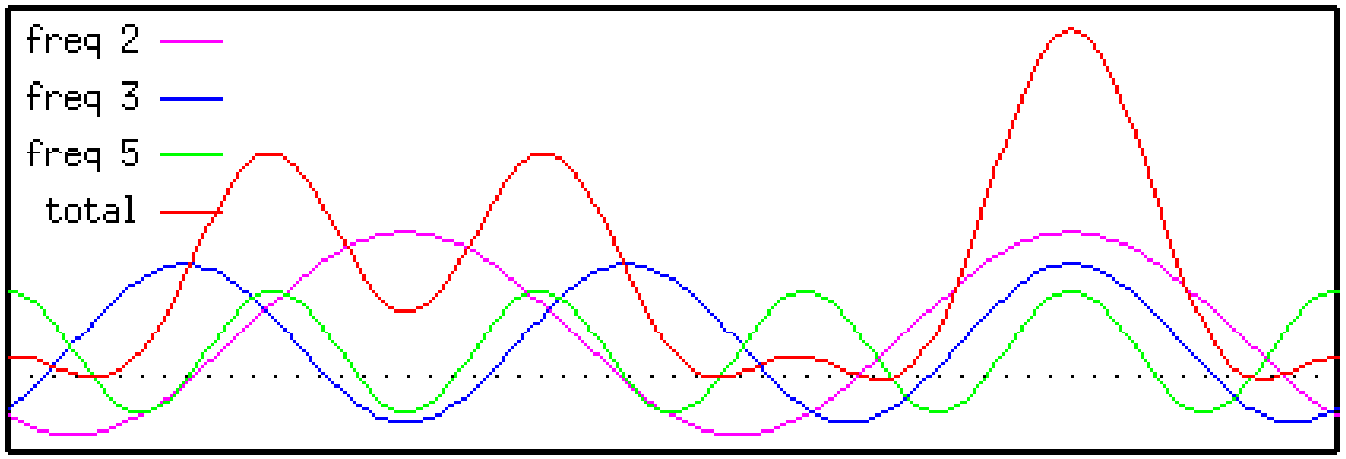
images and X-rays

- A charged particle which is accelerated will emit electromagnetic radiation



The wavelength of the radiation determines the maximal resolution

- By the use of visible light (350-700 nm) details to about 500nm may be seen
  - Ideally $\lambda/2$
- Atoms in molecules have a typical distance of 1-2 Å – therefore the choice is X-rays

X-ray microscope/phase problem

- Need a lens which can focus light with a wavelength comparable to the atomic distances in the lens
  - doesn't exist

- Instead we put a detector where the lens should have been and measure the energy/intensity of the scattered light
  - We loose the phase of the radiation

Why crystals?

- A single molecule would be burned up by the radiation before it was observed

- Irradiation of crystals, where the signal from many molecules is added

  (we can afford to harm single molecules, when we have millions that are ok)

Scattering of X-rays

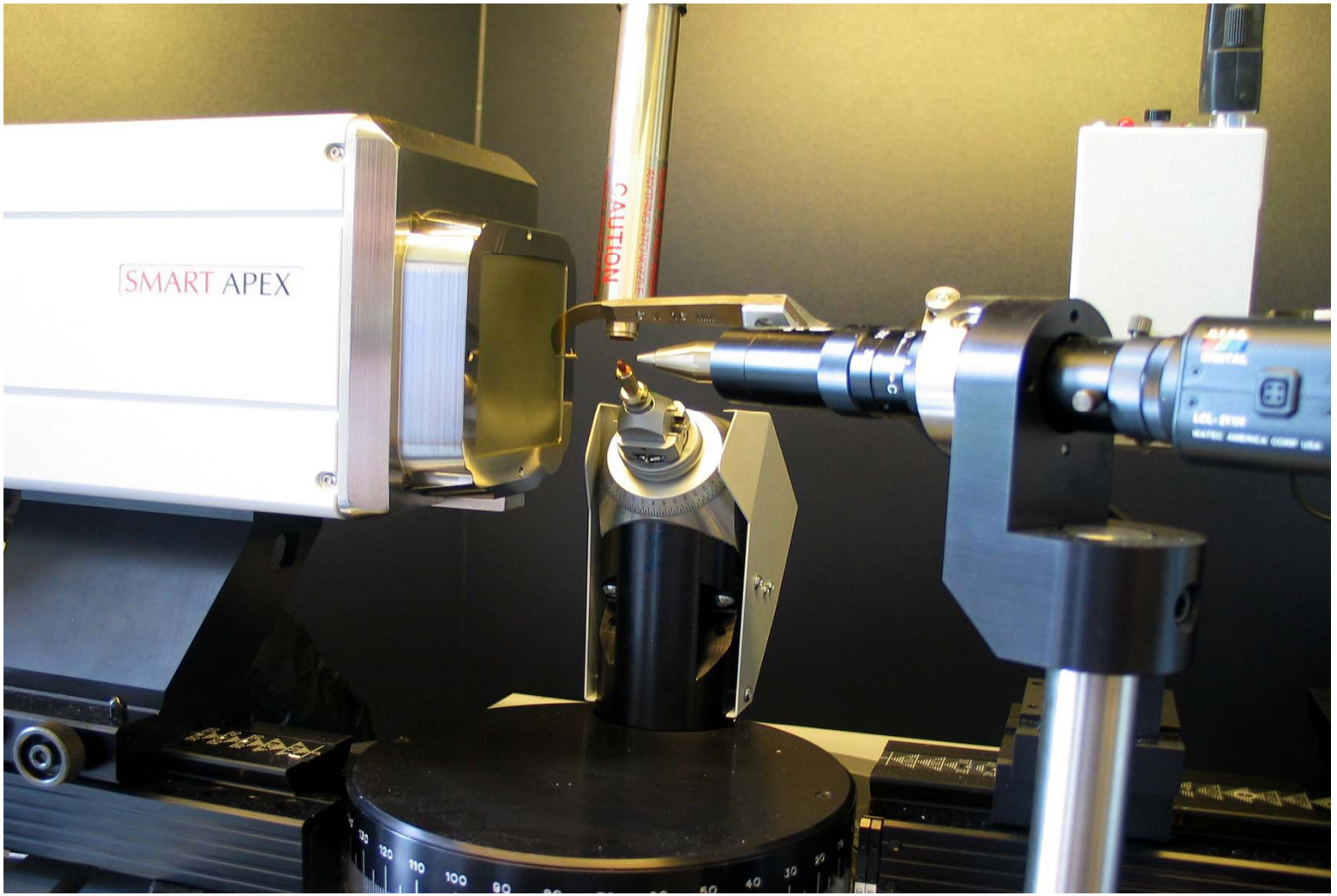
- Charged material scatter X-rays

  A crystal may be described as a three dimensional lattice, where each unit cell contains identical matter

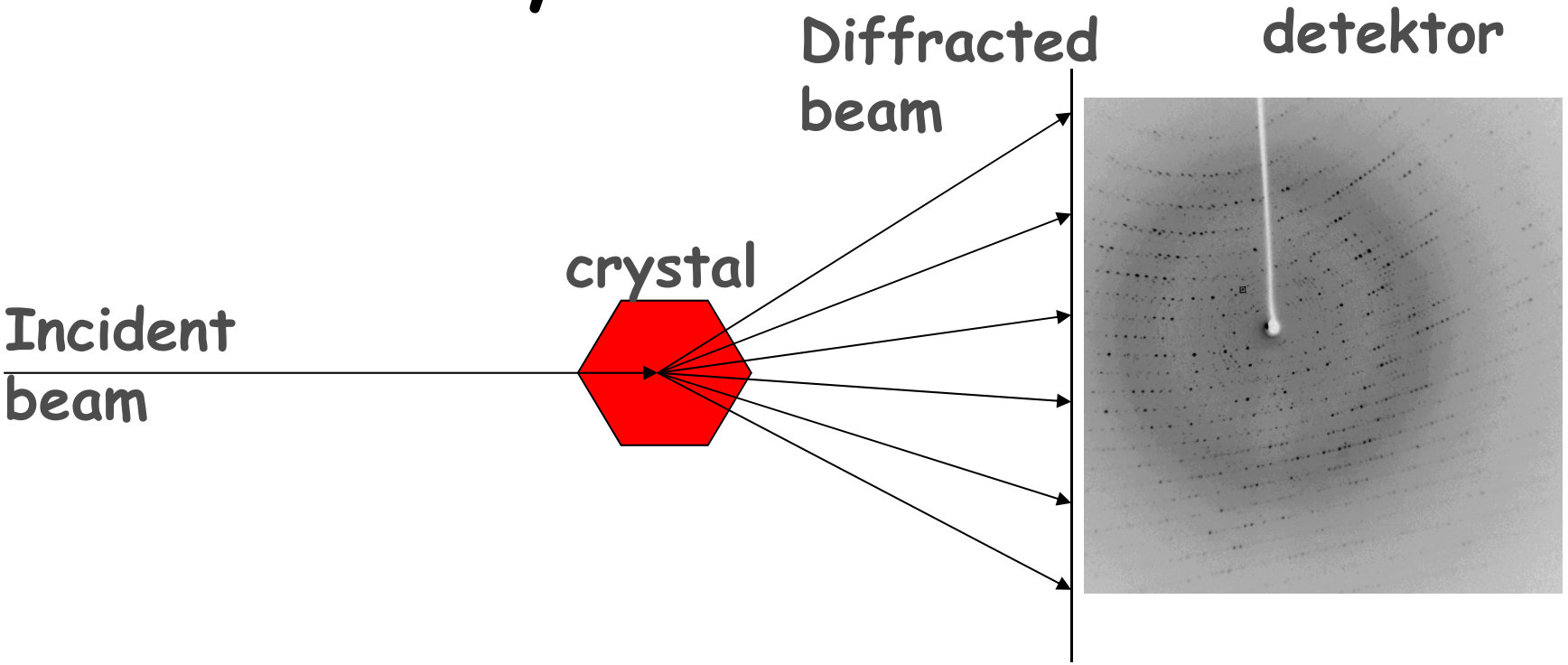
- Matter consists of Nucleii and electrons – charged particles

matter ≡ electron density

experiment



X-ray diffraction



Analogy

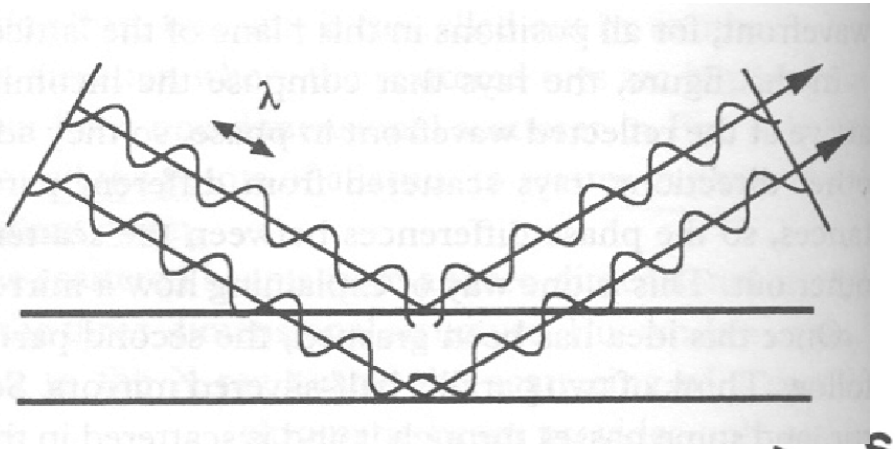
The laser	→	The X-ray beam
The lattice	→	The protein crystal
The wall	→	The detector

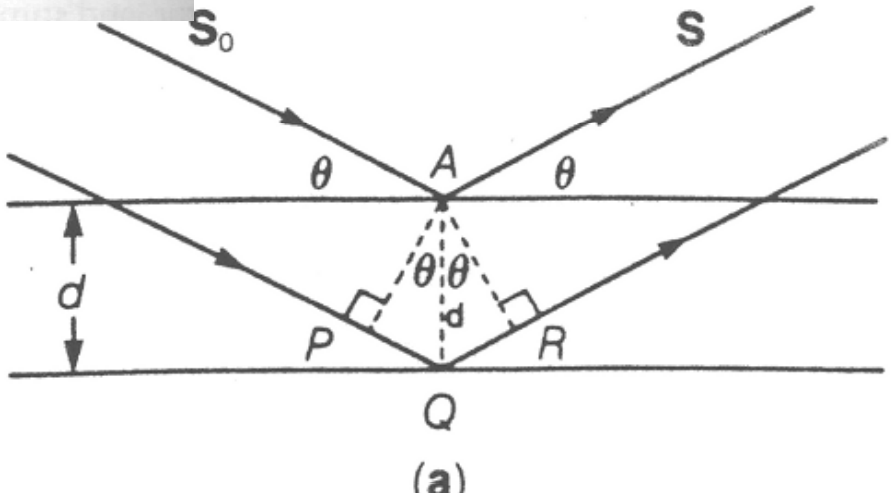
The experiment is successful because the wavelength of the X-rays is comparable with the lattice dimensions in a crystal

The **position of the spots** on the detector depends on the **lattice dimensions**

eg. laser experiment and Bragg's law

How does it depend on the lattice?





$$2d\sin\theta = n\lambda \Rightarrow 2(d/n)\sin\theta = \lambda \Rightarrow 2d_{hkl}\sin\theta = \lambda$$

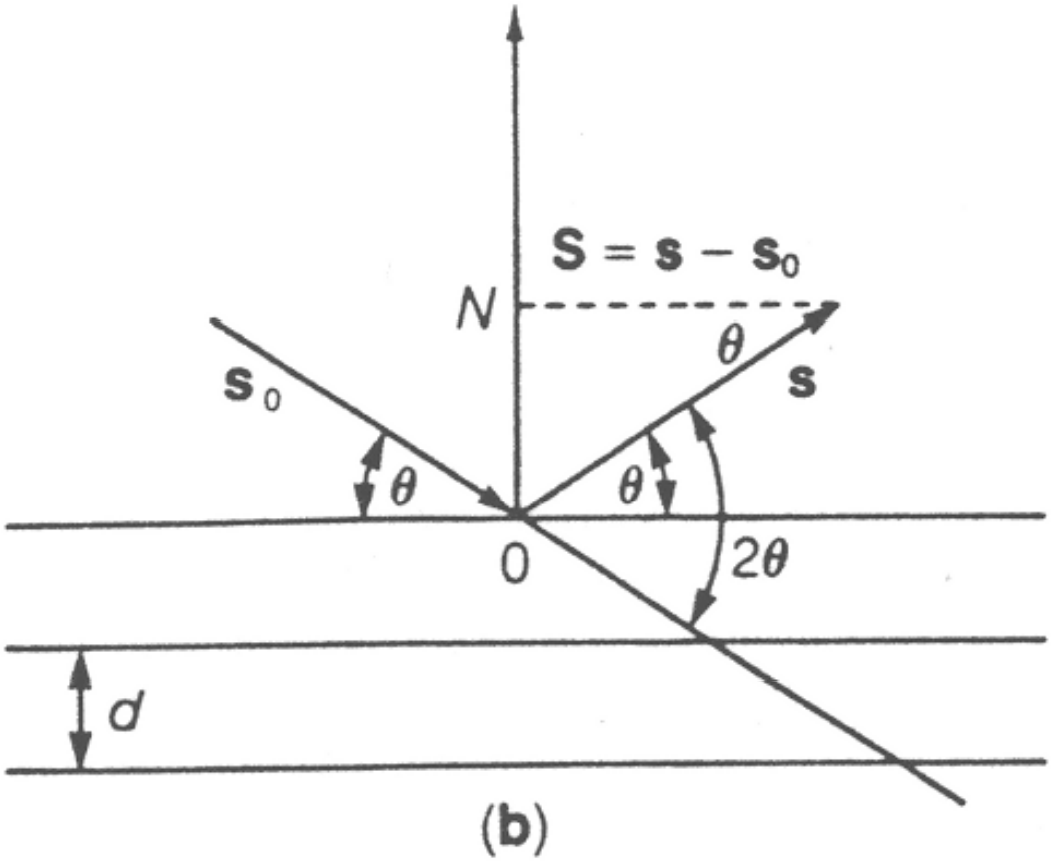
Bragg's lov

- The scattering angle 2θ depends on the distance between the planes d_{hkl}

$$\lambda = 2d_{hkl} \sin\theta \quad \text{(Bragg's lov)}$$

- Larger 2θ means smaller d_{hkl}

- Small d_{hkl} – more details,
  - *i.e. better resolution* $d_{hkl} = \lambda/(2\sin\theta)$



$|\boldsymbol{s_0}|=|\boldsymbol{s}|=1/\lambda$

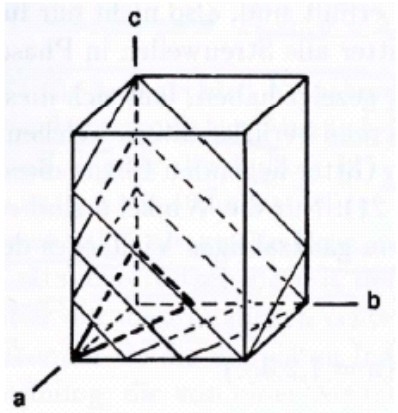
$|\boldsymbol{s}-\boldsymbol{s_0}|=\boldsymbol{S}=\boldsymbol{G}$

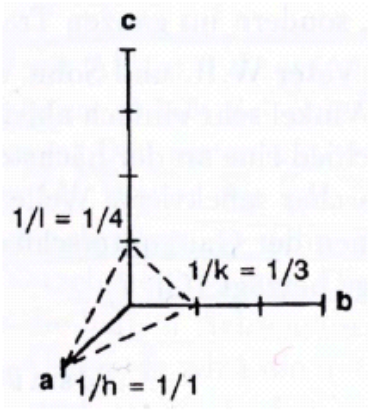
Many different notations

***G** is perpendicular to the Bragg planes*
$|\boldsymbol{G}|=1/d_{hkl}$.

$$2|\boldsymbol{s}|\sin\theta=|\boldsymbol{s}-\boldsymbol{s_0}| \Rightarrow 2(1/\lambda)\sin\theta=|\boldsymbol{s}-\boldsymbol{s_0}| \Rightarrow |\boldsymbol{s}-\boldsymbol{s_0}|=1/d_{hkl}$$

da $2d_{hkl}\sin\theta=\lambda$





- Each set of Bragg planes is named with Miller indices, *hkl*
- From each set of Bragg planes there is **one** reflection
- Each reflection is identified by the Miller indices, *(hkl)*
- The reflections make another lattice **the reciprocal lattice**
- The basis vectors in the reciprocal lattice are **a*,b*,c***, each reflection is seen at lattice point $\boldsymbol{G}=h\boldsymbol{a}^*+k\boldsymbol{b}^*+l\boldsymbol{c}^*$

Example for Miller plane (100)

The Bragg planes are parallelt to the ***bc***-plane

$\boldsymbol{d^*}=\boldsymbol{G}=h\boldsymbol{a^*}=\boldsymbol{a^*}$ *(k,l =0,0)*

$\boldsymbol{a^*} \perp \boldsymbol{b},\boldsymbol{c}$ (perpendicular to the 100 Miller plane)

The angle between ***a*** and ***bc***-plane is φ

$\Rightarrow$ the distance between the planes is $d=|\boldsymbol{a}|\sin\varphi$

$\Rightarrow|\boldsymbol{a^*}|=\mathbf{G}= 1/d=1/(|\boldsymbol{a}|\sin\varphi)$

$\Rightarrow \boldsymbol{a}\cdot\boldsymbol{a^*}=(1/(|\boldsymbol{a}|\sin\varphi)|\boldsymbol{a}|\cos(90°-\varphi)=1$

$\Rightarrow \boldsymbol{a}\cdot\boldsymbol{a^*}=1 \quad og\ \boldsymbol{a}\cdot\boldsymbol{b^*}=0\ og\ \boldsymbol{a}\cdot\boldsymbol{c^*}=0$

The reflections span a lattice

the reciprocal lattice:

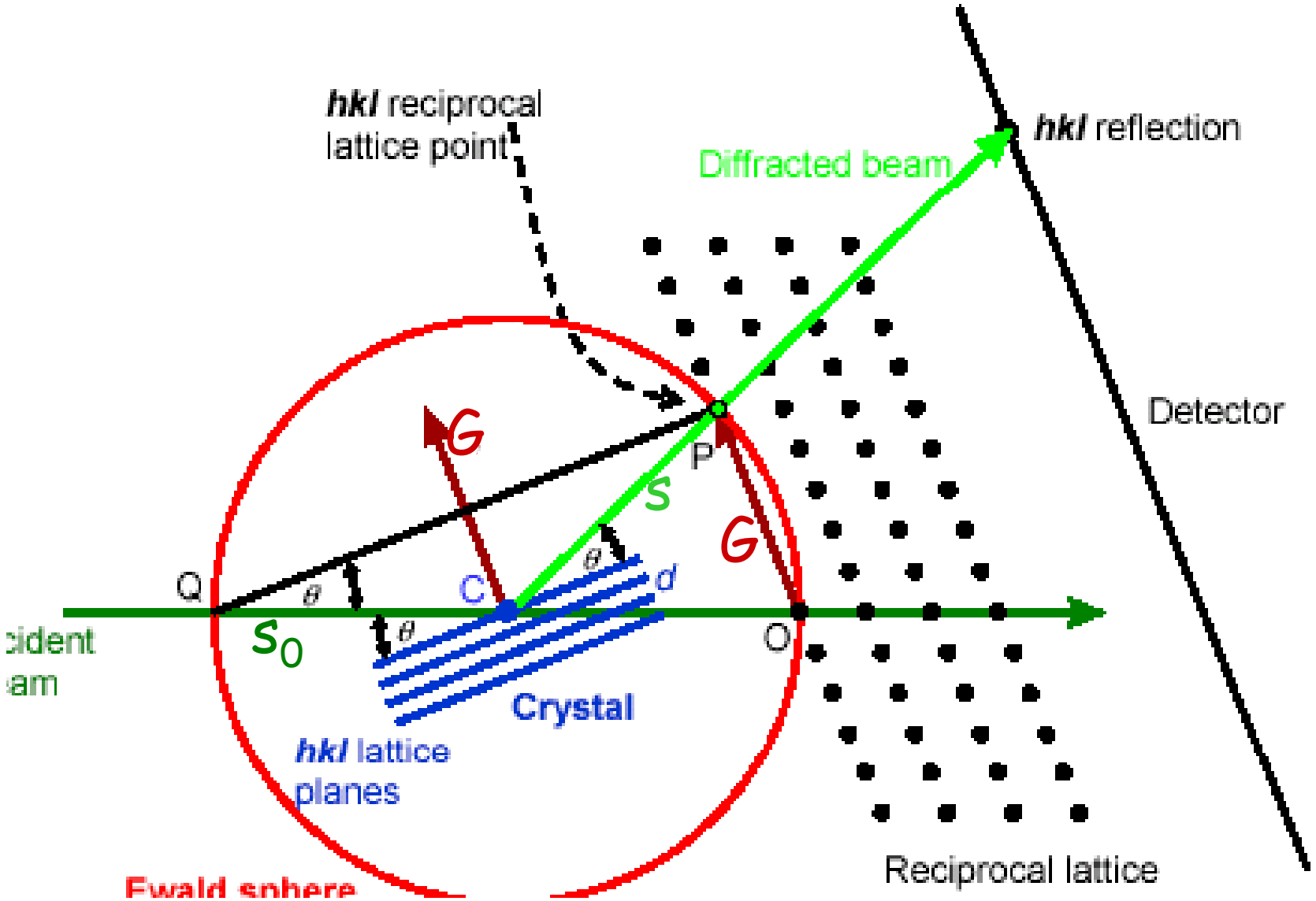
$$\underline{G} = h\underline{a}^* + k\underline{b}^* + l\underline{c}^*$$

h, k, l: Miller indices (integers)

$$\mathbf{a}^* = \frac{\mathbf{b} \times \mathbf{c}}{\mathbf{a} \cdot \mathbf{b} \times \mathbf{c}}$$

$$\mathbf{b}^* = \frac{\mathbf{c} \times \mathbf{a}}{\mathbf{a} \cdot \mathbf{b} \times \mathbf{c}}$$

$$\mathbf{c}^* = \frac{\mathbf{a} \times \mathbf{b}}{\mathbf{a} \cdot \mathbf{b} \times \mathbf{c}}$$


hkl reciprocal lattice point
Diffracted beam
hkl reflection
Detector
G
P
S
G
θ
Q
θ
C
d
θ
S0
O
cident
am
Crystal
hkl lattice planes
Ewald sphere
Reciprocal lattice

if we place one electron in each lattice point

(very simple and unrealistic crystal)

the comparison to the laser experiment becomes straightforward

Instead the electron distribution in the unit cell is a number density $\rho(\underline{r})$, so that the scattering from each atom is:

$$f(\mathbf{H}) = \int \rho(\mathbf{r}) \exp(2\pi i \mathbf{H} \cdot \mathbf{r}) d\mathbf{r}$$

f(H) is the atomic form factor

(the Fourier transformation of the electron distribution of the atom)

- To calculate the scattering from the crystal we sum over all atoms, *j*, and over all lattice points R_n:

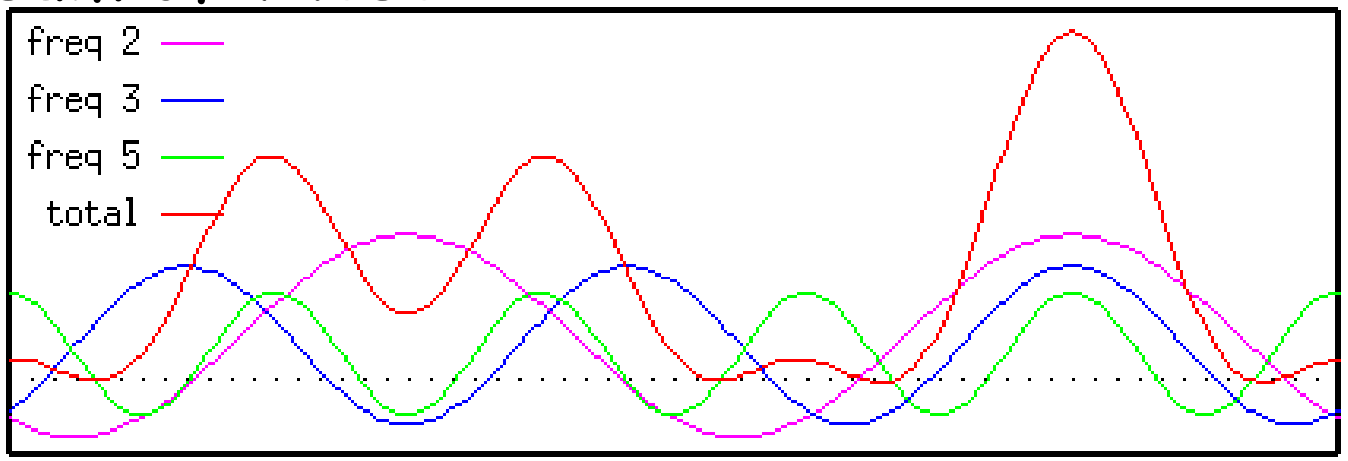
$$\mathbf{F(H)} = \sum_{\mathbf{r}_j} f_j(\mathbf{H}) \exp(2\pi i \mathbf{H}\cdot\mathbf{r}) \sum_{\mathbf{R_n}} \exp(2\pi i \mathbf{H}\cdot\mathbf{R_n})$$

- F(H) is called the structure factor

only ≠0 when H is a reciprocal lattice vector

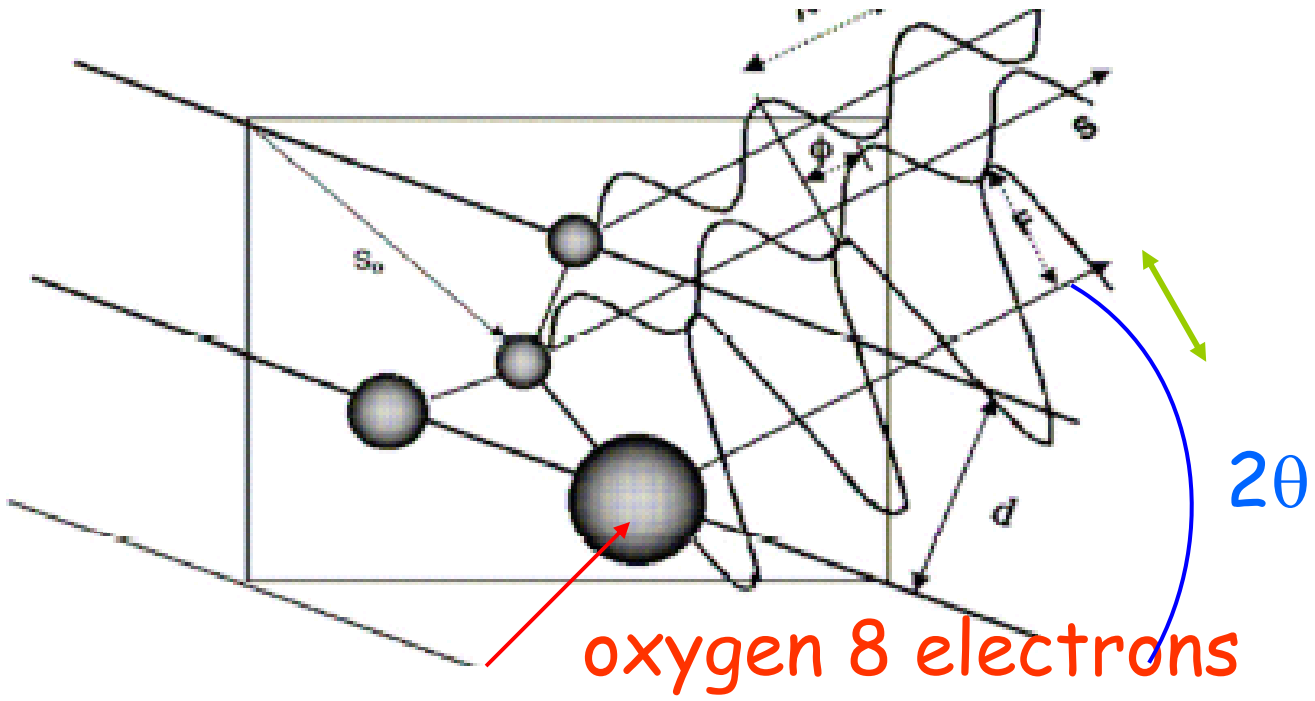
$$\mathbf{F(H)} = \left|\mathbf{F(H)}\right| \exp(i\varphi)$$

- From different atoms in the unit cell waves with different phases and amplitudes (but the same frequency) are scattered. The Structure Factor is the sum of these



The symmetry of the crystal is observed in the diffraction pattern

- the amplitude depends on the number of electrons
- the amplitude depends on the scattering angle 2θ
- the phase depends on the atomic position



In each reciprocal lattice point we measure a reflection with a given intensity

The measured intensity $I(\underline{H})$

$$I(\mathbf{H}) \propto |\mathbf{F}(\mathbf{H})|^2$$

F(H) is the structure factor

- this intensity depends on the contents of the unit cell in the lattice

¡ phase problem !

The electron density of the unit cell may be written as:

$$\rho(\mathbf{r}) = \frac{1}{V}\sum_{\mathbf{H}} \mathbf{F}(\mathbf{H}) \exp(-2\pi i \mathbf{H}\cdot\mathbf{r})$$

where

$$\mathbf{F}(\mathbf{H}) = \left|\mathbf{F}(\mathbf{H})\right| \exp(i\varphi)$$

Recall

$$I(\mathbf{H}) \propto \left|\mathbf{F}(\mathbf{H})\right|^2$$

we loose the phase

To remember from this lecture

The **position of the spots** on the detector depends on the **lattice dimensions**

eg. laser experiment

The **distribution of the intensities** reflects the **symmetry** (contents) of the crystal

we loose the phase information in the experiment