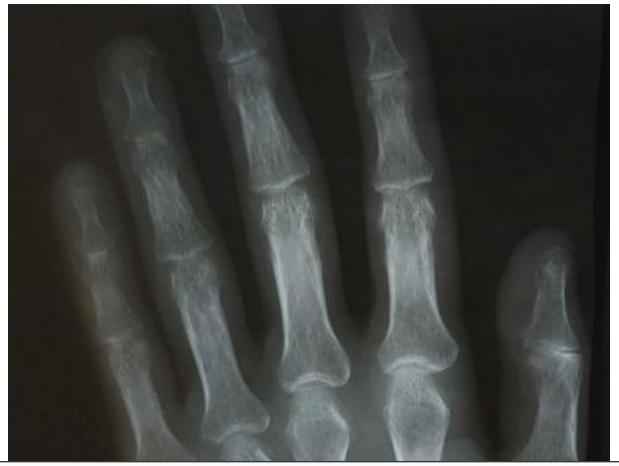
Solid state physics for Nano

Lecture 2: X-ray diffraction

Prof. Dr. U. Pietsch

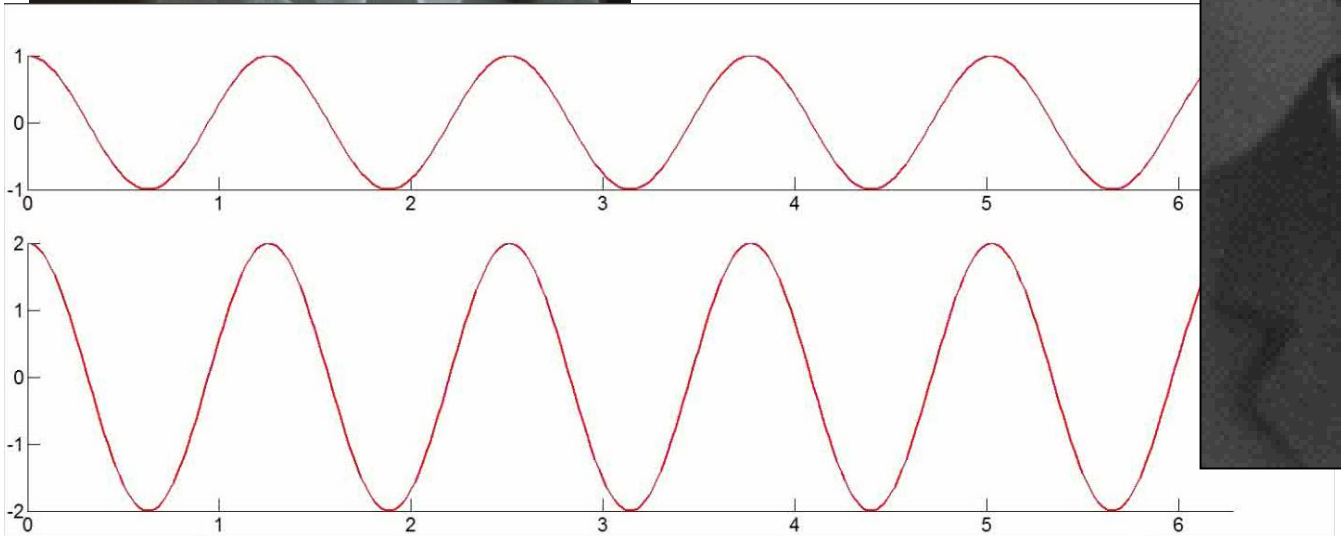
The mean aim of Max von Laue (1912)

X-rays are electromagnetic wave with wave length much smaller than wave length of visible light. X-rays are diffracted a crystal lattice

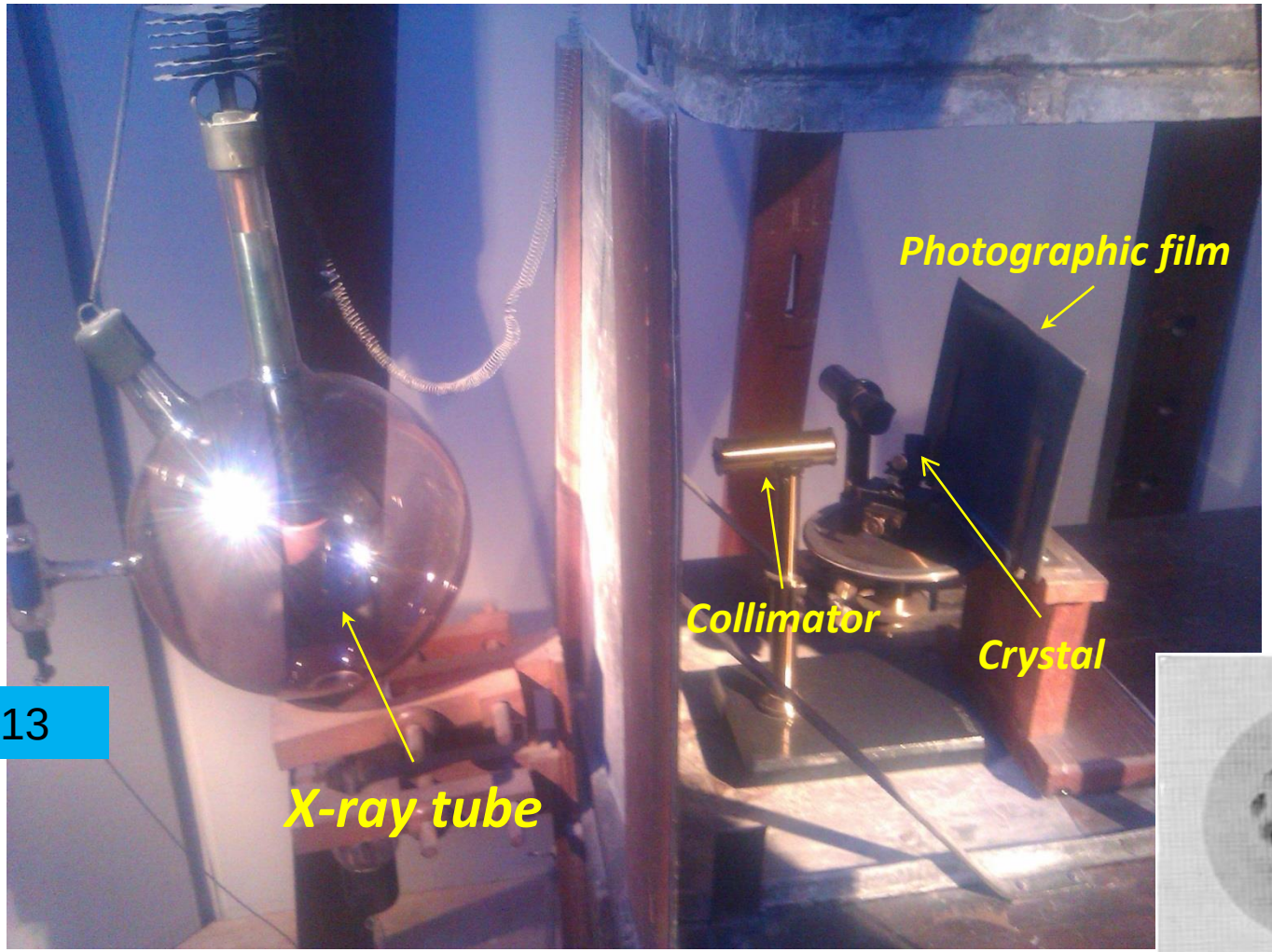


1914

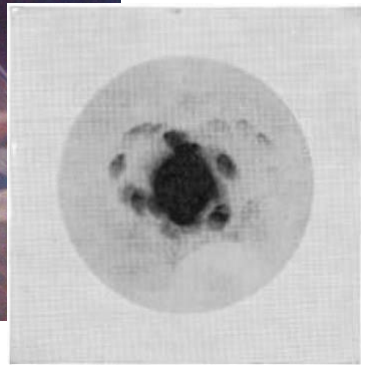
Nobelpreis für Physik



Original experiment von Laue, Friedrich und Knipping

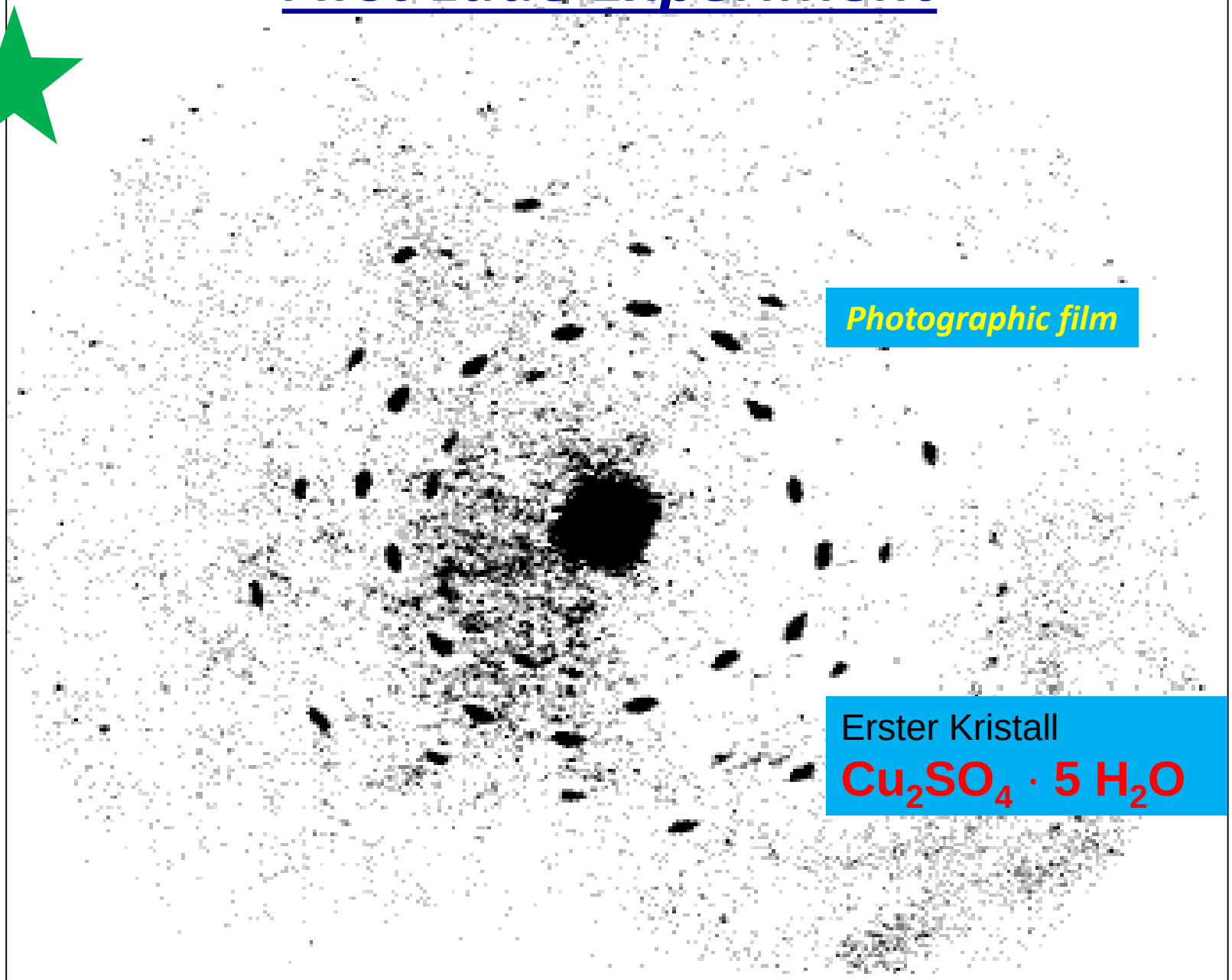


20.April 1913



Ausgestellt im Deutschen Museum in München

First Laue Experiment



Photographic film

Erster Kristall

$Cu_2SO_4 \cdot 5\ H_2O$

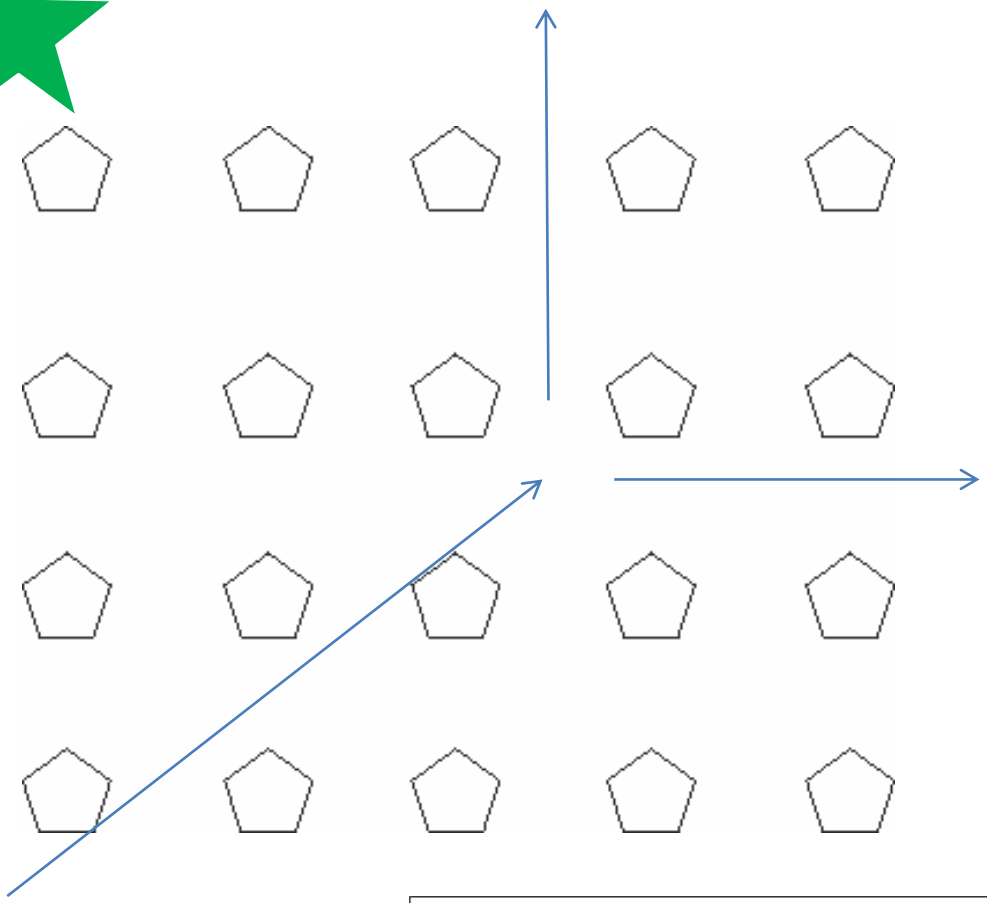
1912: Begin of modern Crystallography

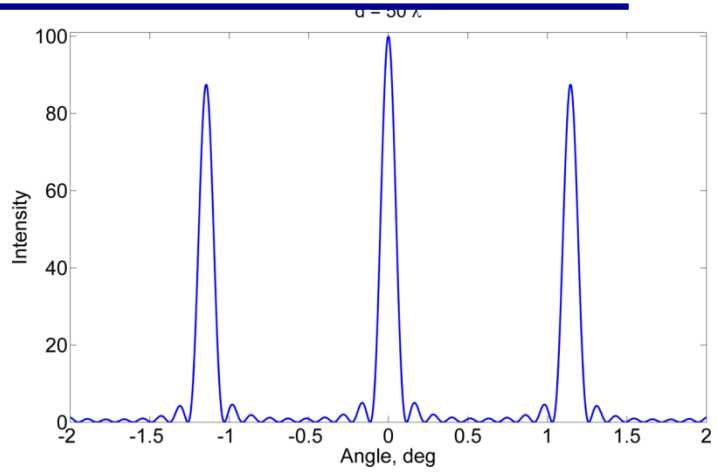
X-rays are electromagnetic waves of very short wavelength (~ 1 Å = 10^{-10} m).

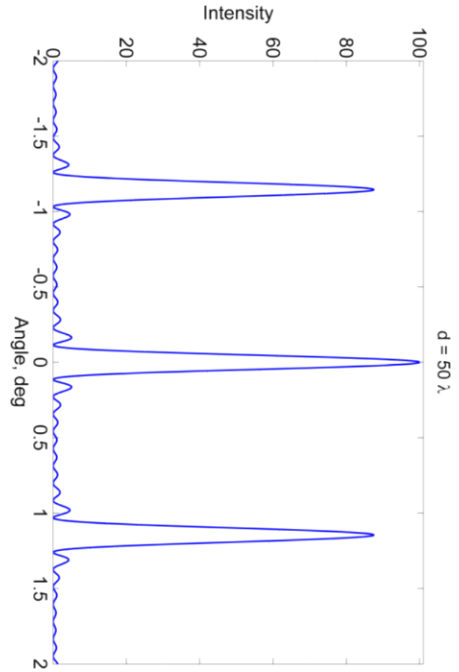
Crystals are periodic structures in 3D : interatomic distances are of similar order of magnitude as x-ray wave length

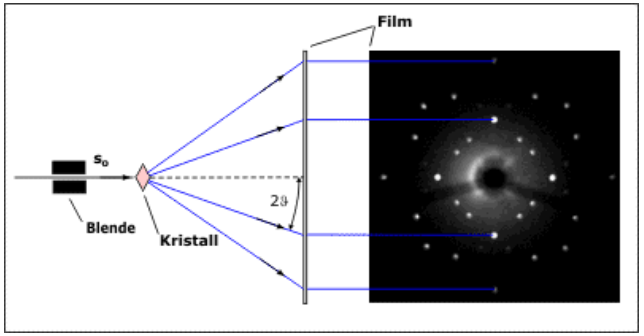
X-ray diffraction is a method to determine the geometric structure of solids !

Erklärung durch Interferenz am 3D Gitter





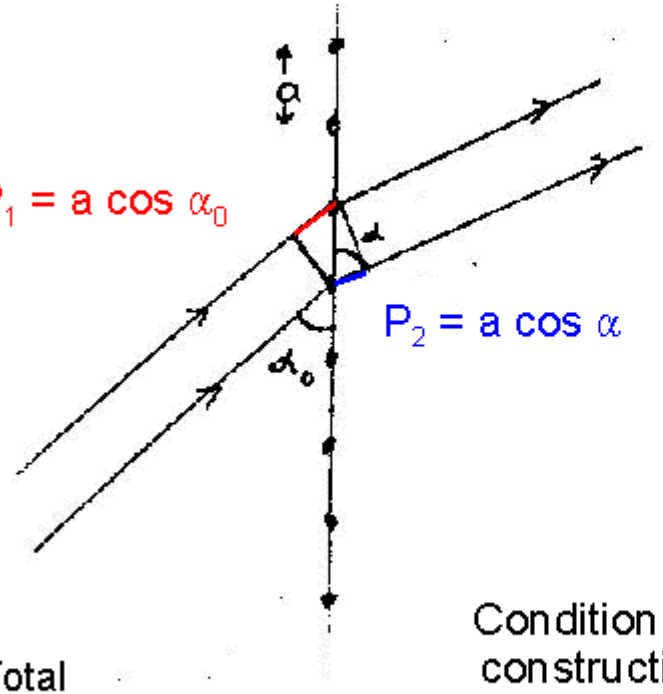




Explanation of Laue pattern

von Laue Equation

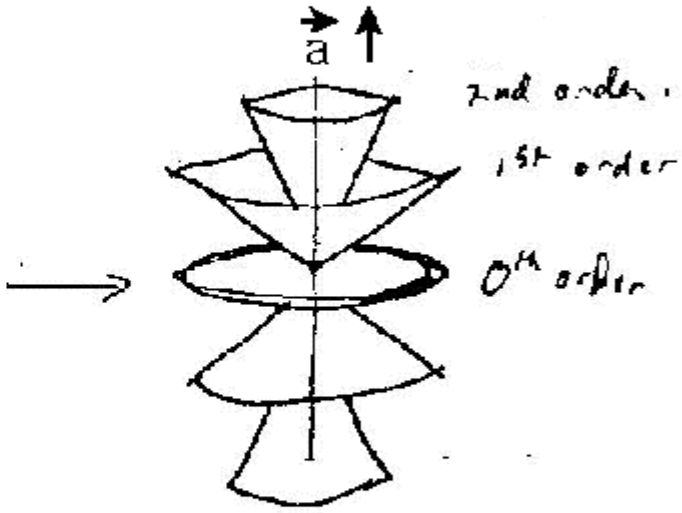
Scattering from a line of atoms along "a"



Total Path difference

Condition for constructive interference

$$P_2 - P_1 = a (\cos \alpha - \cos \alpha_0) = h \lambda$$

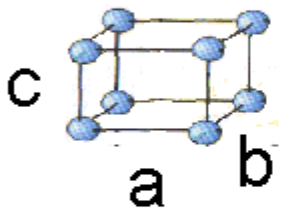


Constructive interference along conical surfaces about a-axis

von Laue Equation

For a crystal with cell parameters

$\vec{a}$, $\vec{b}$, $\vec{c}$



We have three von Laue equations

$$a (\cos \alpha - \cos \alpha_0) = h \lambda$$
$$b (\cos \beta - \cos \beta_0) = k \lambda \qquad ①$$
$$c (\cos \gamma - \cos \gamma_0) = l \lambda$$

Where $\cos \alpha_0$, $\cos \beta_0$, $\cos \gamma_0$ are the direction cosines of the incident ray and $\cos \alpha$, $\cos \beta$, $\cos \gamma$ are the direction cosines of the reflected ray in the crystal axis.

So, we must also satisfy

$$\cos^2 \alpha_0 + \cos^2 \beta_0 + \cos^2 \gamma_0 = 1$$
$$\cos^2 \alpha + \cos^2 \beta + \cos^2 \gamma = 1 \qquad ②$$

Using that the angle between the incident and reflected ray is 2θ

③ $\cos 2\theta = \cos \alpha \cos \alpha_0 + \cos \beta \cos \beta_0 + \cos \gamma \cos \gamma_0$

von Laue Equation

We square the von Laue Equations

$$\frac{h^2\lambda^2}{a^2} = \cos^2\alpha - 2\cos\alpha\cos\alpha_0 + \cos^2\alpha_0$$

①^2

$$\frac{k^2\lambda^2}{b^2} = \cos^2\beta - 2\cos\beta\cos\beta_0 + \cos^2\beta_0$$

$$\frac{l^2\lambda^2}{c^2} = \cos^2\gamma - 2\cos\gamma\cos\gamma_0 + \cos^2\gamma_0$$

$$\left(\frac{h^2}{a^2}+\frac{k^2}{b^2}+\frac{l^2}{c^2}\right)\lambda^2 = 1 - 2\left(\cos\alpha\cos\alpha_0 + \cos\beta\cos\beta_0 + \cos\gamma\cos\gamma_0\right) + 1$$

Using eq. ③

$$\left(\frac{h^2}{a^2}+\frac{k^2}{b^2}+\frac{l^2}{c^2}\right)\lambda^2 = 2(1-\cos 2\theta)$$

Trig. Identity

$$\left(\frac{h^2}{a^2}+\frac{k^2}{b^2}+\frac{l^2}{c^2}\right)\lambda^2 = 4\sin^2\theta$$

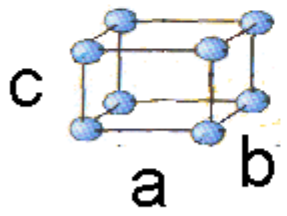
General Bragg law

$$\left(\frac{h^2}{a^2}+\frac{k^2}{b^2}+\frac{l^2}{c^2}\right)^{1/2}\lambda = 2\sin\theta$$

Reciprocal Lattice

For a crystal with cell parameters

$\vec{a}, \vec{b}, \vec{c}$



A vector connecting 2 lattice points in reciprocal space can be written

Reciprocal lattice is constructed using vectors

$\vec{a}^*, \vec{b}^*, \vec{c}^*$

$\vec{a}^*$ is normal to the bc plane and $|\vec{a}^*| = \frac{2\pi}{a}$

$\vec{b}^*$ is normal to the ac plane and $|\vec{b}^*| = \frac{2\pi}{b}$

$\vec{c}^*$ is normal to the ab plane and $|\vec{c}^*| = \frac{2\pi}{c}$

recip. lattice vector $\vec{G} = h\vec{a}^* + k\vec{b}^* + l\vec{c}^*$

$$|\vec{G}| = \left[\left(h\vec{a}^*\right)^2 + \left(k\vec{b}^*\right)^2 + \left(l\vec{c}^*\right)^2\right]^{1/2} = 2\pi\left(\frac{h^2}{a^2}+\frac{k^2}{b^2}+\frac{l^2}{c^2}\right)^{1/2}$$

General Bragg law

$$2\pi\left(\frac{h^2}{a^2}+\frac{k^2}{b^2}+\frac{l^2}{c^2}\right)^{1/2}=\frac{4\pi}{\lambda}\sin\theta$$

$\vec{G}$ are the reciprocal vectors of the reciprocal lattice

$$|\vec{G}|=\frac{4\pi}{\lambda}\sin\theta$$

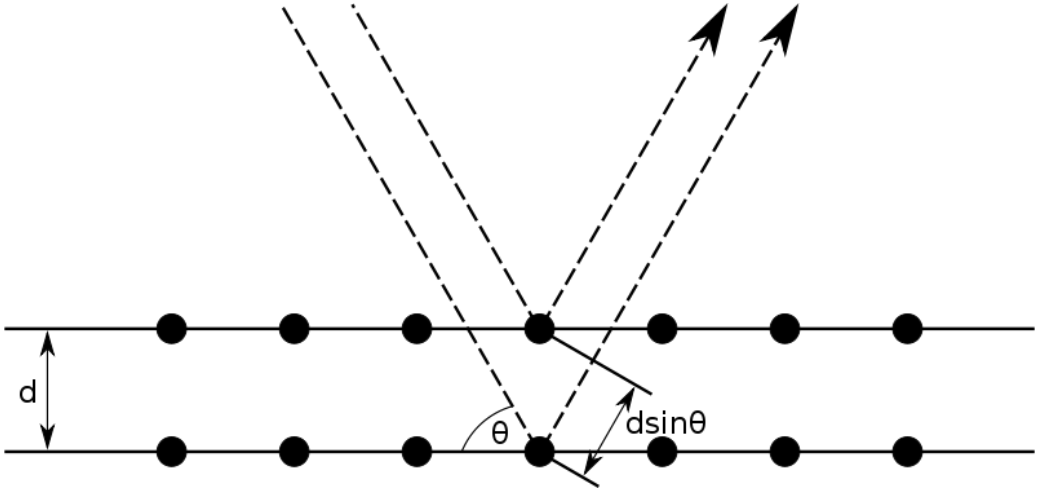
$a=b=c$

$$2\pi\frac{\sqrt{h^2+k^2+l^2}}{a}=\frac{4\pi}{\lambda}\sin\theta$$

$$\lambda=2\frac{a}{\sqrt{h^2+k^2+l^2}}\sin\theta$$

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

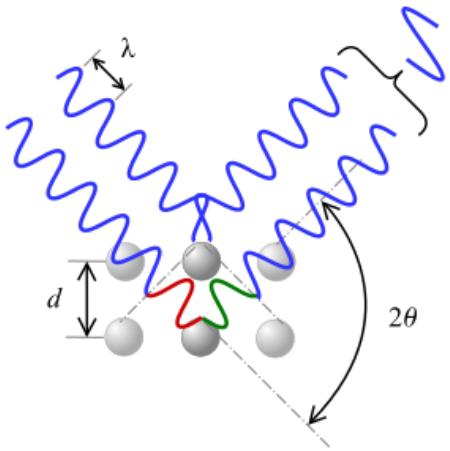
Alternative description of Laue-pattern by W.H.Bragg und W.L.Bragg

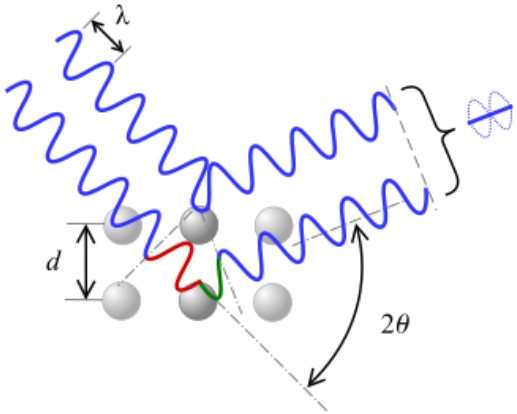


Interference at dense backed „lattice planes“

Bragg equation

$$N\lambda = 2d\sin\Theta$$





Reciprocal space, Ewald construction

$$a^* a = 2\pi$$

$$b^* b = 2\pi$$

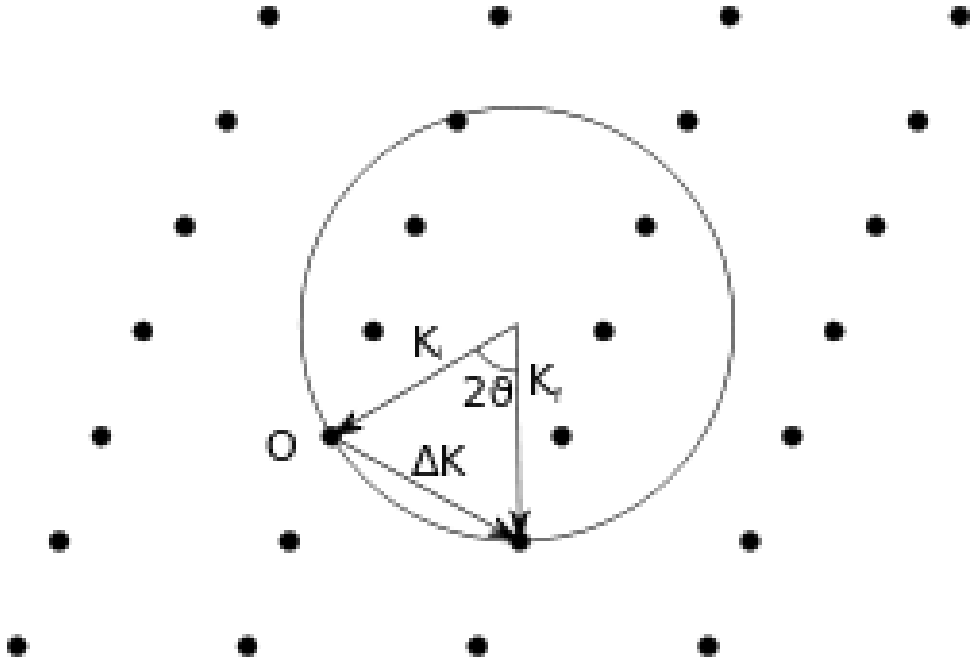
$$c^* c = 2\pi$$

$$a^* b = 0, b^* c = 0, \ldots.$$

$$a^* = \frac{b \times c}{a(b \times c)}$$

$$b^* = \frac{c \times a}{a(b \times c)}$$

$$c^* = \frac{a \times b}{a(b \times c)}$$

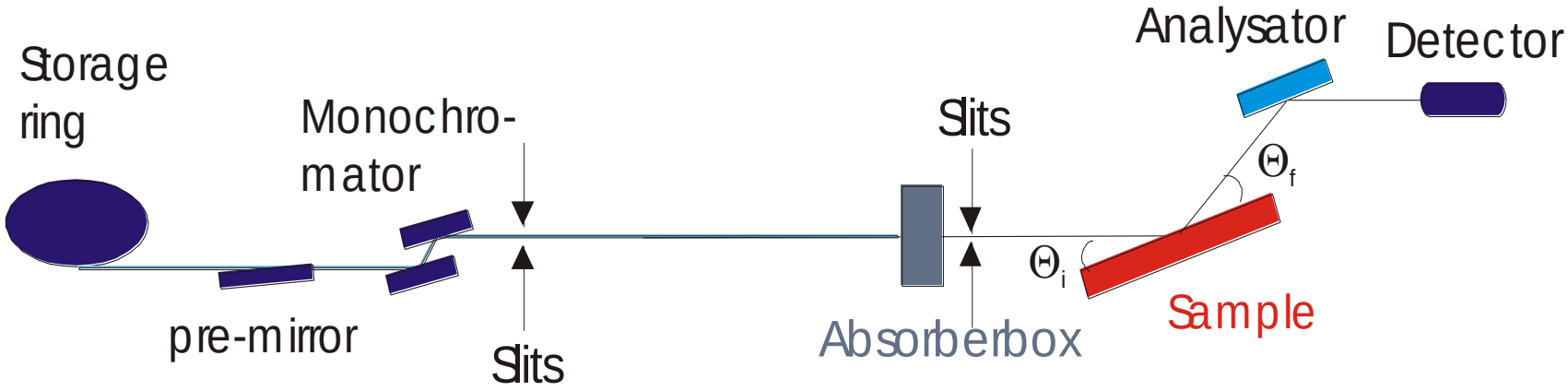


$$k_i = k_f = \frac{2\pi}{\lambda}$$

$$G = \frac{2\pi}{d(hkl)}$$

$$\Delta K = G = 2\pi(ha^* + kb^* + lc^*)$$

Setup of modern diffraction experiment

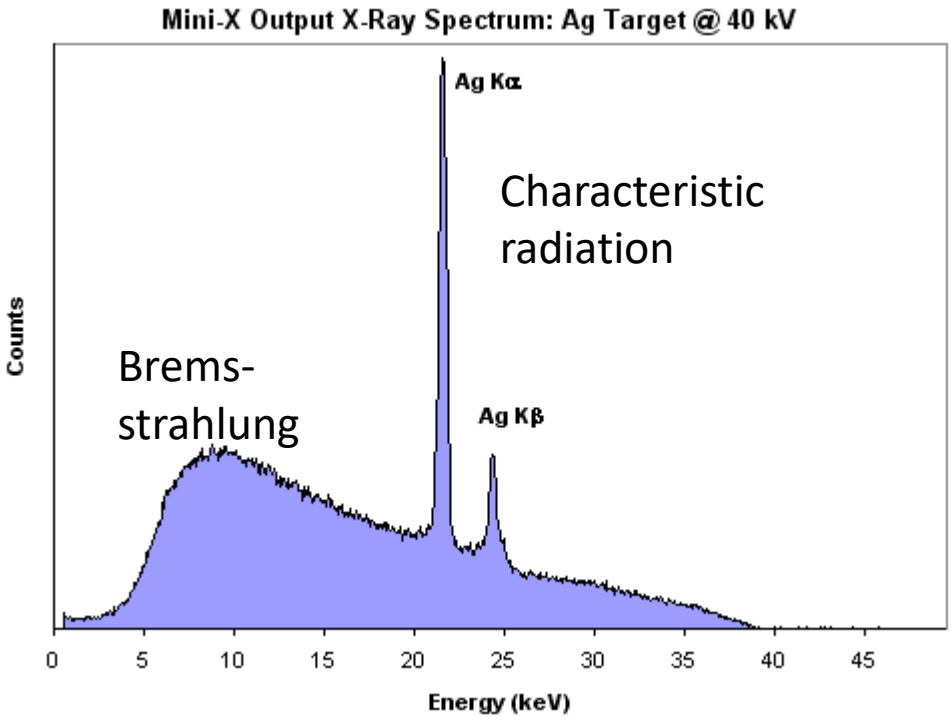


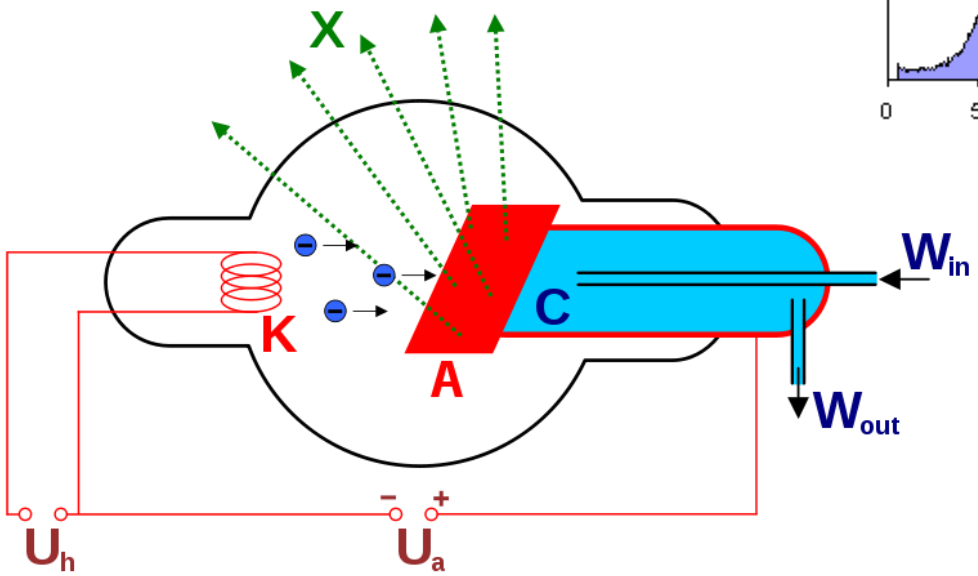
X-ray tube and tube spectrum

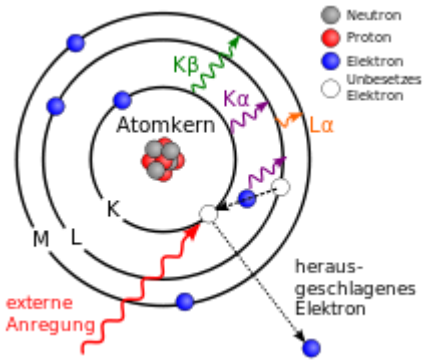
$E = h\,\nu = e\,U$

$\lambda_{min} = h\,c / e\,U_a$

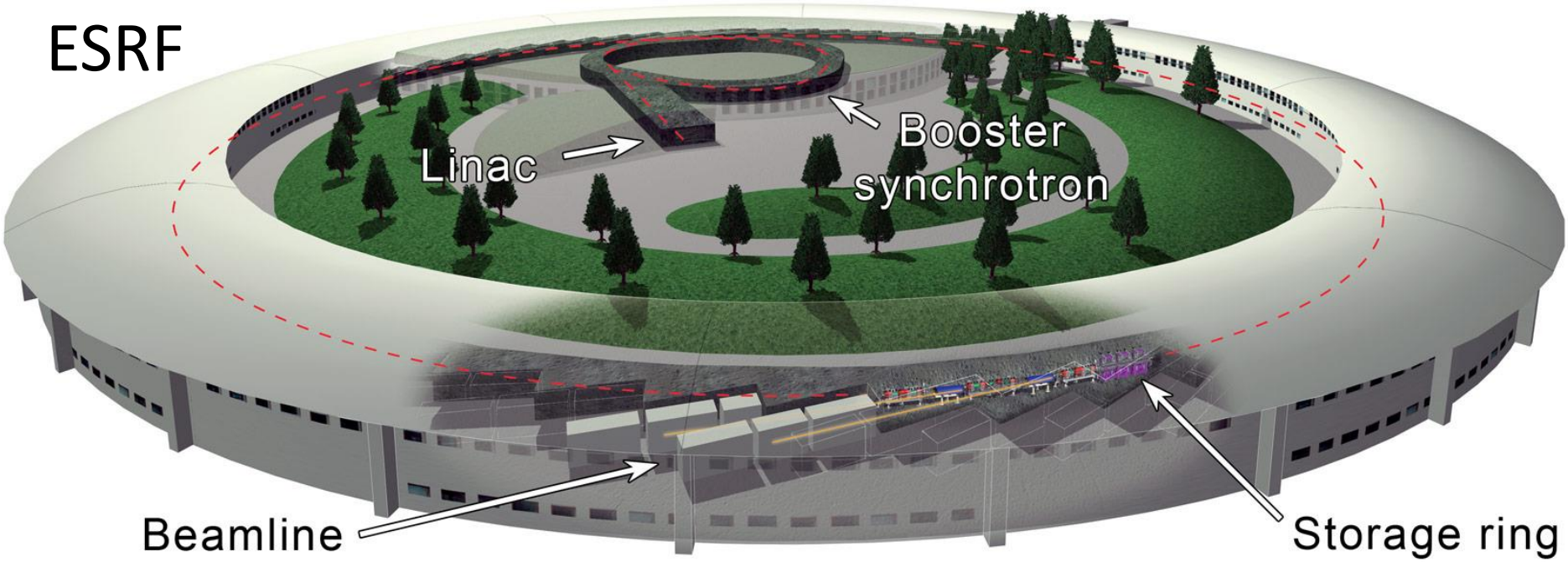
$\lambda_{min} = 12.4/U_a$

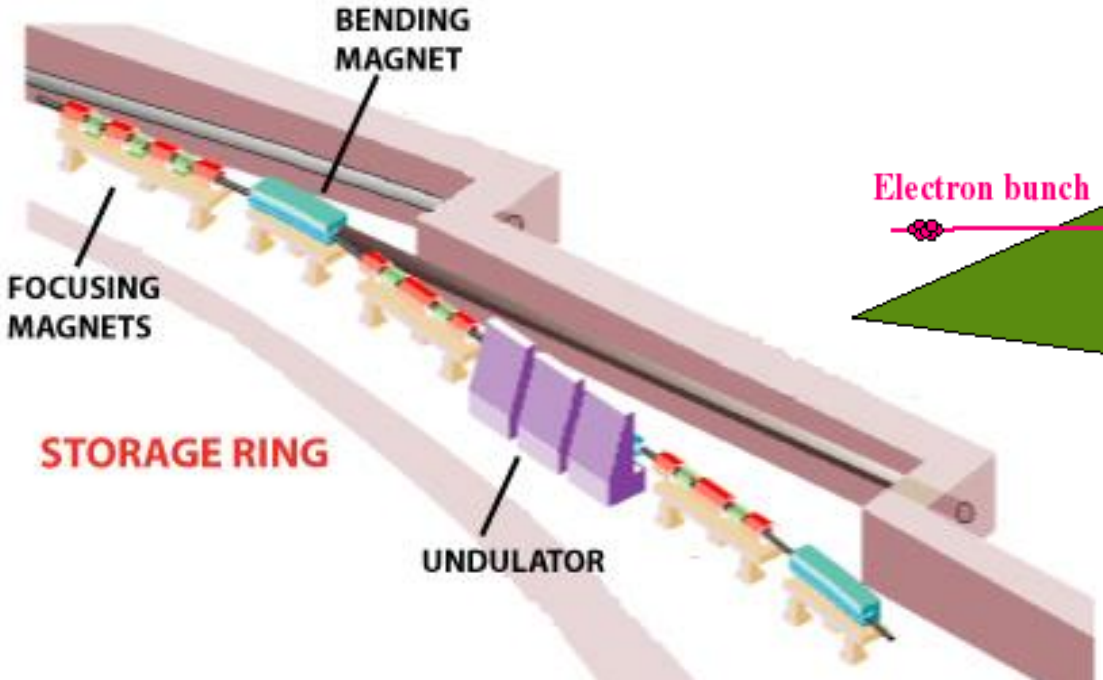


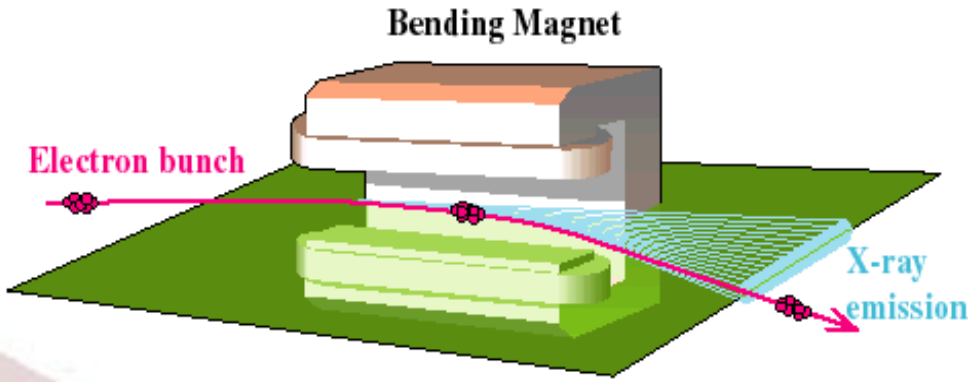




ESRF

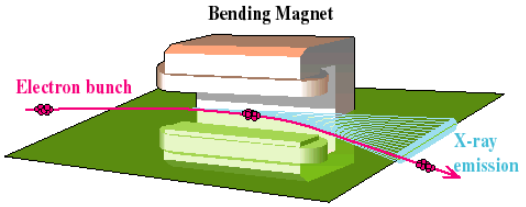

Linac
Booster synchrotron
Beamline
Storage ring


BENDING MAGNET
FOCUSING MAGNETS
STORAGE RING
UNDULATOR


Bending Magnet
Electron bunch
X-ray emission

Generation of Synchrotron radiation

Electron circulates with relatvististic energy in orbit of storage ring with orbit frequency $\omega = 10^6$ Hz → E_e = 5 GeV



$$E_e = \frac{m_0 c^2}{\sqrt{1 - \frac{v^2}{c^2}}} = \frac{m_0 c^2}{\sqrt{1 - ß^2}}$$

E_e is much larger compared to rest mass energy mc^2, γ = 5GeV/ 0.511 GeV≈ 10^4

$$\gamma = \frac{E_e}{m_o c^2} = \frac{1}{\sqrt{1 - ß^2}}$$

value $1/\gamma$ is the vertical open angle

Using γ one can estimate the electron velocity

$$ß = [1 - \frac{1}{\gamma^2}]^{1/2} \approx 1 - \frac{1}{2\gamma^2} = 1 - 6 * 10^{-9} \qquad v \approx 1 - 6 * 10^{-9} c$$

Generation of Synchrotron radiation

Supposing the circulating electron emits a photon at point A of orbit. M Elektron proceeds to point C via B on orbit. At point C it emits a second photon. For the electron the length

AC (electron) = v* dt .

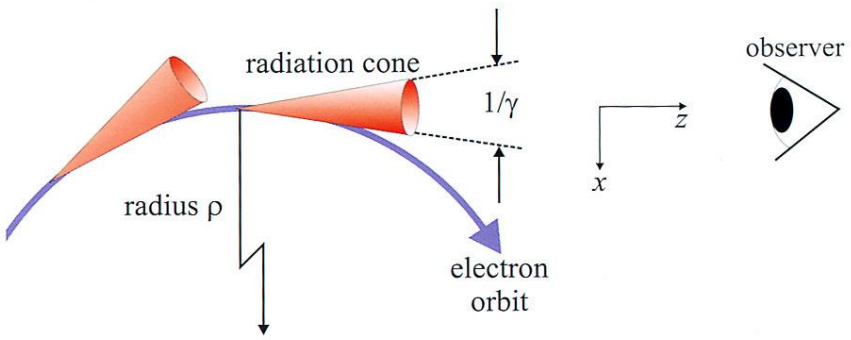
For the photon emitted in A reaches this distance is

AC(photon = c *dt

The spatial distance between both waves : (c-v) dt

An observer at point C the light pulse has a length

$$\Delta t = \frac{(c-v)dt'}{c} = (1-\beta^2)dt'$$



Generation of Synchrotron radiation

Considering the opening angle $\alpha = 1/\gamma$ due to electron orbit

$$\Delta t = (1-\beta\cos\alpha)dt' = [1-(1-\frac{1}{2\gamma^2})(1-\frac{\alpha^2}{2})]dt' \approx \frac{1+(\alpha\gamma)^2}{2\gamma^2}dt'$$

For $\alpha = 0$

$$\Delta t = \approx \frac{1}{2\gamma^2}dt' \approx 10^{-8}dt'$$

Dilatation of time a consequences for spectral distribution of photon emission

Orbit time of electron along AC differs from time of photon

$$\Delta t'(electron) = \frac{1}{2\pi\gamma}T = \frac{1}{\gamma\omega} \approx 10^{-10}s$$

$$\Delta t(photon) = \frac{1}{2\gamma^2}\frac{1}{\gamma\omega}T = \frac{1}{2\gamma^3\omega} \approx 10^{-18}s$$

Generation of Synchrotron radiation

Inverse pulse length determines the spectral with of light emission

$$\Delta\omega_c = \frac{3}{2}\gamma^3\omega \approx 10^{18}\,Hz$$

The emission spectrum has a critical wave length given by

$$\lambda_c = \frac{c}{\upsilon} = \frac{10^8}{10^{18}} = 10^{-10}m$$

This is x-ray range. In energy :

$$\hbar\omega_c = \frac{3}{2}\hbar\omega\gamma^3 \approx 0.655 * E_e^2(GeV)B(T)$$

Generation of Synchrotron radiation

Bending radius R of electron orbit is

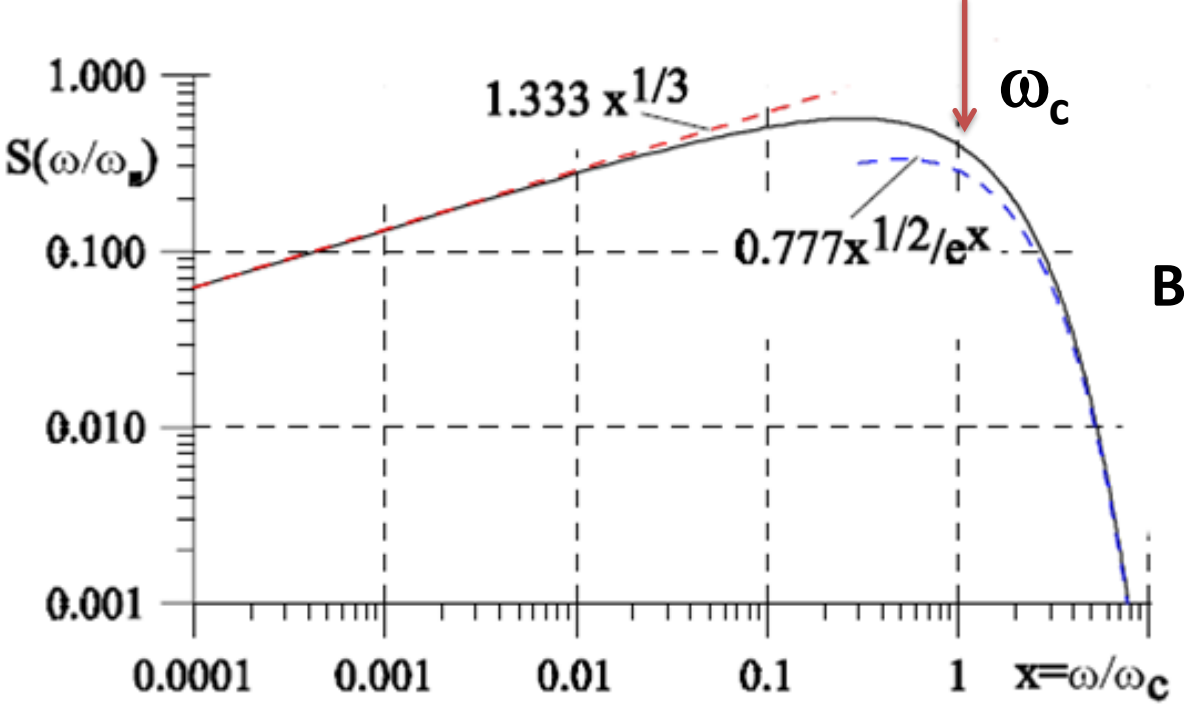
$$\gamma mv = \mathrm{Re}\, B \qquad R = \frac{\gamma mc}{eB} = \frac{E_e}{mc^2}\frac{mc}{eB} = 3.3 * \frac{E_e(GeV)}{B(T)}$$

Emission power is

$$P(kW) = 1.266 * E_e^2(GeV) B^2(T) R\alpha(m) I(mA)$$

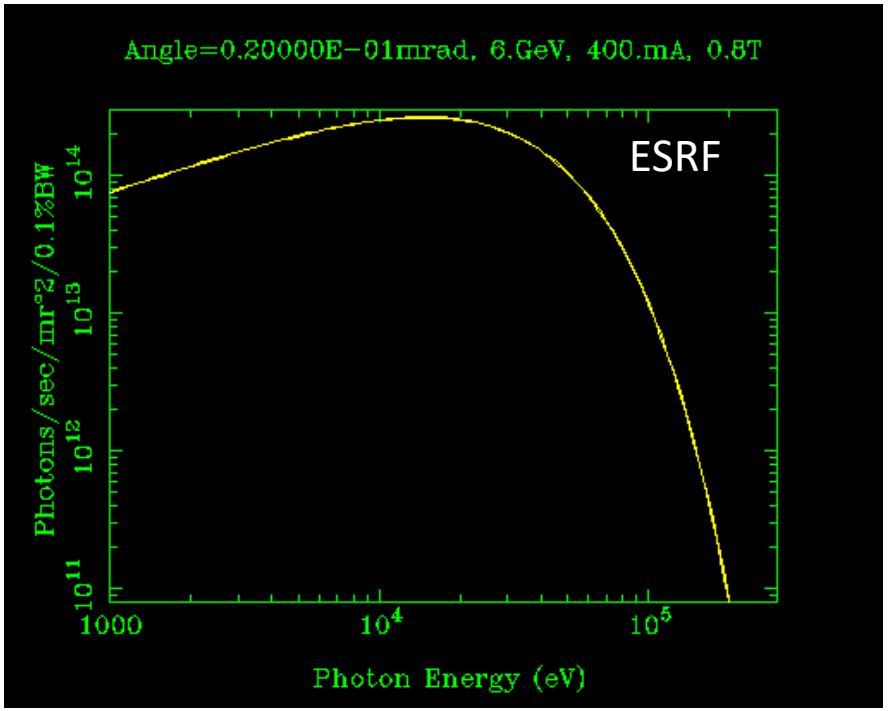
For ESRF, E=6GeV, B=0.8T → R= 24.8m

$$P(kW) = 1.266 * 6_e^2(GeV) 0.8^2(T) 24.8m + 0.05mrad * 100mA = 7.3W$$



Bend magnet spectrum

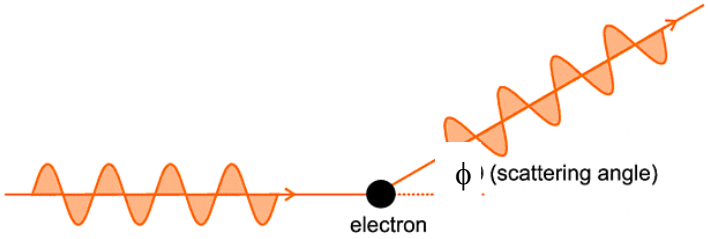
Well predictable



Kinematic X-ray scattering

Dipole scattering of x-ray wave by an electron: Electron excites dipole radiation

$$I =< E^2 >=< E_o^2 > \frac{e^2}{mc^2}\frac{1}{R^2}\left(\frac{1+\cos^2\phi}{2}\right)$$



Superposition of dipole radiation generated by two electrons at positions X_1 and X_2

$$E = E_0 \frac{e^2}{mc^2}\frac{1}{X}\exp(i[\omega t - \frac{2\pi}{\lambda}(X_1 - X_2)])$$

For n electrons

$$E = E_0 \frac{e^2}{mc^2}\frac{1}{R}\exp(2\pi i[\upsilon t - \frac{R}{\lambda}]\sum_n \exp(\frac{2\pi}{\lambda}[\vec{S} - \vec{S}_0]) \qquad k_f - k_i = \frac{2\pi}{\lambda}(S - S_0)$$

Stotal scattering amplitude of one atom : → atomic form factor

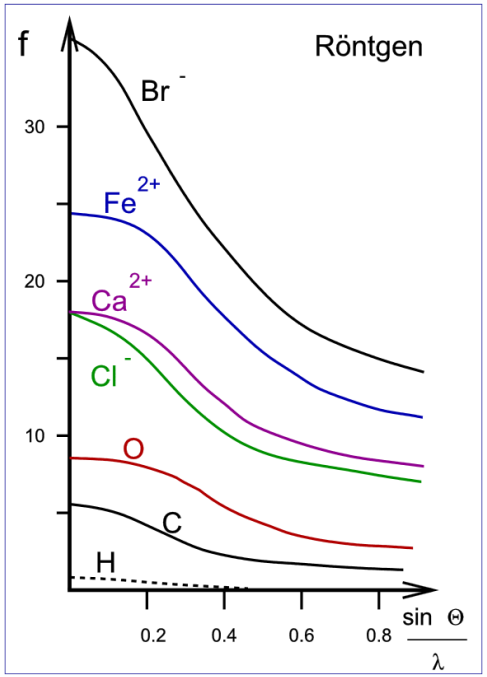
Kinematic X-ray scattering

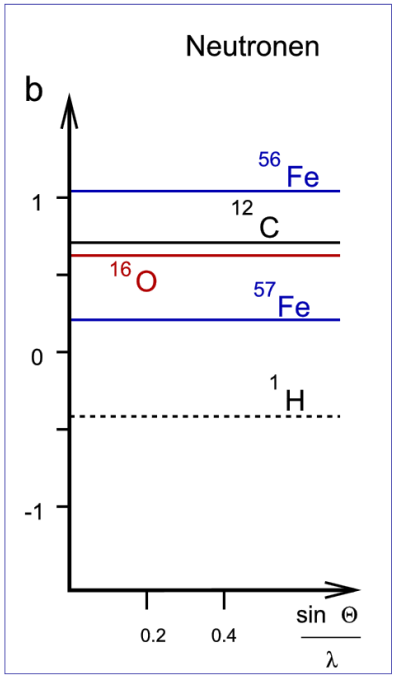
Scattering by all electrons of one atom : → atomic formfactor

$$E = E_0 \frac{e^2}{mc^2} \frac{1}{R} \exp(2\pi i[\upsilon t - \frac{R}{\lambda}] \sum_n \exp(\frac{2\pi}{\lambda}[\vec{S} - \vec{S}_0])$$

$$e * \sum_n \exp(i[\frac{2\pi}{\lambda} r(\vec{S} - \vec{S}_0)]) = \int \exp(2\pi i[\frac{\vec{s} - \vec{s}_0}{\lambda} \vec{r}]) \rho dV$$

Form factor $f[(s\text{-}s_0)/\lambda]$ result from quantun mechanical calculations
$f(0) = Z$; $f[(s\text{-}s_0)/\lambda]$ decays continuosly as function of $(s\text{-}s_0)/\lambda$





Kinematic X-ray scattering

Scattering by two atoms :

$$E \approx f_1 \exp(2\pi i[\upsilon t - \frac{R}{\lambda}] + f_2 \exp(2\pi i[\upsilon t - \frac{R-(S-S_0)R_2}{\lambda}]) = \exp(2\pi i[\upsilon t + \frac{R}{\lambda}](f_1 + f_2 \exp(2\pi i[\frac{R_2}{\lambda}(\vec{S}-\vec{S}_0)])$$

Scattering by many disordered atoms :

$$I \approx E * E^* = f_1^2 + f_2^2 + 2 f_1 f_2 \cos[\frac{2\pi}{\lambda}(\vec{S}-\vec{S}_0)]$$

$$< \exp \frac{2\pi i}{\lambda}[\vec{S}-\vec{S}_0]r_{nm}] > \rightarrow \frac{\sin(kr_{nm})}{kr_{nm}} \rightarrow k = \frac{2\pi}{\lambda}$$

$$I = \sum_{n,m} f_m f_n \frac{\sin(kr_{nm})}{kr_{nm}}$$

Debye´sche Streugleichung Debye equation

Kinematic X-ray scattering

Scattering by „small“ crystal: $r_{nm} = R_{nm} + r_n$ distances between unit cells → shape factor, distances betwen atoms within one unit cell → structure factor

$$\boldsymbol{R}_{nm} = \boldsymbol{m}_1\boldsymbol{a}_1 + \boldsymbol{m}_2\boldsymbol{a}_2 + \boldsymbol{m}_3\boldsymbol{a}_3$$

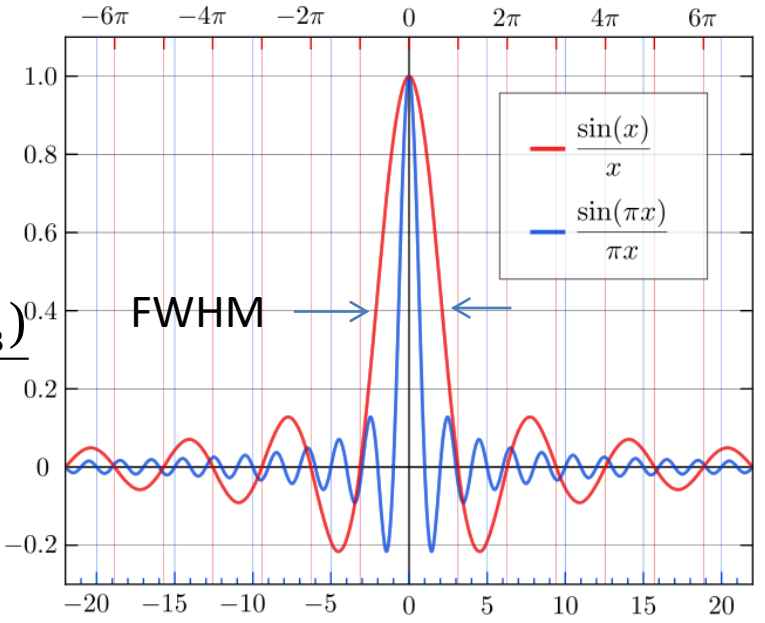
$$E \approx f_n \exp(i\omega t)\exp(-2\pi i\frac{R}{\lambda})\exp(\frac{2\pi i}{\lambda}(\vec{S}-\vec{S}_0)[m_1a_1 + m_2a_2 + m_3a_3]$$

Summation over all unit cells
→ N_1a_1 , N_2a_2 , N_3a_3

$$K = k_f - k_i \qquad |K| = \frac{2\pi}{\lambda}$$

$$E \approx F^2 \frac{\sin(\frac{1}{2}N_1Ka_1)}{\sin(\frac{1}{2}Ka_1)}\frac{\sin(\frac{1}{2}N_2Ka_2)}{\sin(\frac{1}{2}Ka_2)}\frac{\sin(\frac{1}{2}N_3Ka_3)}{\sin(\frac{1}{2}Ka_3)}$$

$$I \approx EE^* = F^2S^2$$



Kinematic X-ray scattering

I <> 0 only in near vicinity of the peak maxima

$$Ka_1 = 2\pi h$$
$$Ka_2 = 2\pi k$$
$$Ka_3 = 2\pi l$$

h,k,l integer

FWHM of a Bragg peak can be approximated

$$I(\Delta x) \approx \frac{\sin^2(N\Delta x)}{\sin^2(\Delta x)} \approx N^2 \exp(-(\Delta x N)^2/\pi) \qquad \Delta x = \frac{1}{2}\Delta k a \qquad \Delta k = \frac{1}{2} B \cos\Theta$$

$$N^2 \exp(-(\pi \frac{N^2 a^2}{\lambda^2}(\frac{B}{2})^2 \cos^2\Theta) = \frac{1}{2}$$

FWHM B(2Θ) is inversely proportional to crystal size L

$$B(2\Theta) = \frac{\sqrt{2(\ln s)/\pi}\lambda}{Na\cos\Theta} = \frac{0.94\lambda}{Na\cos\Theta} = \frac{0.94\lambda}{L\cos\Theta}$$

Structure factor F

$$F = \sum_{i=1}^{n} f_i \exp(-i(kr_i))$$

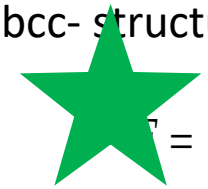
$$k = 2\pi(ha^* + kb^* + lc^*) \qquad r_i = x_i a + y_i b + z_i c$$

$$F = \sum_{i=1}^{n} f_i \exp(-2\pi i(ha^* + kb^* + lc^*)(x_i a + y_i b + z_i c))$$

$$F = \sum_{i=1}^{n} f_i \exp(-2\pi i(hx_i + ky_i + lz_i))$$

Examples →

bcc- structure: xyz = 000, ½ ½ ½



$$F = f(1+\exp(-\pi i(h+k+l))$$

F= 2f if h+k+l = even;
F= 0 if h+k+l odd

fcc- structure: xyz = 000, ½ ½ 0, ½ 0 ½ , 0 ½ ½

$$F = f(1+\exp(-\pi i(h+k)+\exp(-\pi i(h+l)+\exp(-\pi i(k+l))$$

F= 4f if h,k,l all are even or odd;
F= 0 if h,k,l are mixed

hcp- structure: xyz = 000, 1/3 2/3 ½

$$F = f(1+\exp(-2\pi i((h+2k)/3+l/2))$$

F= 2f if h+2k =3n, l even;
F= √3f if h+2k= 3n+1, l odd
F= 0 if h+2k= 3n+1 l even

Extinktion rules

Not all combinations of h,k,l are „allowed“ , Bragg peak intensity can be vanishing due to crystal (point group) symmetry

In fcc system, only reflections appear with $h^2+k^2+l^2 = 2,4,8,11,12….$

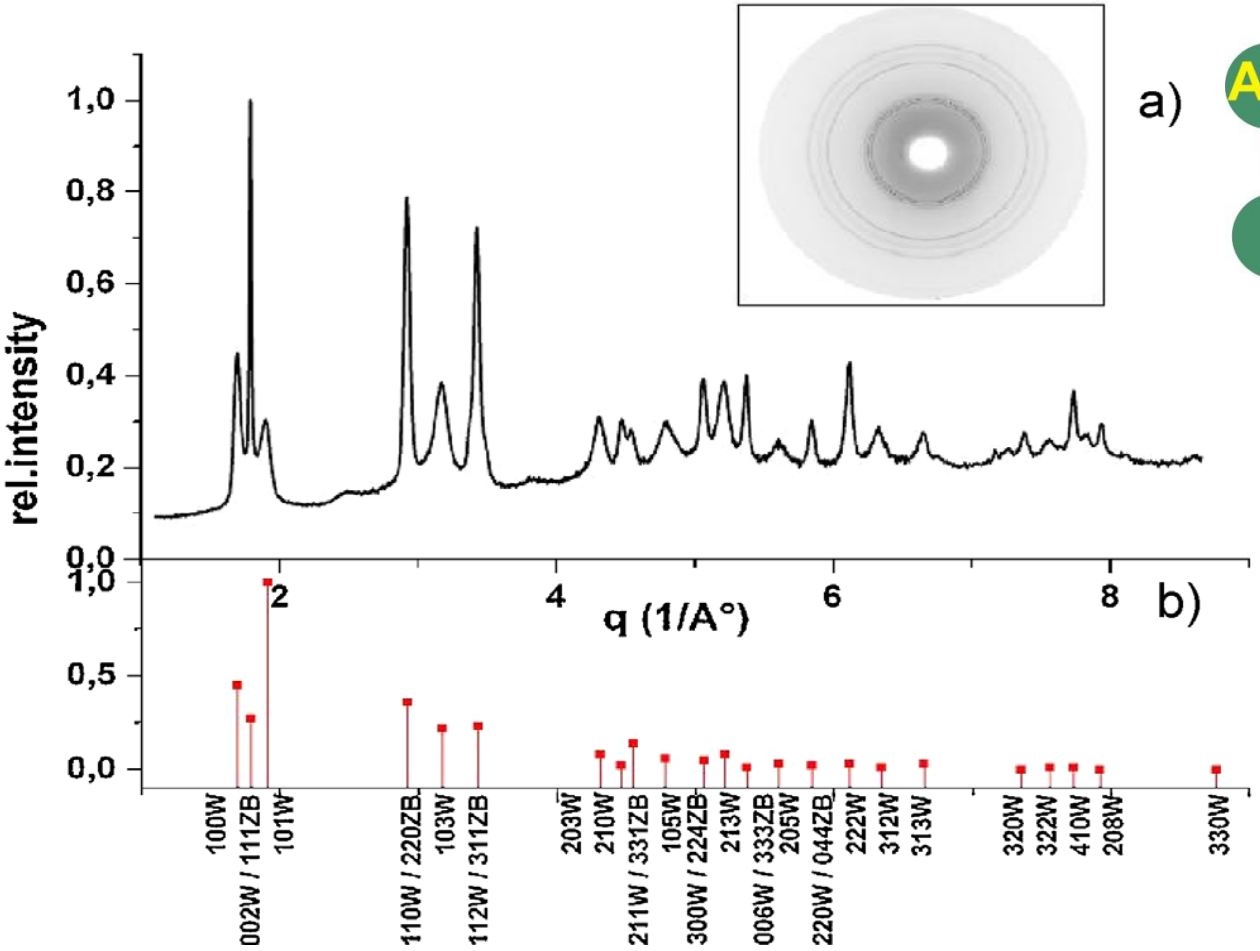
= 111, 200, 220, 311, 222,…..

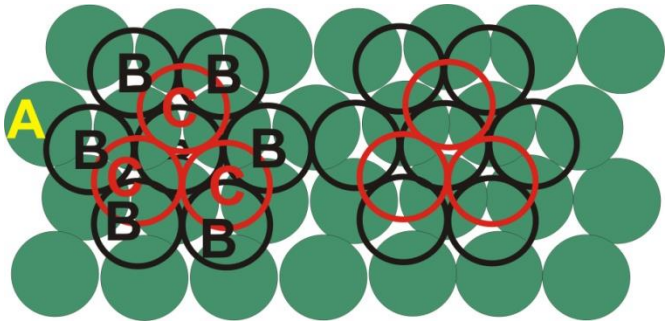
In NaCl 111, 311….. Are weak reflectons
220, 400….. Are strong reflections

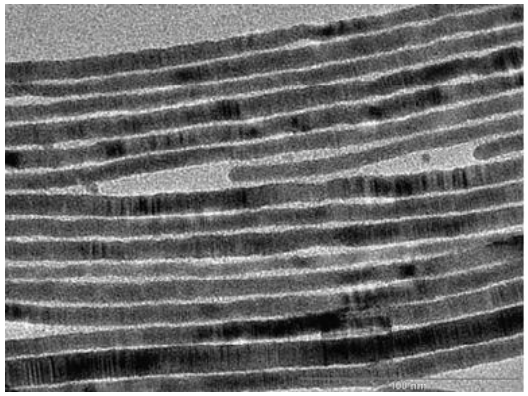
In ZnSe 220, 400…….strong
111, 311…….middle
200, 222…….weka

Structure (point group) identification considering extinktion rules and Bragg peak intensities

Powder diffraction pattern from CdSe Nanowires







Debye-Waller Factor

Due to thermal atom oscillations

$$\left\langle \exp(ik(r+\Delta r)) \right\rangle = \exp(ikr)\left\langle \exp(ik\Delta r) \right\rangle$$

$$\left\langle \exp(ix) \right\rangle = 1 + i\left\langle x \right\rangle - \frac{1}{2}\left\langle x^2 \right\rangle + \ldots = \exp(-\frac{1}{2}\left\langle x^2 \right\rangle)$$

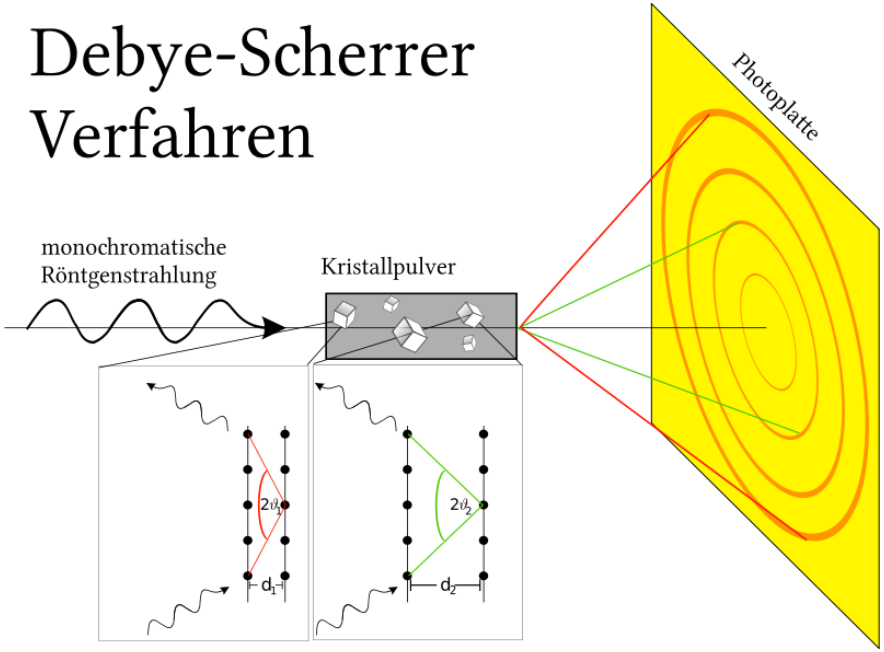
$$\left\langle \exp(ik\Delta r) \right\rangle \approx \exp(-\frac{1}{2}k^2\left\langle \Delta r^2 \right\rangle) = \exp(-2M)$$

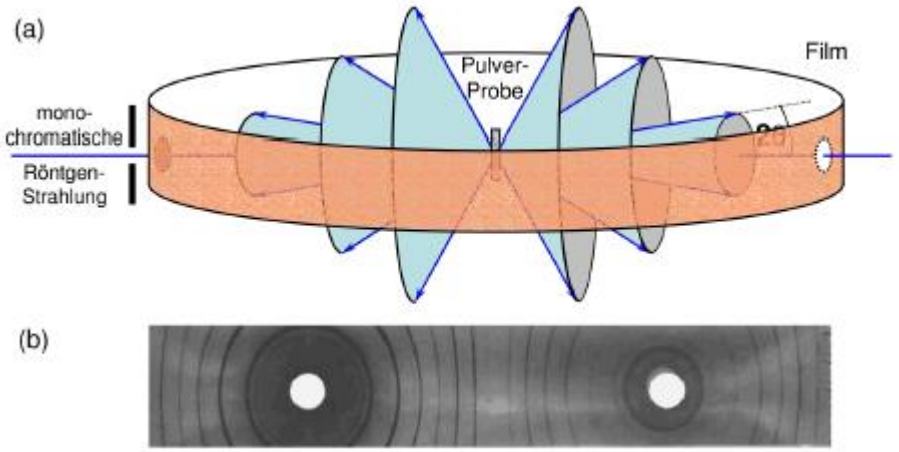
$$2M = 16\pi^2\left\langle u^2 \right\rangle \frac{\sin^2\theta}{\lambda^2}$$

$$F(T) = F\exp(-2M)$$

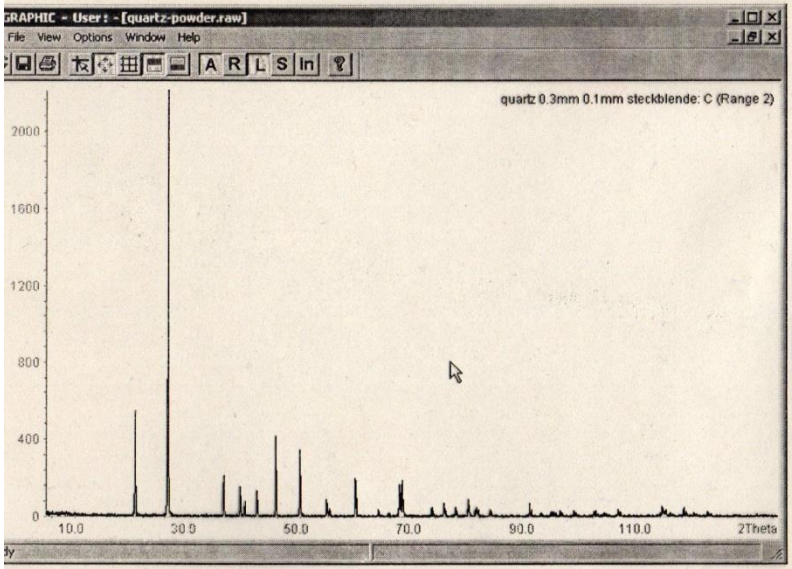
X-ray intensity becomes damped, Bragg peaks exit

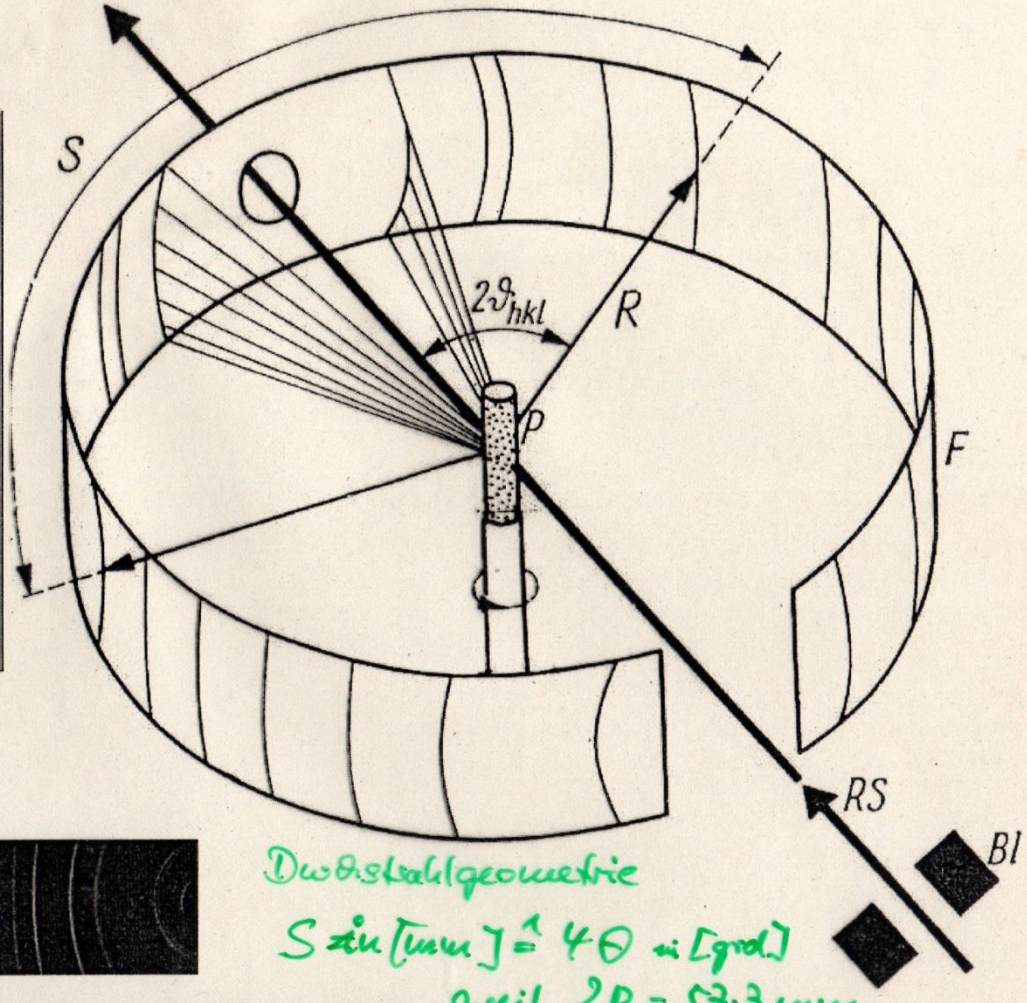
Debye-Scherrer Verfahren





Debye-Scherrer Experiment

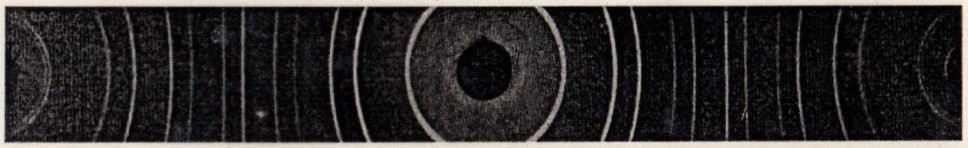




Debyestabilgeometrie

S ≙ [mm] ≙ 4Θ ≙ [grad]

weil 2R = 57.3 mm



Data evaluation

Table 5.1

POWDER DIFFRACTOMETER PATTERN OF NaCl ($\lambda = 1.542$ A)

1	2	3	4	5	6	7	8	9	10	11	12	13	14
2θ	$\frac{4\sin^2\theta}{\lambda^2}$	$h^2 + k^2 + l^2$	hkl	$a(A)$	$\frac{\sin\theta}{\lambda}$	f_{Cl}	f_{Na}	F^2	m	(LP)	$\frac{F^2 m(\mathrm{LP})}{1000}$	A, arb. unit	Col. 12 corrected
27.3	0.0940	3	111	5.65	0.154	13.50	8.90	338	8	33.5	91	116	102
31.7	0.1255	4	200	5.65	0.177	12.70	8.70	7330	6	24.0	1057	1260	1160
45.5	0.2516	8	220	5.64	0.251	10.50	7.65	5280	12	10.9	690	694	697
53.9	0.3455	11	311	5.64	0.294	9.60	7.00	107	24	7.4	19	23	18
56.5	0.3768	12	222	5.64	0.307	9.35	6.75	4150	8	6.6	219	200	201
66.3	0.503	16	400	5.64	0.354	8.65	6.10	3490	6	4.7	98	92	82
73.2	0.598	19	331	5.64	0.386	8.30	5.65	112	24	3.8	10	13	8
75.4	0.629	20	420	5.64	0.396	8.20	5.50	3010	24	3.60	260	198	195
84.1	0.755	24	422	5.64	0.434	7.85	5.05	2660	24	3.05	195	136	136
90.6	0.849	27	511 333	5.64	0.461	7.60	4.75	130	24 8	2.80	12	10	8

Electron charge density distribution from x-ray diffraction data

$$\rho(r) = \int_{-\infty}^{\infty} F(k)\exp(-ikr)dk$$

$$\rho_i(r) = \frac{2}{V}\sum_{-h}^{h}\sum_{-k}^{k}\sum_{-l}^{l}\Delta F_i(H)\exp(-2\pi Hr); \qquad H = \frac{1}{a}(hkl)$$

$$i = \begin{cases} \text{VED using } F_i(\boldsymbol{H}) = F_{\text{obs}}(\boldsymbol{H}) - F_{\text{core}}(\boldsymbol{H}); & hkl = 000 \ldots 12\,12\,0\,, \\ \text{DED using } F_i(\boldsymbol{H}) = F_{\text{obs}}(\boldsymbol{H}) - F_{\text{sph}}(\boldsymbol{H}); & hkl = 111 \ldots 12\,12\,0\,, \\ \text{FRD using } F_i(\boldsymbol{H}) = F_{\text{obs}}(\boldsymbol{H}); & hkl = 222,\ 442,\ 622\,, \\ \text{DX using } F_i(\boldsymbol{H}) = F_{\text{All}}(\boldsymbol{H}) - F_{\text{TB}}(\boldsymbol{H}); & hkl = 111 \ldots 880\,. \end{cases}$$

Electronic charge density of silicon

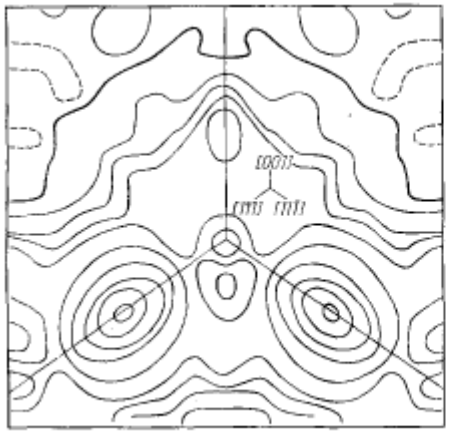


Fig. 1

Valence charge density

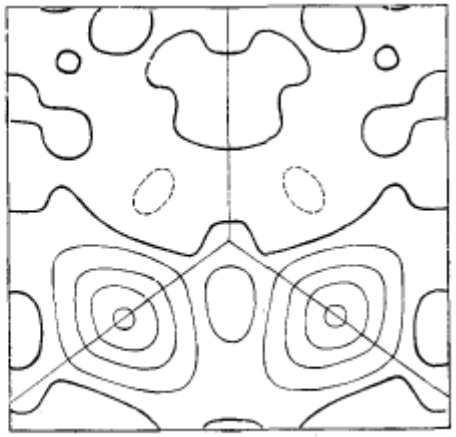
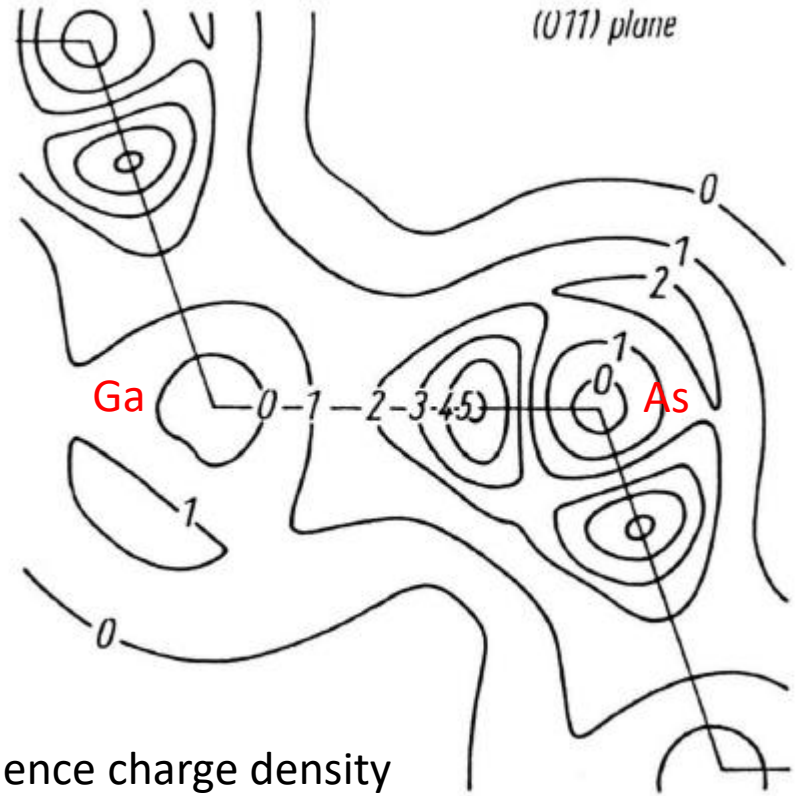


Fig. 2

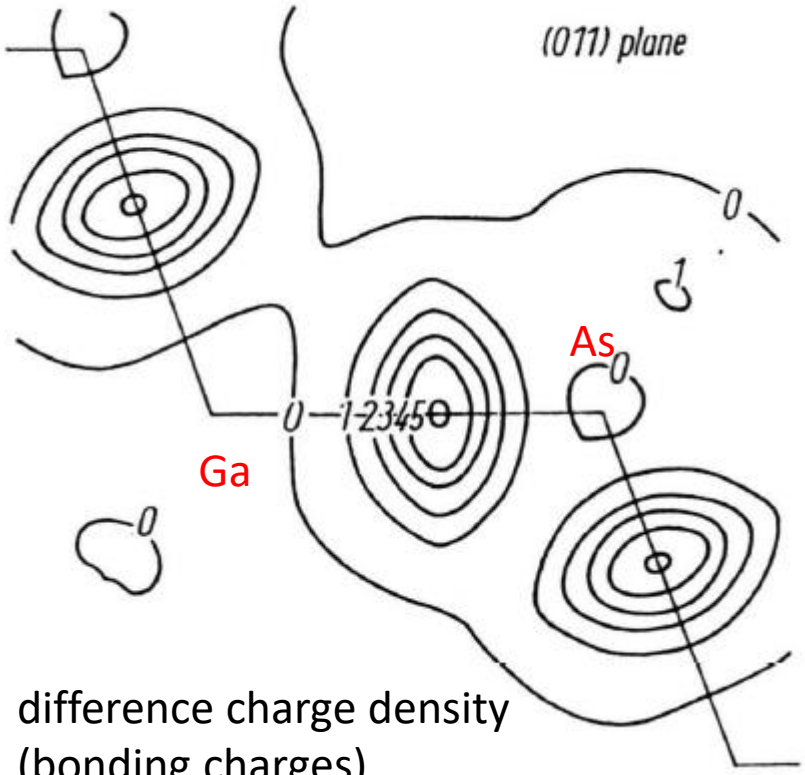
difference charge density (bonding charges)

U.Pietsch
phys.stat.sol.(b)
137, 441,(1986)

Electron density distribution of GaAs from x-ray diffraction data



Valence charge density



difference charge density
(bonding charges)

Ullrich Pietsch
Z. Naturforsch. **48a**, 29–37 (1993)