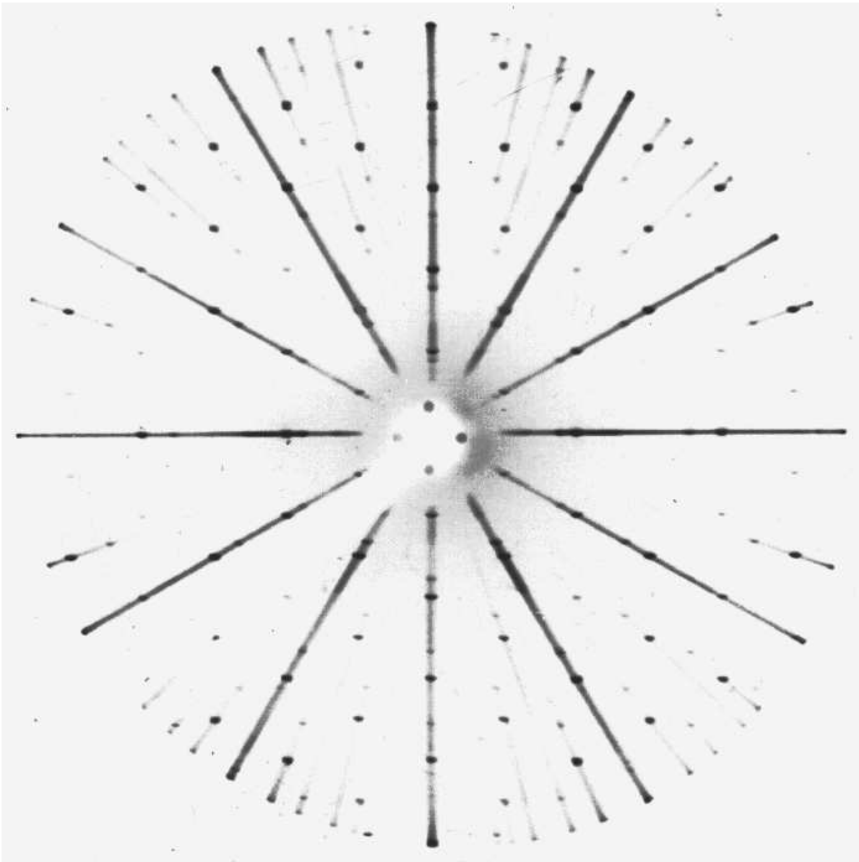
Experimental Determination of Crystal Structures

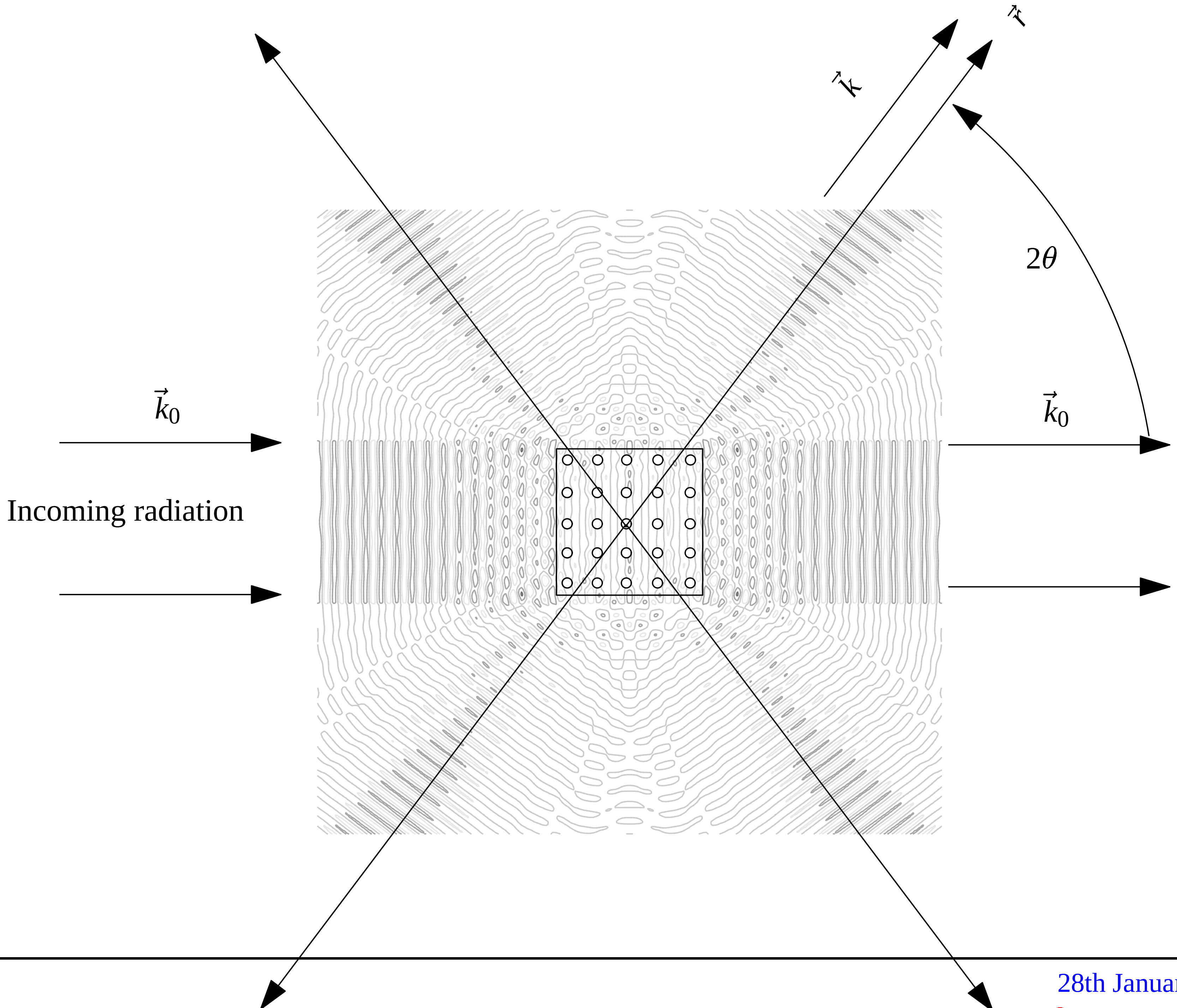


Experiments and theory in 1912 finally revealed locations of atoms in crystalline solids.
Essential ingredients:

- Theory of diffraction grating.
- Skiing, and physics table at Café Lutz.
- Willingness to disobey supervisor, and belief that "experiment was safer than theory."
- X-ray tubes, photographic plates, and experience with their use.
- Persistence.
- Coherent experiments dragging incoherent theory along behind.

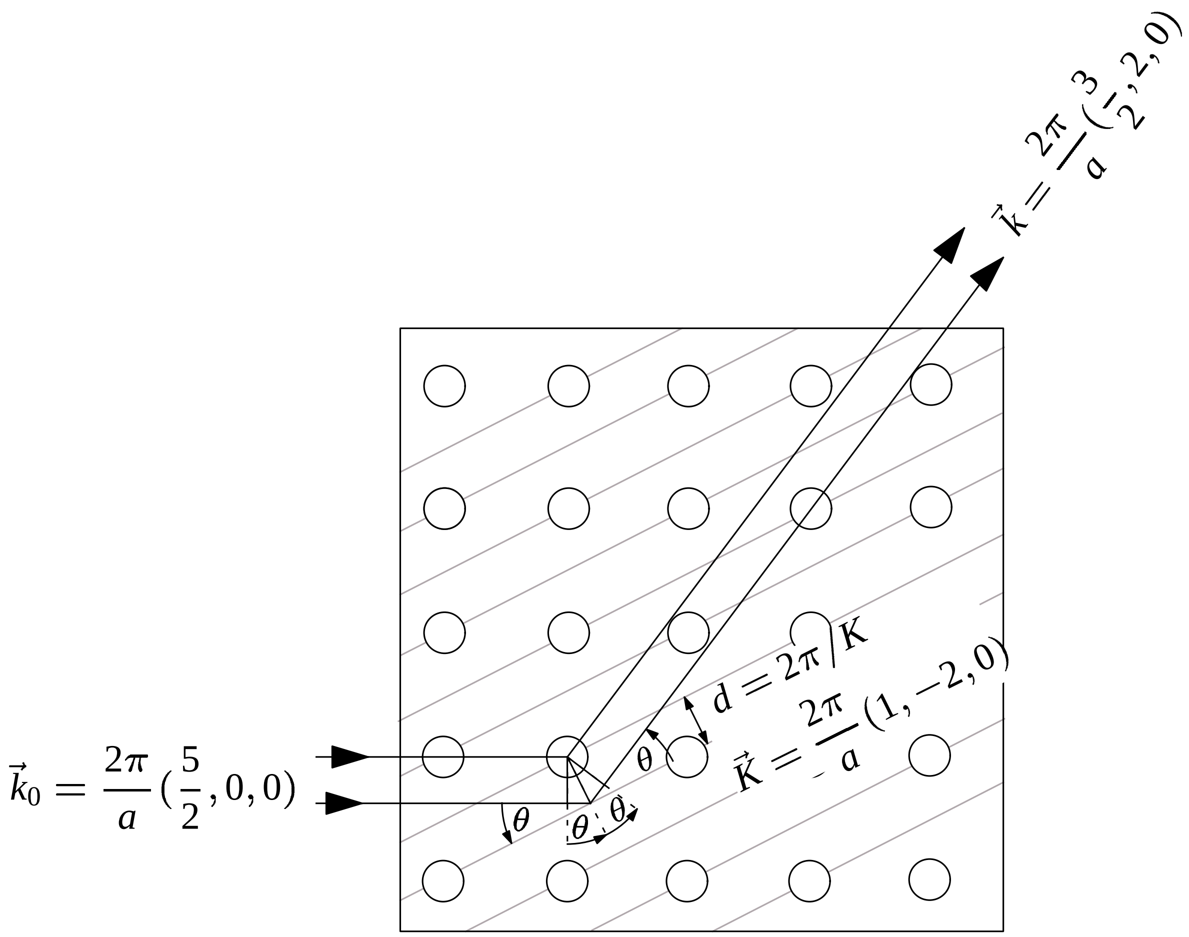
Terms

- Bragg scattering, elastic and inelastic
- Bragg angle
- Bragg peak
- Bragg planes
- Atomic form factor
- Reciprocal lattice
- Miller indices
- Structure factor
- Extinctions
- Ewald construction
- Laue method
- Debye-Scherrer method, powder diffraction



$\vec{r}$
$\vec{k}$
2θ
$\vec{k}_0$
Incoming radiation
$\vec{k}_0$

Scattering Theory



Plane wave travels toward solid, scatters off atoms. Coherent scattering pattern reveals crystalline pattern.

Schiff page 115 or Jackson Eq. 9.8

$$\psi \approx A e^{-i\omega t}[e^{i\vec{k}_0\cdot\vec{r}} + f(\hat{r})\frac{e^{ik_0 r}}{r}] \tag{L1}$$

$$I_{\rm atom} \equiv \frac{d\sigma}{d\Omega}_{\rm atom} = |f(\hat{r})|^2 \tag{L2}$$

f is atomic form factor.

Scattering from particle at $\vec{R}$

$$\psi \sim Ae^{-i\omega t}e^{i\vec{k}_0\cdot\vec{R}}[e^{i\vec{k}_0\cdot(\vec{r}-\vec{R})} + f(\hat{r})\frac{e^{ik_0|\vec{r}-\vec{R}|}}{|\vec{r}-\vec{R}|}]. \tag{L3}$$

For sufficiently large r,

$$k_0|\vec{r}-\vec{R}| \approx k_0 r - k_0\frac{\vec{r}}{r}\cdot\vec{R}. \tag{L4}$$

Using Eq. (L4) and defining

$$\vec{k} = k_0\frac{\vec{r}}{r}, \tag{L5}$$

and

$$\vec{q} = \vec{k}_0 - \vec{k} \tag{L6}$$

gives

$$\psi \sim Ae^{-i\omega t}[e^{i\vec{k}_0\cdot\vec{r}} + f(\hat{r})\frac{e^{ik_0 r + i\vec{q}\cdot\vec{R}}}{r}]. \tag{L7}$$

Note that

$$q = 2k_0\sin\theta. \tag{L8}$$

Assume multiple scattering and inelastic scattering can be ignored

$$\psi \sim Ae^{-i\omega t}\left[e^{i\vec{k}_0\cdot\vec{r}} + \sum_l f_l(\hat{r})\frac{e^{ik_0 r + i\vec{q}\cdot\vec{R}_l}}{r}\right]. \qquad \text{(L9)}$$

Look away from incoming beam

$$\psi \sim Ae^{-i\omega t}\left[\sum_l f_l(\hat{r})\frac{e^{ik_0 r + i\vec{q}\cdot\vec{R}_l}}{r}\right]. \qquad \text{(L10)}$$

Intensity per unit solid angle

$$I = \sum_{l,l'} f_l f_{l'}^* e^{i\vec{q}\cdot(\vec{R}_l - \vec{R}_{l'})}. \qquad \text{(L11)}$$

Eq. (L11) is true no matter how atoms are arranged.

Scattering from crystal

$$I = I_{\text{atom}} |\sum_l e^{i\vec{q}\cdot\vec{R}_l}|^2. \tag{L12}$$

Laue condition: find $\vec{q}$ so that for all atom locations $\vec{R}_l$

$$\exp(i\vec{q}\cdot\vec{R}_l) = 1 \tag{L13}$$

One-Dimensional Sum

$$\Sigma_q = \sum_{l=0}^{N-1} e^{ilaq}. \tag{L14}$$

$$\Sigma_q = \sum_{l=0}^{N-1} e^{ilaq} \tag{L15}$$

$$\Rightarrow e^{iaq}\Sigma_q = \sum_{l=0}^{N-1} e^{i(l+1)aq} \tag{L16}$$

$$= \sum_{l=0}^{N-1} e^{ilaq} - 1 + e^{iNaq} \tag{L17}$$

$$= \Sigma_q - 1 + e^{iNaq} \tag{L18}$$

$$\Rightarrow \Sigma_q = \frac{e^{iNaq}-1}{e^{iaq}-1} \tag{L19}$$

$$= \frac{e^{iNaq/2}}{e^{iaq/2}} \frac{\sin Naq/2}{\sin aq/2} \tag{L20}$$

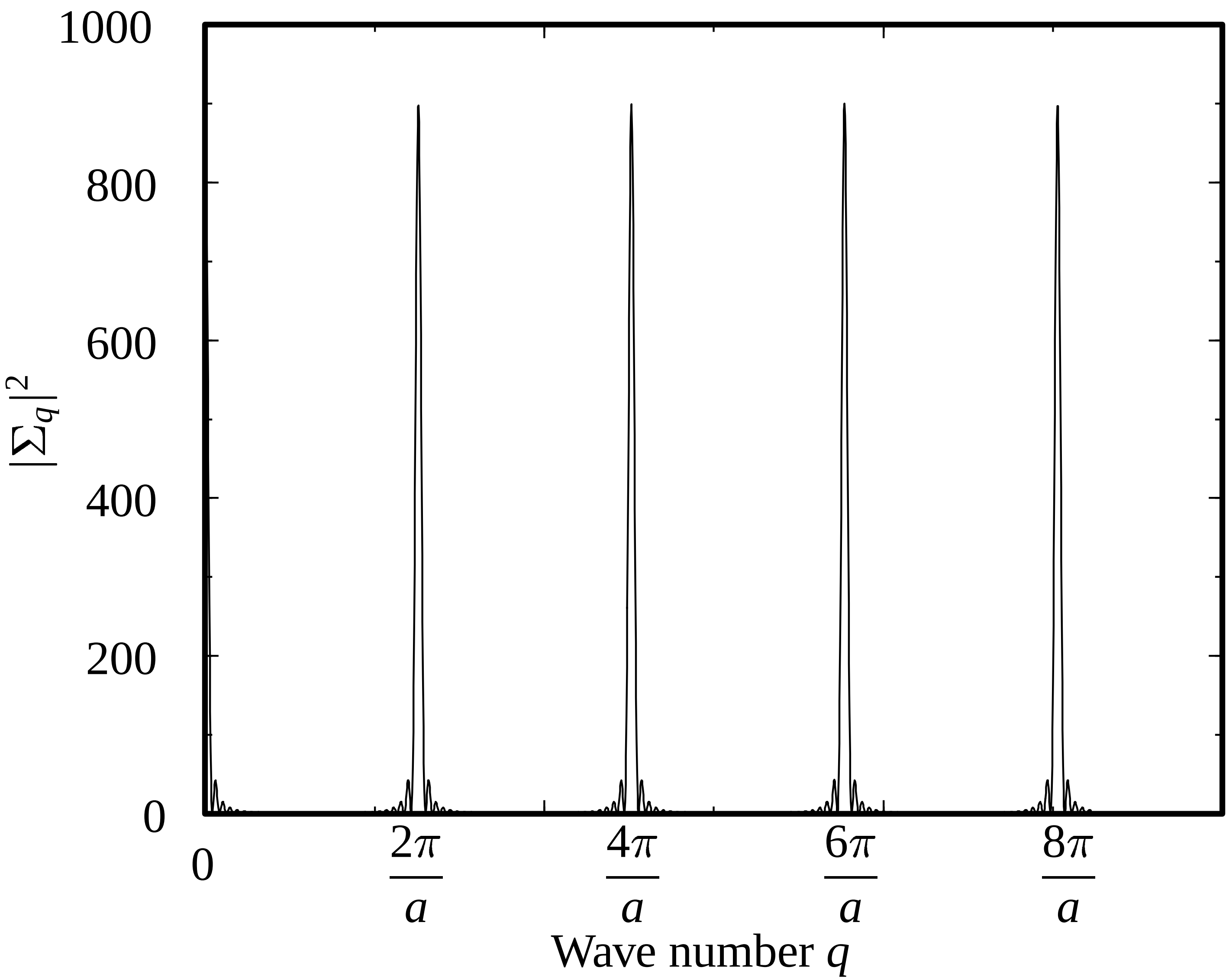
One-Dimensional Sum

$$\Rightarrow |\Sigma_q|^2 = \frac{\sin^2 Naq/2}{\sin^2 aq/2}. \tag{L21}$$

$$\Sigma_q = \frac{e^{iNaq}-1}{e^{iaq}-1} \tag{L22}$$

$$|\Sigma_q|^2 = \frac{\sin^2 Naq/2}{\sin^2 aq/2}. \tag{L23}$$

One-Dimensional Sum



Peaks when

$$aq/2 = l\pi \Rightarrow q = 2\pi l/a. \tag{L24}$$

View as sum of delta functions:

$$\sum_{l=0}^{N-1} e^{ilaq} = \sum_{l'=-\infty}^{\infty} N\frac{2\pi}{L}\delta(q - 2\pi l'/a). \tag{L25}$$

Main result: when $\vec{q} = \vec{k}_0 - \vec{k} = \vec{K}$ satisfies

$$\exp[i\vec{K}\cdot\vec{R}] = 1 \text{ or } \vec{K}\cdot\vec{R} = 2\pi l \tag{L26}$$

there is a strong scattering peak.

The scattering sum can be rewritten

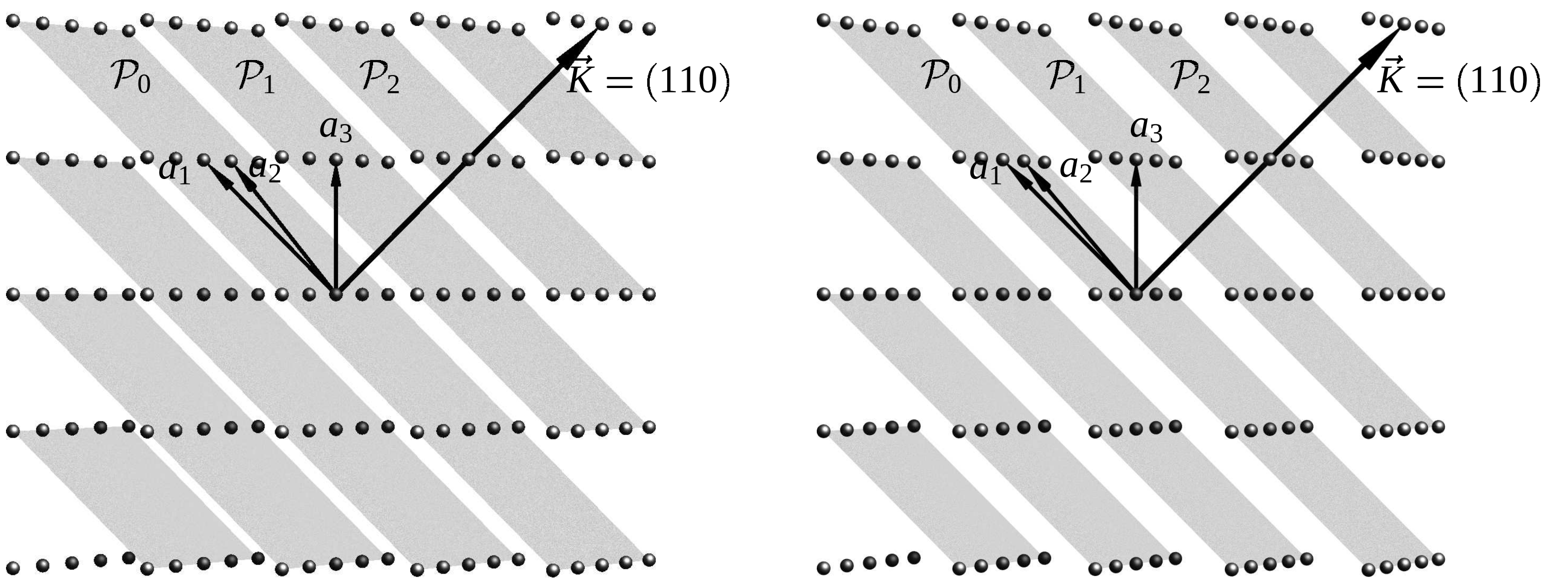
$$\sum_{\vec{R}} e^{i\vec{R}\cdot\vec{q}} = \sum_{\vec{K}} N\frac{(2\pi)^3}{\mathcal{V}}\delta(\vec{q}-\vec{K}), \tag{L27}$$

When the vectors $\vec{R}$ lie in a Bravais lattice, then vectors $\vec{K}$ satisfying Eq. (L26) also lie in a lattice— the reciprocal lattice.

First consider

$$\vec{K}\cdot\vec{R}=0 \tag{L28}$$

Once the direction of $\vec{K}$ is chosen, the $\vec{R}$ satisfying this condition lie in a plane passing through the origin



Scattering in three dimensions

The magnitude of $\vec{K}$ is restricted by the need to satisfy Eq. (L28) for all Bragg planes. In the plane,

$$l_1\vec{a}_1 + l_2\vec{a}_2, \tag{L29}$$

For any $\vec{a}_3$ in an adjacent plane, suppose

$$\vec{a}_3 \cdot \vec{K} = 2\pi. \tag{L30}$$

Then

$$\vec{K}\cdot\vec{R} = \vec{K}\cdot(l_1\vec{a}_1 + l_2\vec{a}_2 + l_3\vec{a}_3) = 2\pi l_3. \tag{L31}$$

Explicit construction:

$$\vec{b}_1 = 2\pi\frac{\vec{a}_2\times\vec{a}_3}{\vec{a}_1\cdot\vec{a}_2\times\vec{a}_3} \quad \vec{b}_2 = 2\pi\frac{\vec{a}_3\times\vec{a}_1}{\vec{a}_2\cdot\vec{a}_3\times\vec{a}_1} \quad \vec{b}_3 = 2\pi\frac{\vec{a}_1\times\vec{a}_2}{\vec{a}_3\cdot\vec{a}_1\times\vec{a}_2} \tag{L32a}$$

$$\vec{K} = \sum_{l=1}^{3} m_l\vec{b}_l. \tag{L32b}$$

Scattering in three dimensions

Reciprocal lattice of a simple cubic lattice of lattice spacing a is another simple cubic lattice, of spacing $2\pi/a$.

The reciprocal lattice of an fcc lattice of spacing a is, however, a bcc lattice of spacing $4\pi/a$

The reciprocal lattice of a bcc lattice of spacing a is an fcc lattice of spacing $4\pi/a$.

- $[ijk]$ refers to a *direction*

$$i\hat{x}+j\hat{y}+k\hat{z} \tag{L33}$$

  in the lattice specified by the three integers i, j, and k.

- (ijk) refers to a *lattice plane* perpendicular to $[ijk]$
- $\{ijk\}$ refers to the family of lattice planes perpendicular to $[ijk]$ and related by symmetry.

Lattice with a Basis

$$\vec{R} = \vec{u}_l + \vec{v}_{l'} \tag{L34}$$

Regrouping of basic sum first carried out by Laue

$$\sum_{\vec{R}} e^{i\vec{q}\cdot\vec{R}} = \sum_{ll'} e^{i\vec{q}\cdot(\vec{u}_l+\vec{v}_{l'})} \tag{L35}$$

$$= \left(\sum_{l} e^{i\vec{q}\cdot\vec{u}_l}\right)\left(\sum_{l'} e^{i\vec{q}\cdot\vec{v}_{l'}}\right) \tag{L36}$$

$$\Rightarrow I \propto \left(\sum_{jj'} e^{-i\vec{q}\cdot(\vec{u}_j-\vec{u}_{j'})}\right)\left(\sum_{ll'} e^{i\vec{q}\cdot(\vec{v}_l-\vec{v}_{l'})}\right). \tag{L37}$$

Structure factor for the unit cell is

$$F_{\vec{q}} \equiv |\sum_{l} e^{i\vec{q}\cdot\vec{v}_l}|^2. \tag{L38}$$

When $F_{\vec{q}}$ vanishes, have an extinction: Laue overlooked this possibility, leading to years of confusion interpreting patterns.

Example: Diamond

$$\vec{v}_1 = (0\ \ 0\ \ 0), \quad \vec{v}_2 = \frac{a}{4}(1\ \ 1\ \ 1). \tag{L39}$$

$$\vec{K} = l_1 \frac{4\pi}{2a}(1\ \ 1\ \ -1) + l_2 \frac{4\pi}{2a}(-1\ \ 1\ \ 1) + l_3 \frac{4\pi}{2a}(1\ \ -1\ \ 1). \tag{L40}$$

Therefore,

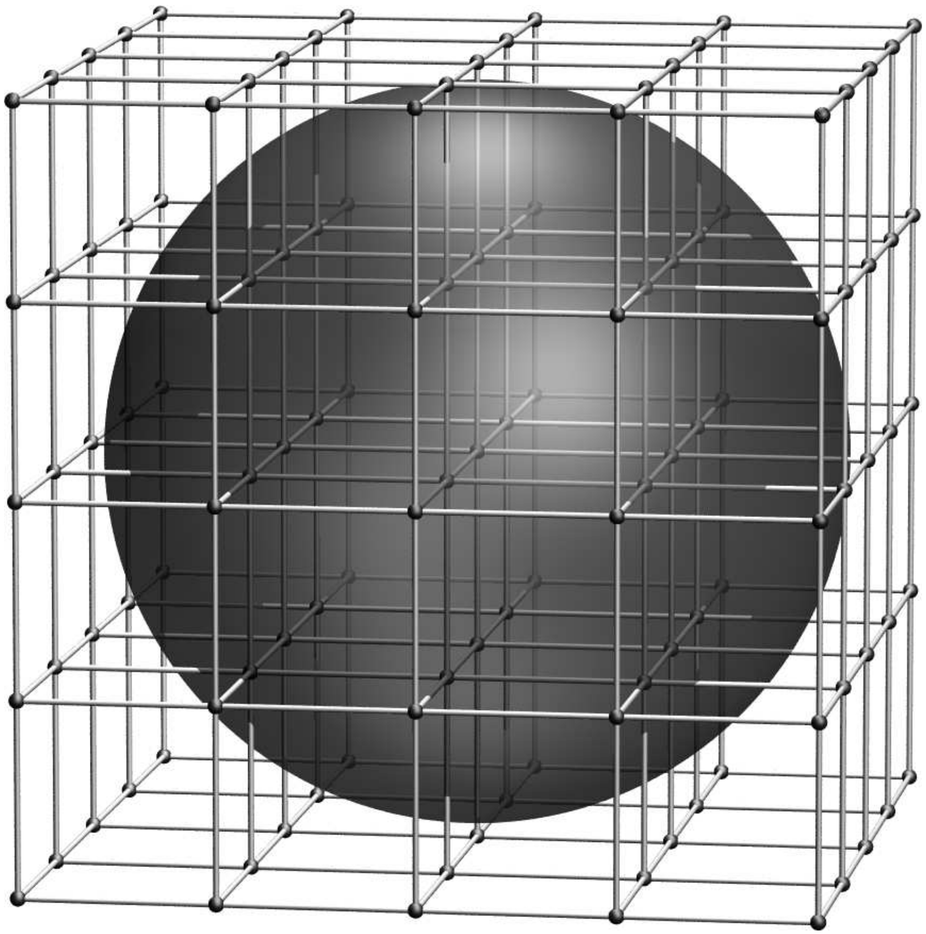
$$\vec{v}_2 \cdot \vec{K} = \frac{\pi}{2}(l_1 + l_2 + l_3), \tag{L41}$$

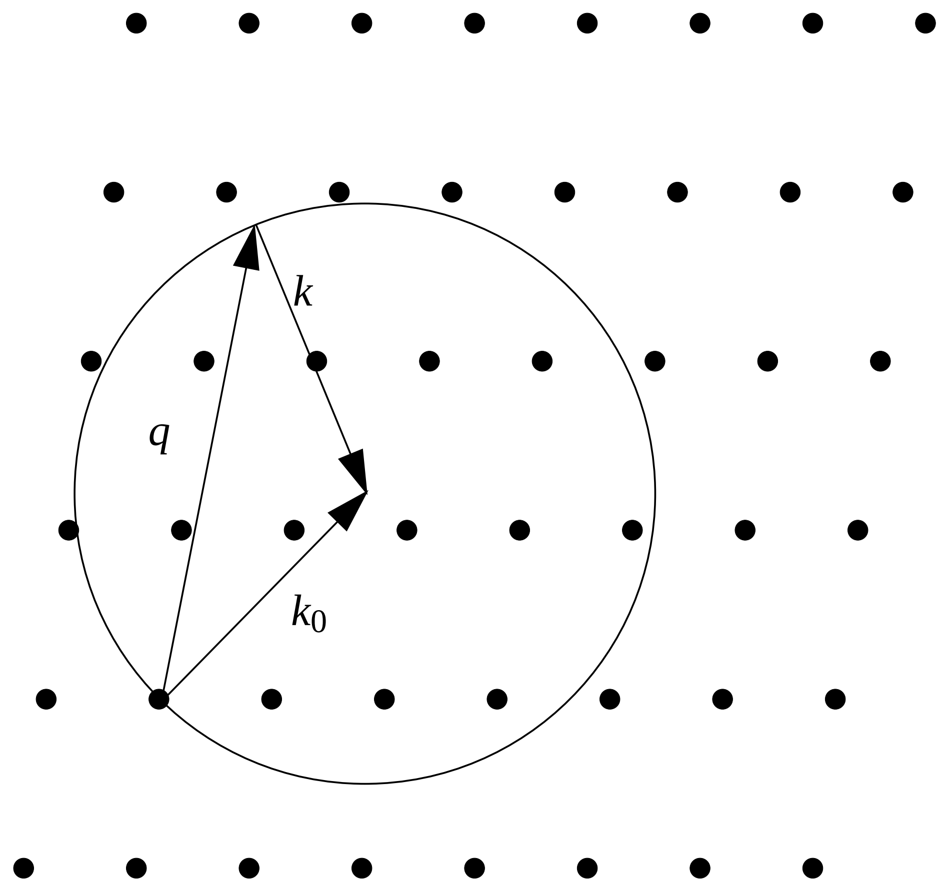
$F_{\vec{K}}$ is

$$F_{\vec{K}} = |1 + e^{i\pi(l_1+l_2+l_3)/2}|^2 \tag{L42}$$

$$= \begin{cases} 4 & \text{if } l_1 + l_2 + l_3 = 4, 8, 12, \ldots \\ 2 & \text{if } l_1 + l_2 + l_3 \text{ is odd} \\ 0 & \text{if } l_1 + l_2 + l_3 = 2, 6, 10, \ldots . \end{cases} \tag{L43}$$

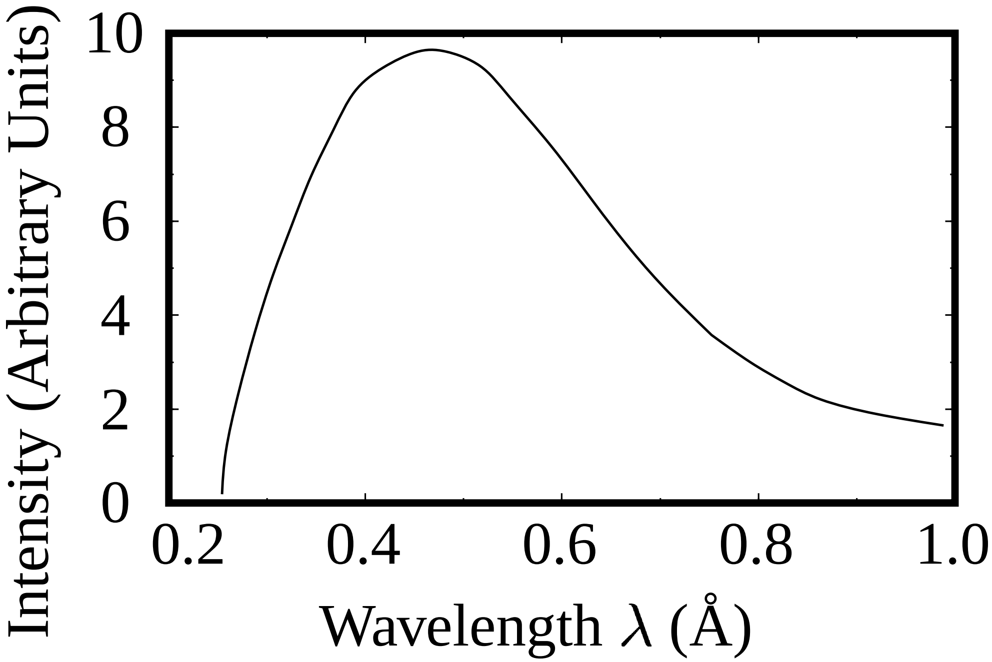
Ewald construction

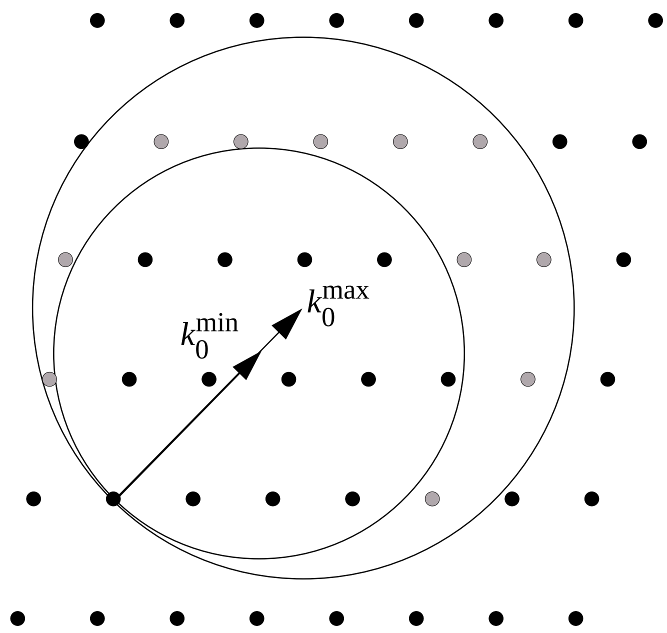




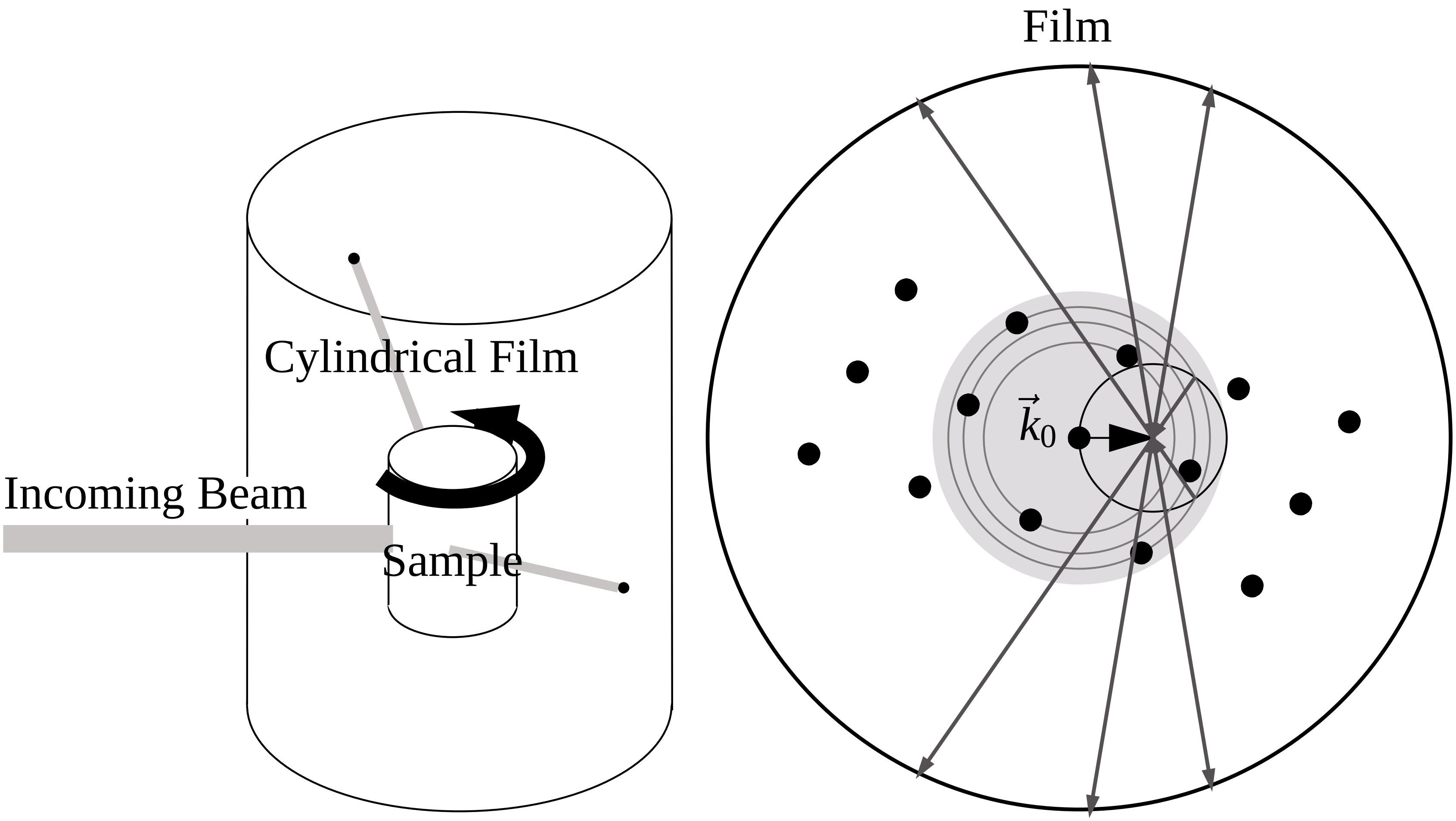
Shining generic monochromatic X-ray upon crystal gives **no scattering peaks**

Laue Method

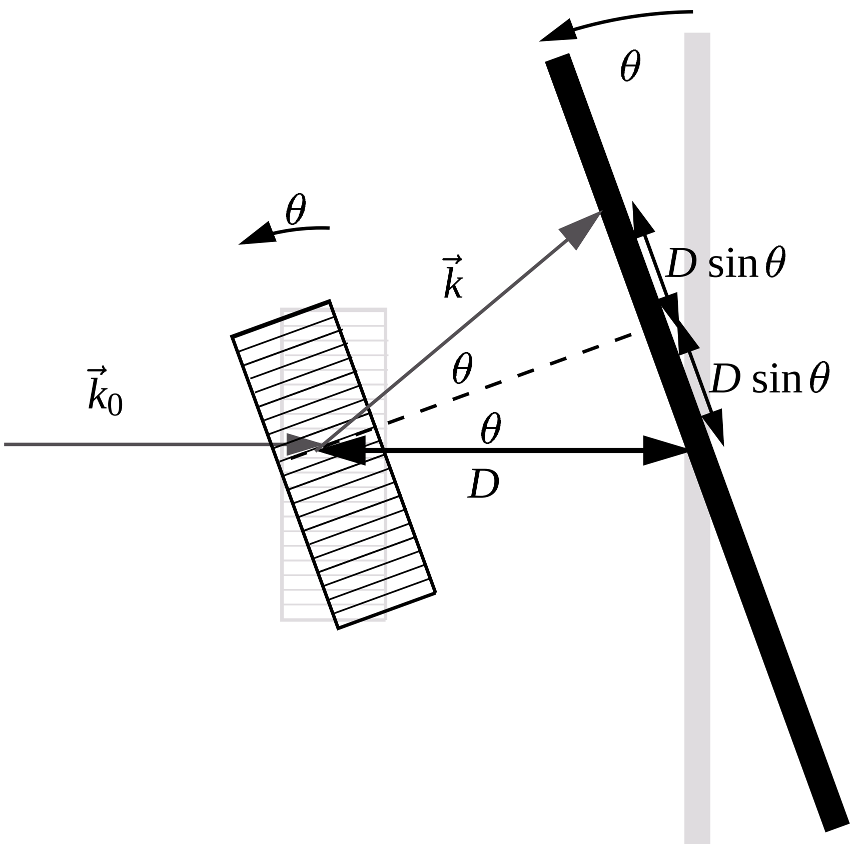

Intensity (Arbitrary Units)
10
8
6
4
2
0
0.2
0.4
0.6
0.8
1.0
Wavelength λ (Å)

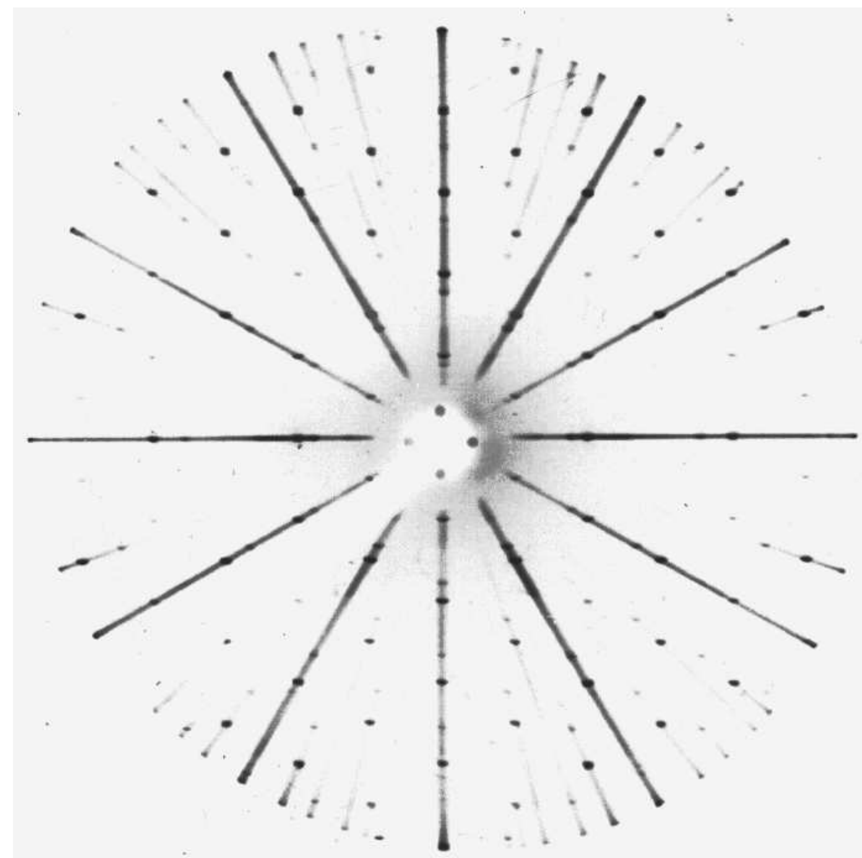

k_0^{min}
k_0^{max}

Rotating Crystal Method

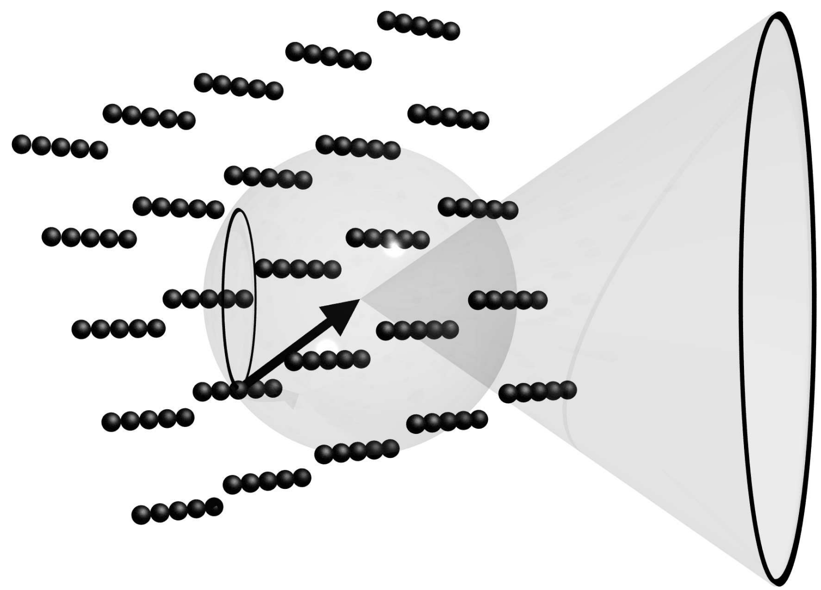


Rotating Crystal Method





Powder Method



$$\theta = \sin^{-1}(K/2k_0) \tag{L44}$$

and the radius r on film of the scattering ring due to reciprocal lattice vector $\vec{K}$ is

$$r = D\tan(2\theta). \tag{L45}$$

More on Scattering Experiments

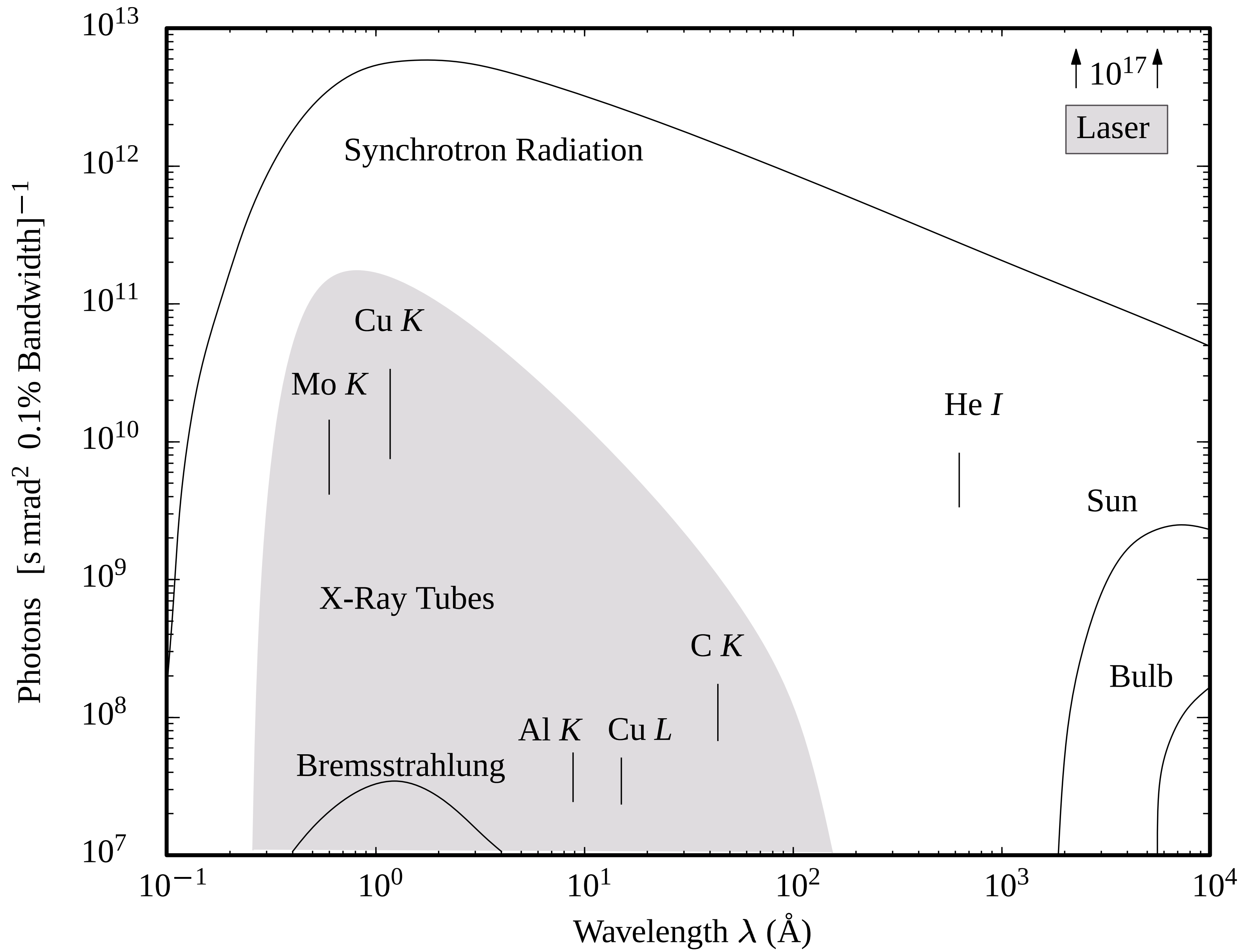
	X-rays	Neutrons	Electrons
Charge	0	0	$-e$
Mass	0	$1.67{\cdot}10^{-27}$ kg	$9.11{\cdot}10^{-31}$ kg
Typical energy	10 keV	0.03 eV	100 keV
Typical wavelength	1Å	1 Å	0.05Å
Typical attenuation length	100 μm	5 cm	1 μm
Typical atomic form factor, f	10^{-3} Å	10^{-4} Å	10 Å

Interactions of X–rays with matter

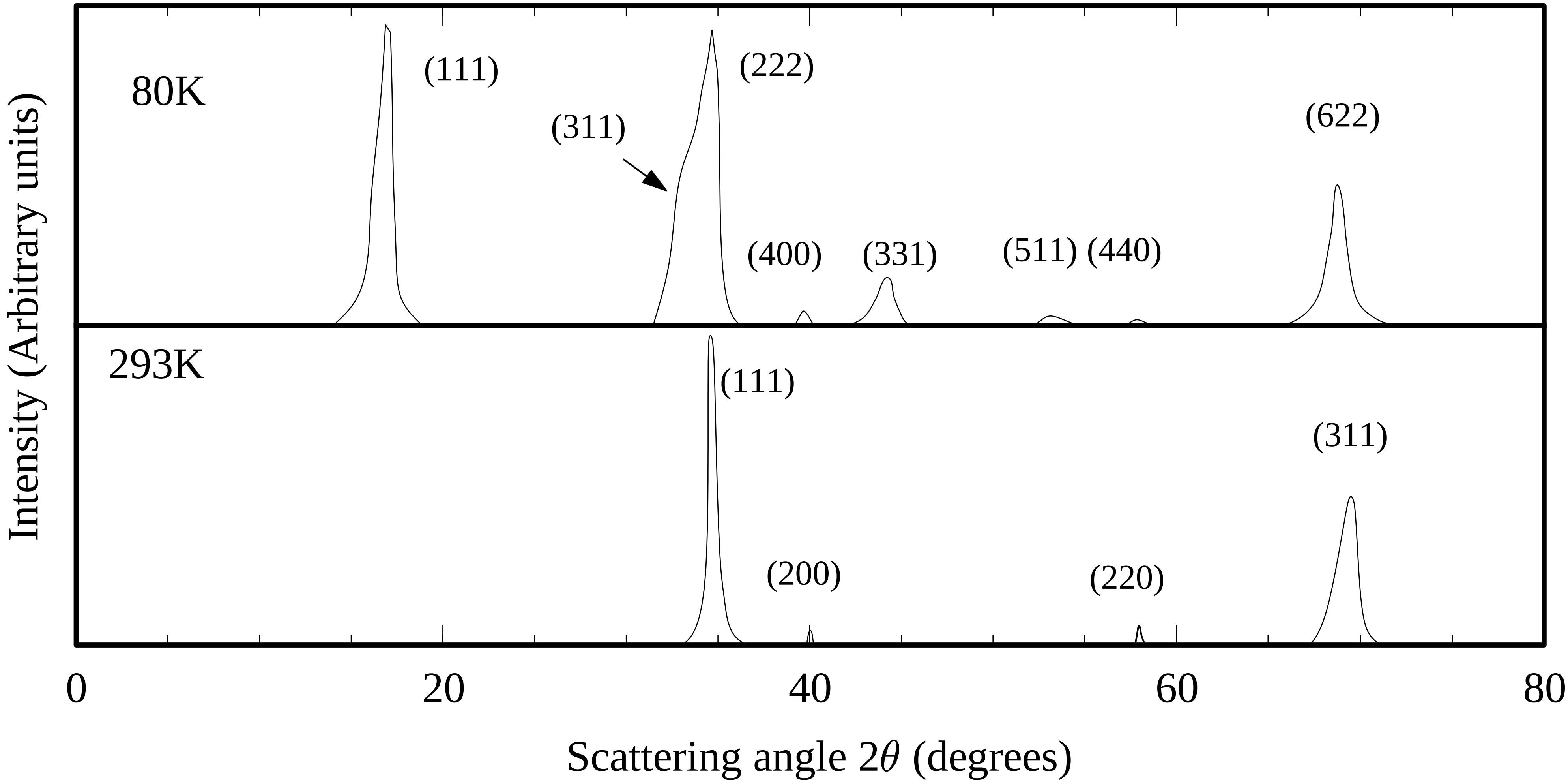
$$I_{\text{atom}}(\hat{r}) = \frac{e^4}{m^2c^4}\frac{(1+\cos^2 2\theta)}{2} \equiv \frac{e^4}{m^2c^4}P(\hat{r}) \tag{L46}$$

$$\Rightarrow f(\hat{r}) = \frac{e^2}{mc^2}\sqrt{P(\hat{r})} = 2.82\cdot 10^{-15}\sqrt{P(\hat{r})}\ \text{m} \tag{L47}$$

More on Scattering Experiments



Neutrons are almost completely isotropic. Elastic scattering (neutrons lose no energy) gives very precise information about static structure. Inelastic scattering gives very precise information about mechanical excitations. Neutrons are sensitive to the spins of the nuclei from which they scatter.



Information on a neutron detector

75 years of further advances...

Insertion of heavy atoms allows extremely complex crystals to be deciphered.

Crystallography Online

Structure of Hemoglobin

rasmol viewer for molecules

Computers do most of the work now (for better or worse)