Mitglied der Helmholtz-Gemeinschaft

JARA Jülich Aachen Research Alliance

JÜLICH FORSCHUNGSZENTRUM

Probing Matter with Scattering Methods

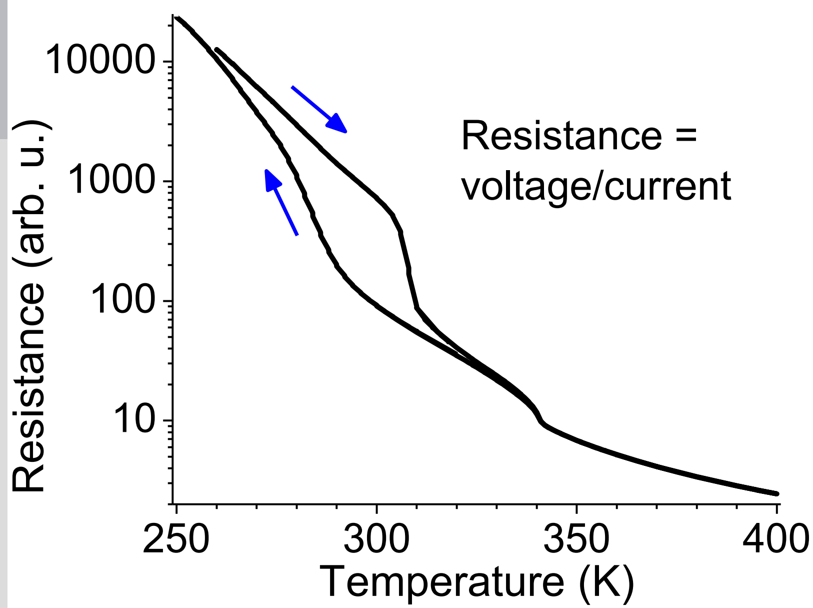
An elementary introduction

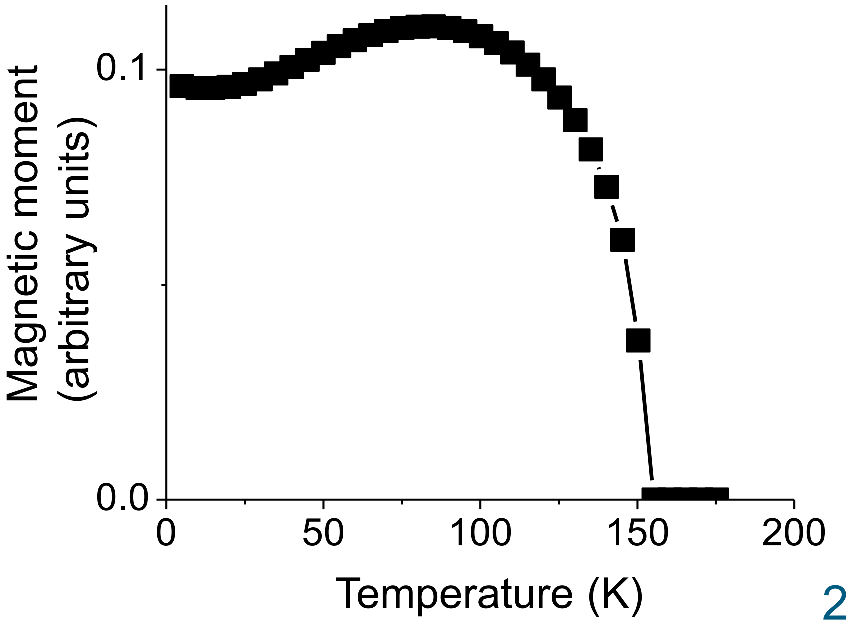
Manuel Angst

1st QUALI-START-UP SCIENCE LECTURES, 11-15 September 2017

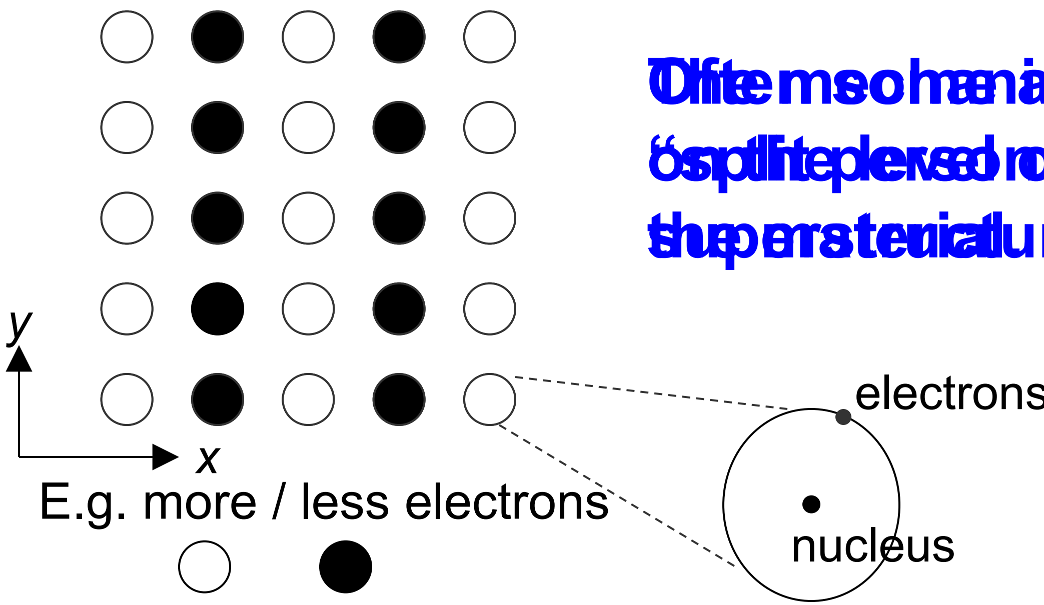
Much of technology relies on phenomena related to electronic properties of materials

These properties can be measured in various ways, but to understand (and then tune) them, the underlying mechanism needs to be investigated





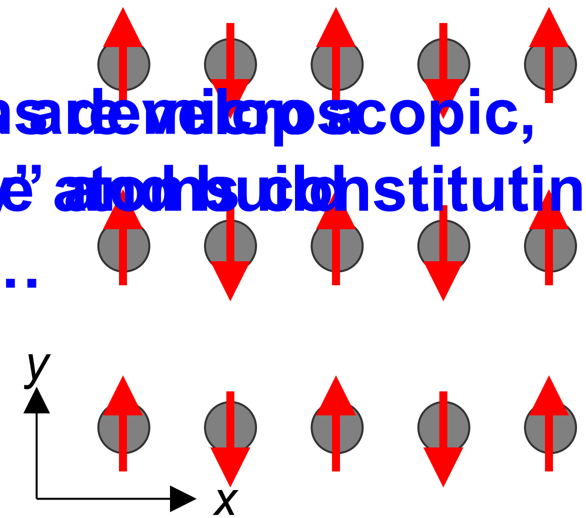
Superstructures



E.g. more / less electrons

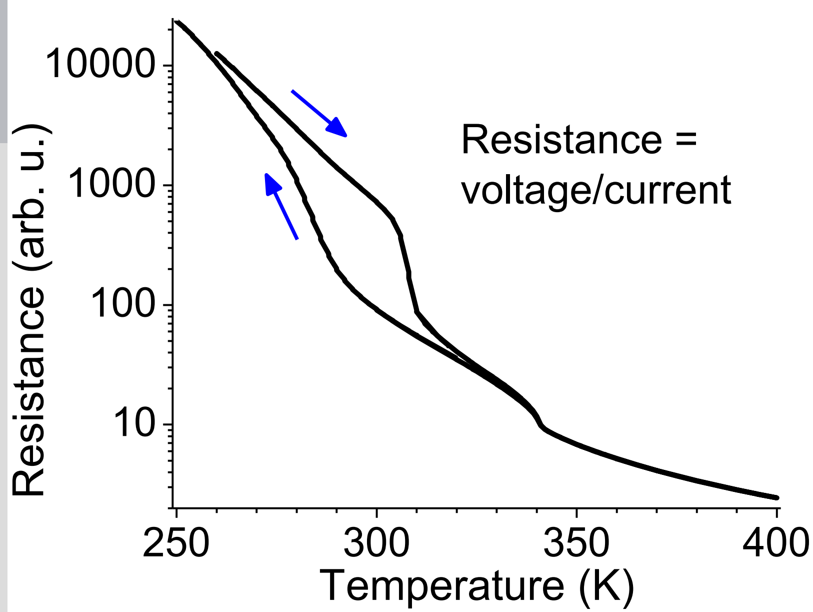
The mechanisms are microscopic, on the level of the atoms constituting the material…

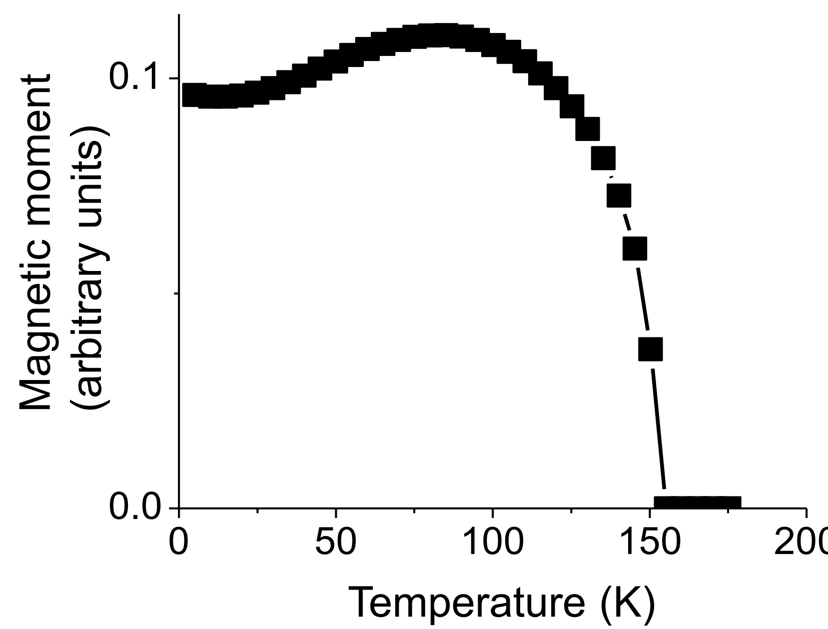
Often atoms develop a “split personality” and such superstructures…



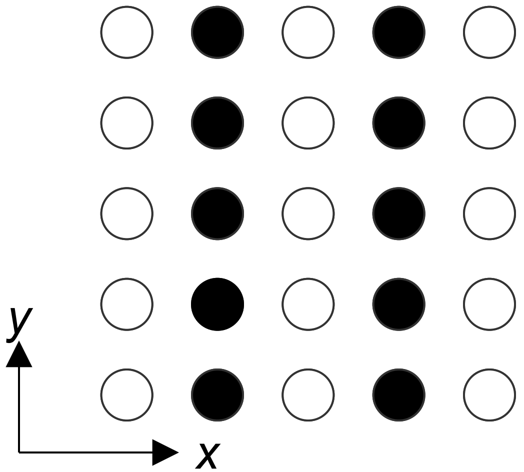
atomic magnetic moment

(anti-ferromagnetism)

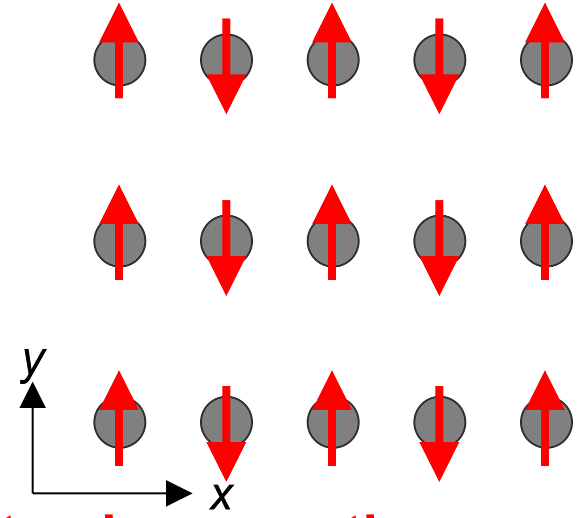




Superstructures



E.g. more / less electrons



atomic magnetic moment

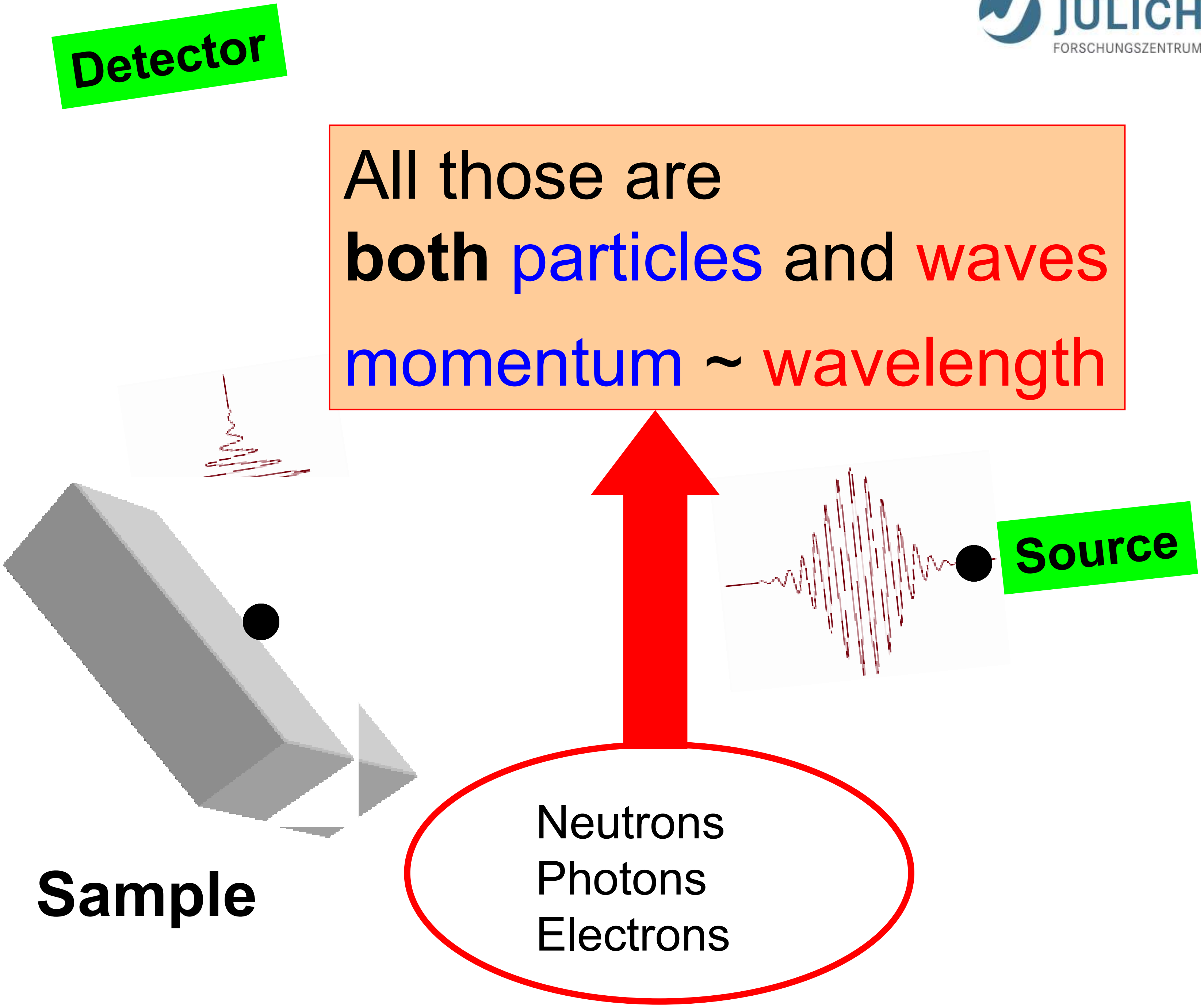
(anti-ferromagnetism)

To really understand what is going on, we should be able to “see” such superstructures

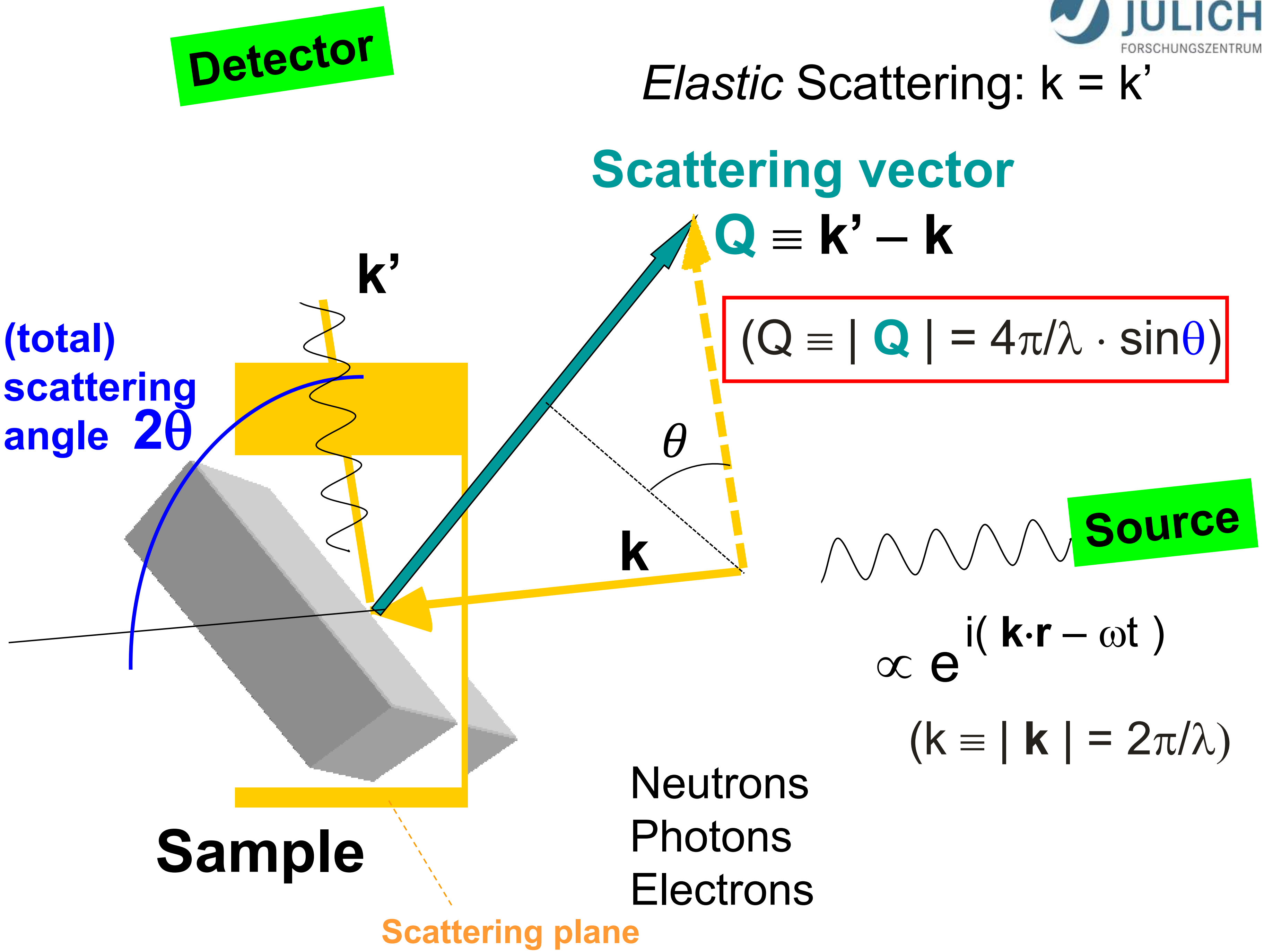
With **scattering methods**, this is possible !

All those are
both particles and waves

momentum ~ wavelength



Elastic Scattering: k = k'

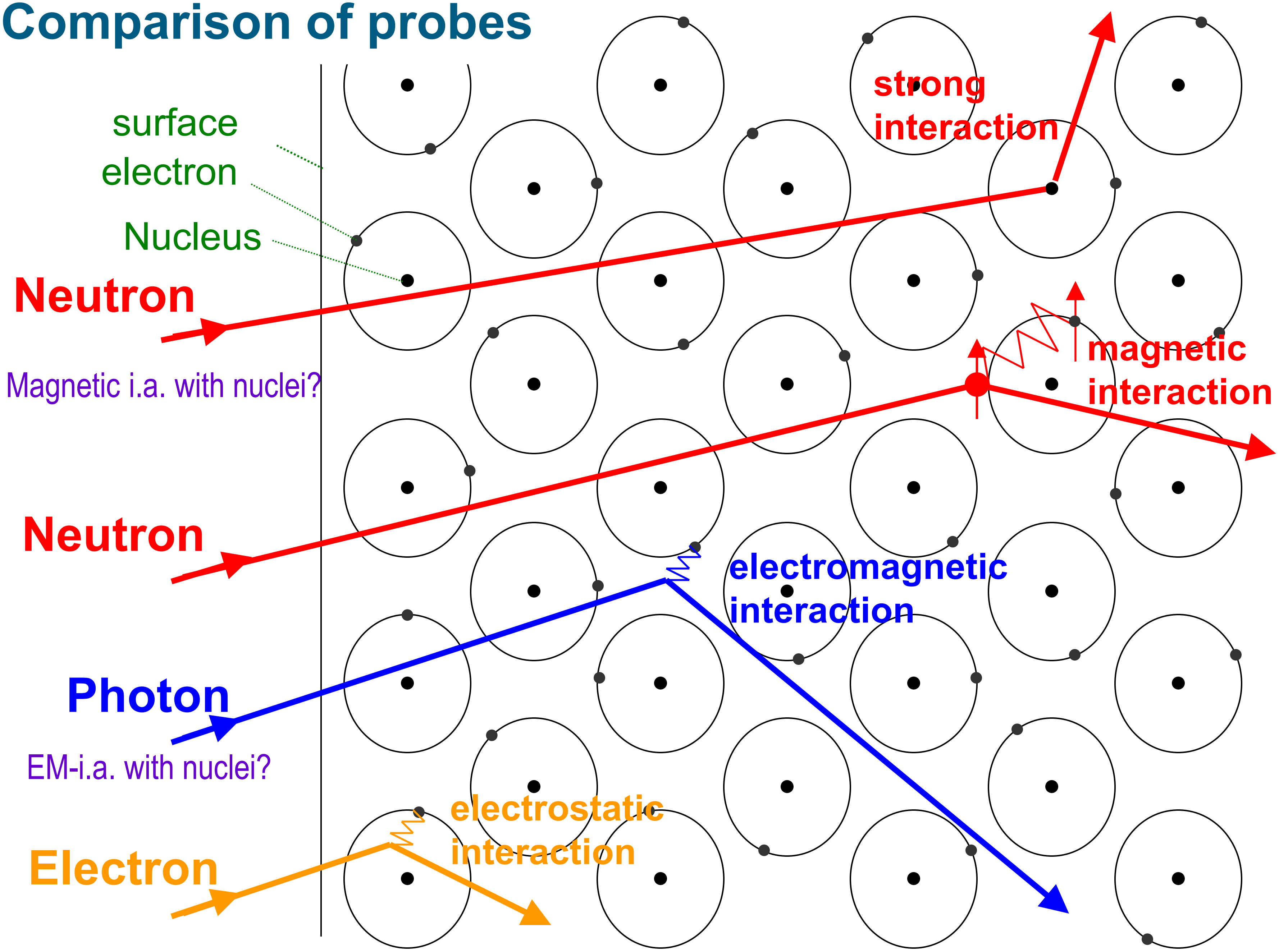


$(Q \equiv |\mathbf{Q}| = 4\pi/\lambda \cdot \sin\theta)$

$\propto e^{i(\mathbf{k}\cdot\mathbf{r} - \omega t)}$

$(k \equiv |\mathbf{k}| = 2\pi/\lambda)$

Comparison of probes



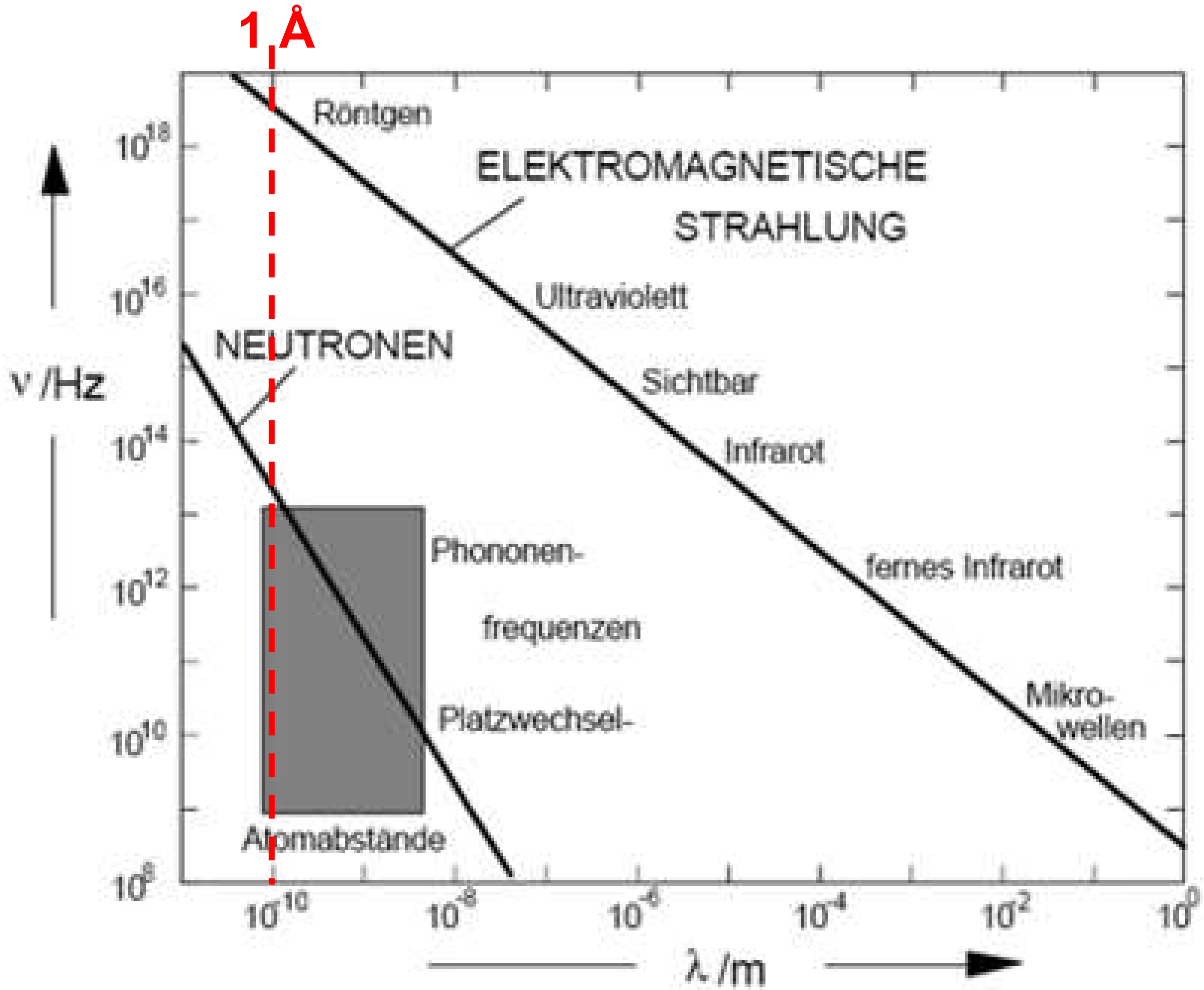
Comparison of probes

Neutrons have simultaneously wave lengths (0.2 – 20 Å) and energies (10^{-3} - 10^{3} meV) corresponding to atomic distances and charakteristic energies in solids (e.g. phonons).

Neutron scattering can answer the question

„Where are the atoms, and how do they move?“.

Relationship between frequency and wave length for neutrons and X-rays ($\nu = c/\lambda$)



Comparison of probes

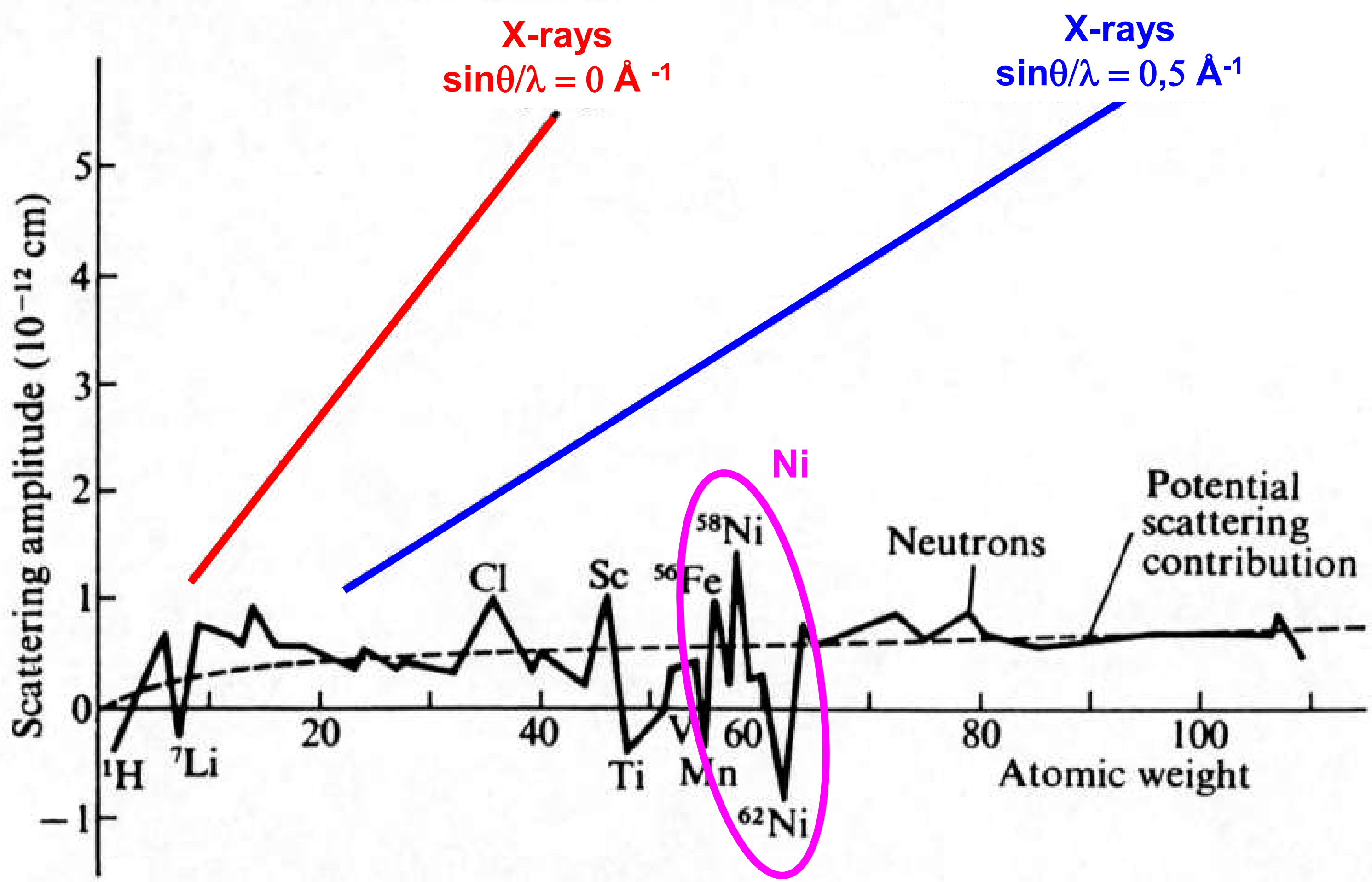


FIG. 22. Irregular variation of neutron scattering amplitude with atomic weight due to superposition of 'resonance scattering' on the slowly increasing 'potential scattering'; for comparison the regular increase for X-rays is shown. (From *Research (London)* 7, 257 (1954).)

Basics of diffraction

Two fundamental principles:

1. Huygens‘ principle:

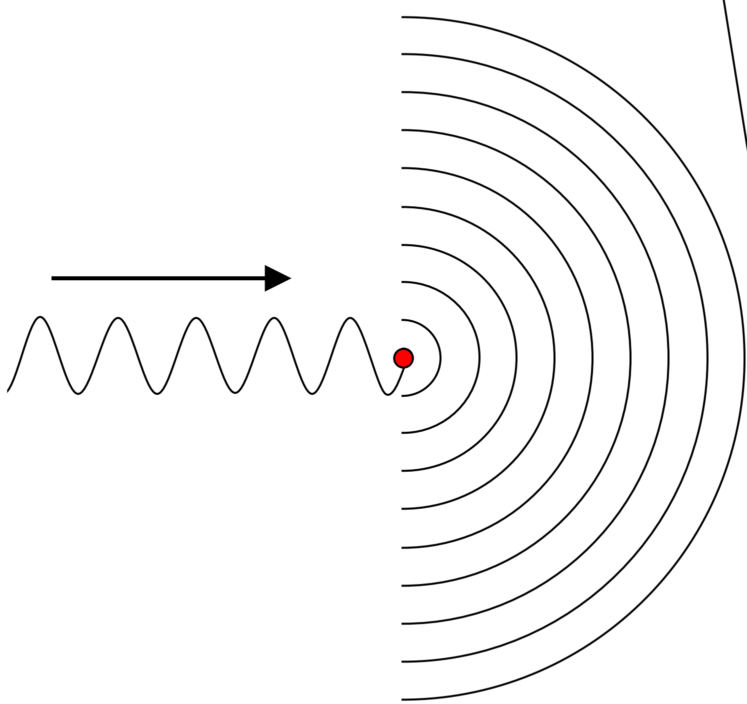
Every point in space reached acts as a source of a spherical wave
(if there are no obstacles except for a point-scatterer, we get a sum of the incoming wave and a spherical wave emitting from the scatterer)

2. Superposition principle:

For several waves of the same frequency traversing the same point, the amplitude at this point is given by the sum of the complex amplitudes (with a phase factor) of the individual waves.

Diffraction: Huygens principle

Small scattering object (atom, nanoparticle, …)
acts as secondary source of
a spherical wave



Intensity of the scattered radiation depends on the details of the interaction with the object.

depends on scattering vector
Q (magnitude and direction!)

What about neutron nuclear
and Thomson scattering ?

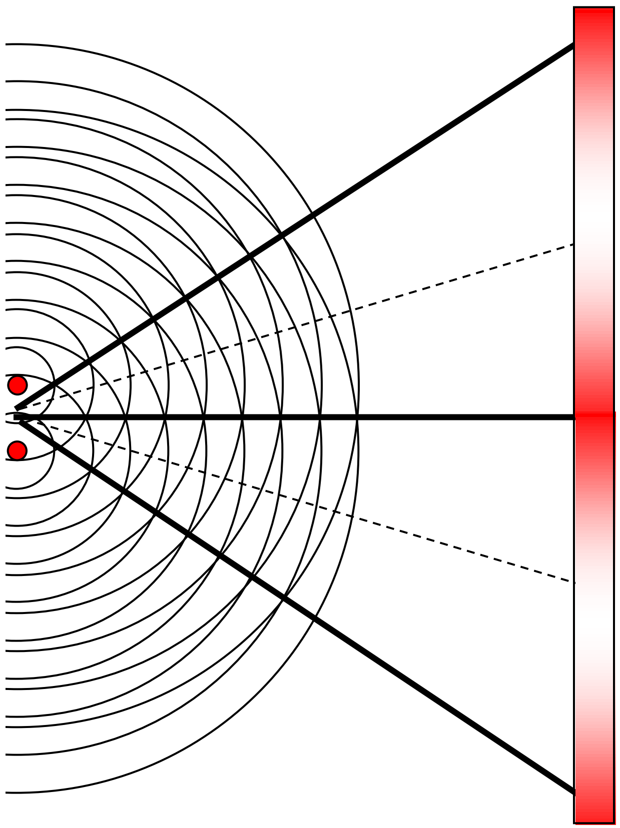
$$I\,(\mathbf{Q}) = |\,f(\mathbf{Q})\,|^2$$

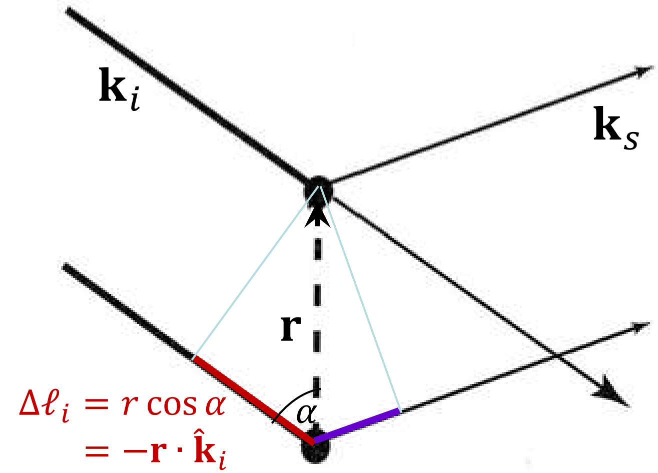
"scattering factor"

Diffraction: Young's '2-slit' interference

Two scattering objects act as **coherent** secondary sources.

Phase-correct summation of the scattering amplitudes (far field / Frauenhofer)





$$\frac{\text{phase difference } \Delta\phi}{2\pi} = \frac{\text{path difference } \Delta\ell}{\text{wave length } \lambda}$$

$$\Delta\phi_i = -\mathbf{r}\cdot\hat{\mathbf{k}}_i \frac{2\pi}{\lambda} = -\mathbf{r}\cdot\mathbf{k}_i$$

$$\Delta\phi_s = \mathbf{r}\cdot\hat{\mathbf{k}}_s \frac{2\pi}{\lambda} = \mathbf{r}\cdot\mathbf{k}_s$$

$$\Delta\phi = \mathbf{r}\cdot(\mathbf{k}_s - \mathbf{k}_i) = \mathbf{r}\cdot\mathbf{Q}$$

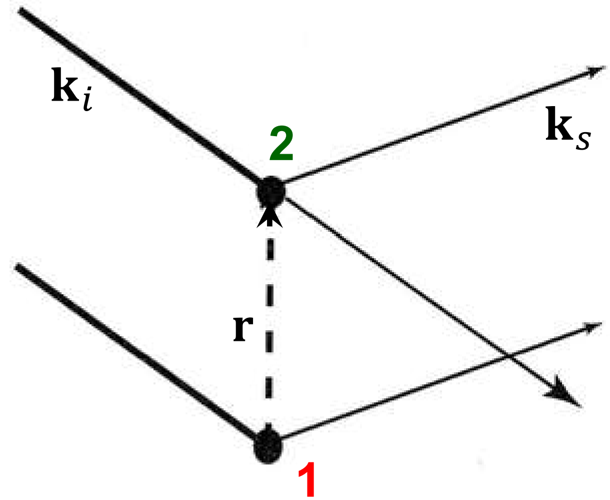
→ Interference pattern due to constructive/destructive inteference

Diffraction: two scatterers

$I(\mathbf{Q}) = |F(\mathbf{Q})|^2 = F(\mathbf{Q})\,F(\mathbf{Q})^*$

Phase-correct summation of the scattering amplitudes (far field / Frauenhofer)

$$F(\mathbf{Q}) = f_1(\mathbf{Q})e^{i\mathbf{Q}\cdot\mathbf{r}_1} + f_2(\mathbf{Q})e^{i\mathbf{Q}\cdot\mathbf{r}_2}$$



$$\frac{\text{phase difference } \Delta\phi}{2\pi} = \frac{\text{path difference } \Delta\ell}{\text{wave length } \lambda}$$

$$\Delta\phi_i = -\mathbf{r}\cdot\hat{\mathbf{k}}_i\,\frac{2\pi}{\lambda} = -\mathbf{r}\cdot\mathbf{k}_i$$

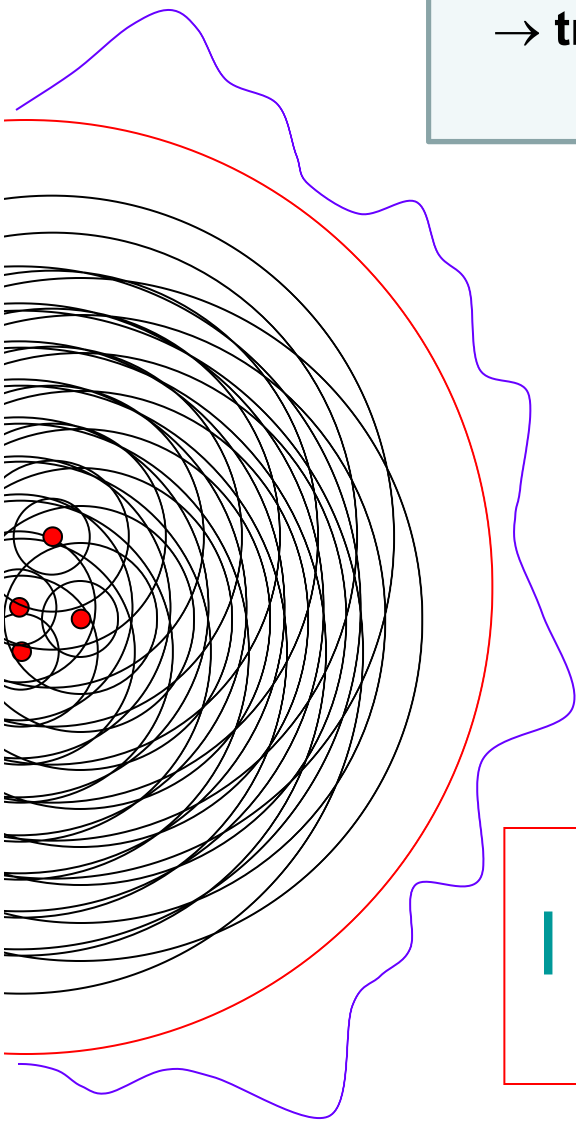
$$\Delta\phi_s = \mathbf{r}\cdot\hat{\mathbf{k}}_s\,\frac{2\pi}{\lambda} = \mathbf{r}\cdot\mathbf{k}_s$$

$$\Delta\phi = \mathbf{r}\cdot(\mathbf{k}_s - \mathbf{k}_i) = \mathbf{r}\cdot\mathbf{Q}$$

Diffraction: many scatterers

What about beam divergence, energy-distribution?

→ **transversal and longitudinal/temporal coherence**
(→ exercises)



Many scatterers analogously act as coherent secondary sources.

Far away: interference pattern

$$F(\mathbf{Q}) = \sum_j f_j(\mathbf{Q}) e^{i\mathbf{Q}\cdot\mathbf{R}_j}$$

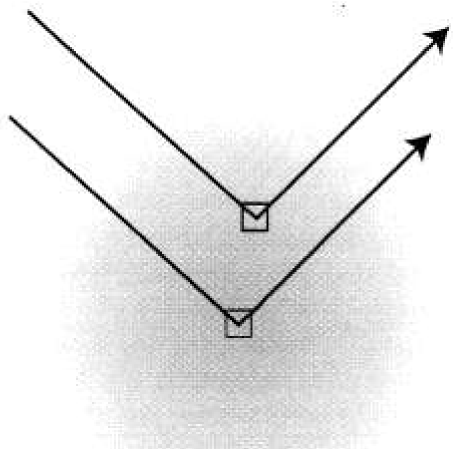
position scatterer j,k

$$I(\mathbf{Q}) = \sum_{j,k} f(\mathbf{Q})_j \, f(\mathbf{Q})_k^* \, e^{i\mathbf{Q}\cdot(\mathbf{R}_j - \mathbf{R}_k)}$$

Continuous scattering distribution

X-ray scattering on an atom:
- Single electron: Thomson-scattering (polarisation factor separates)
- Electrons have a continuous probability density $|\psi(\mathbf{r})|^2$

$$F(\mathbf{Q}) = \sum_j f_j(\mathbf{Q}) e^{i\mathbf{Q}\cdot\mathbf{R}_j}$$



$$f(\mathbf{Q}) = \int |\psi(\mathbf{r})|^2 e^{i\mathbf{Q}\cdot\mathbf{r}} \, d^3r$$

Fourier transform !

in general: scattering length density ρ_s

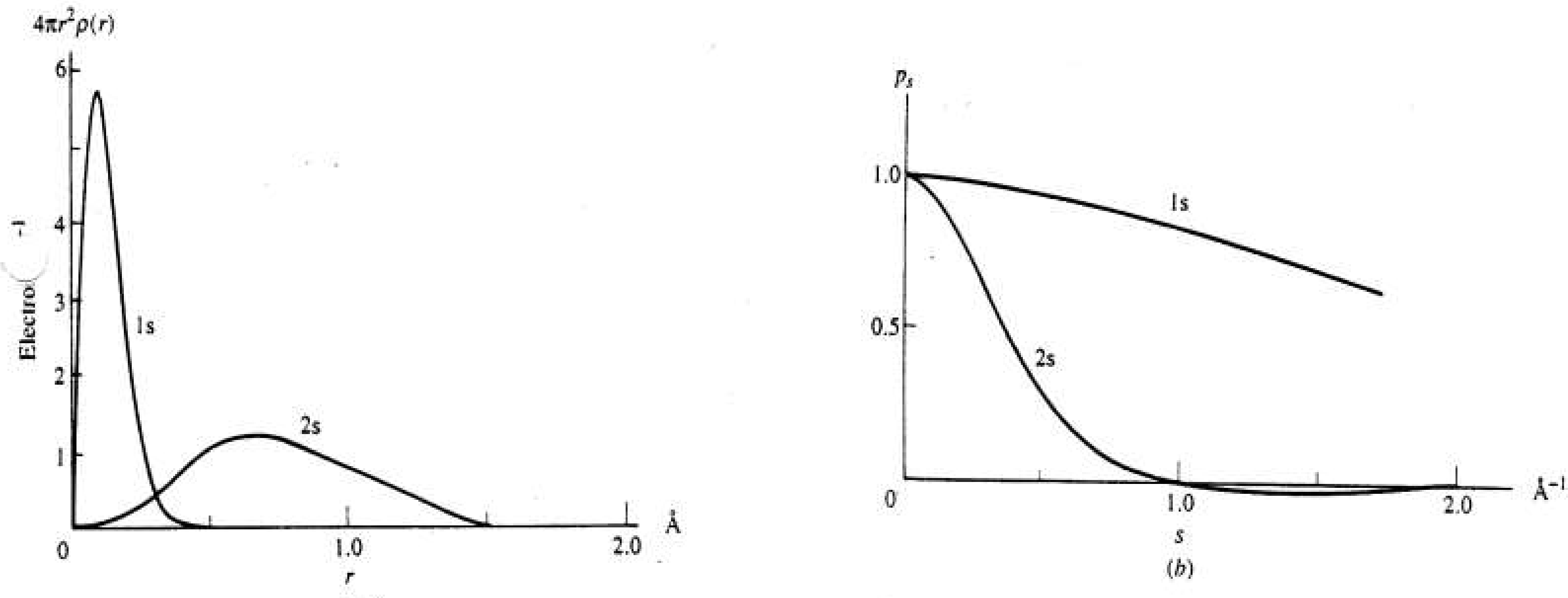
form factor (generally: scattering amplitude)

Atomic form factor

$$f(\mathbf{Q}) = \int |\psi(\mathbf{r})|^2 e^{i\mathbf{Q}\cdot\mathbf{r}} \, d^3r$$

Example: Carbon

Contribution of different shells to the scattering amplitude



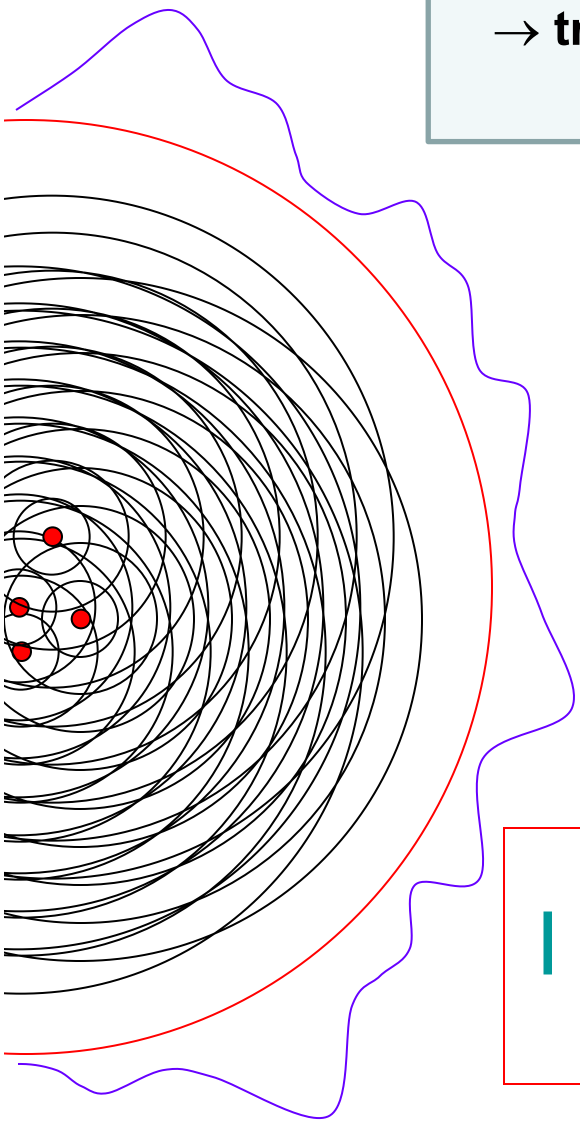
localised in real space ↔ extended in reciprocal space

Diffraction: many scatterers

JÜLICH FORSCHUNGSZENTRUM

What about beam divergence, energy-distribution?

→ **transversal and longitudinal/temporal coherence** (→ exercises)



Many scatterers analogously act as coherent secondary sources.

Far away: interference pattern

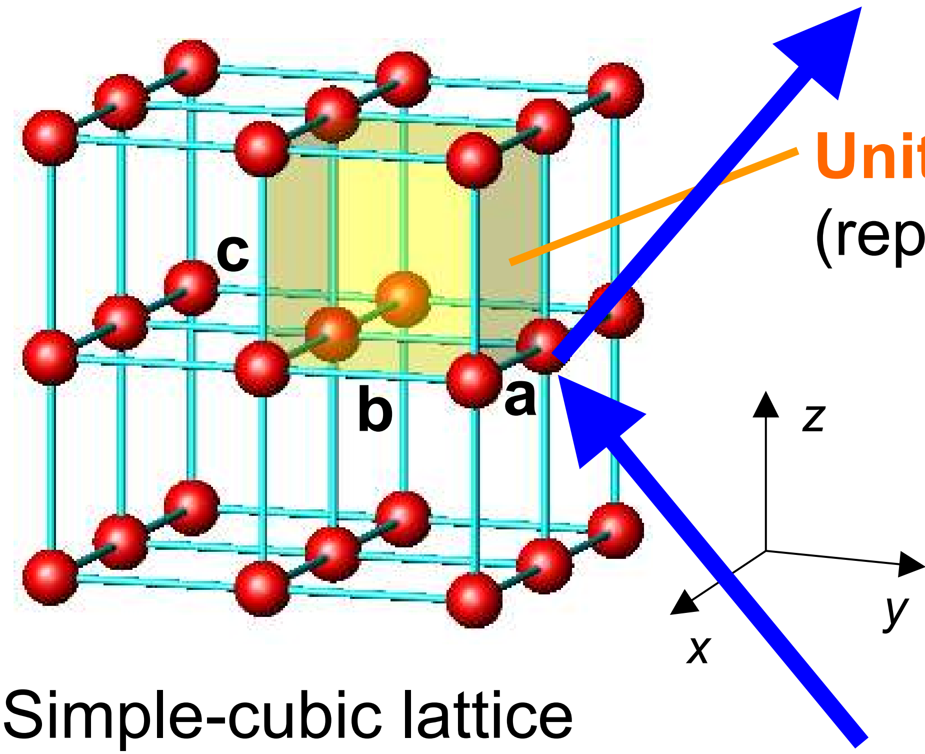
$$F(\mathbf{Q}) = \sum_j f_j(\mathbf{Q}) e^{i\mathbf{Q}\cdot\mathbf{R}_j}$$

position scatterer j,k

$$I(\mathbf{Q}) = \sum_{j,k} f(\mathbf{Q})_j \, f(\mathbf{Q})_k^{*} \, e^{i\mathbf{Q}\cdot(\mathbf{R}_j - \mathbf{R}_k)}$$

Crystalline Matter

Atoms in matter usually arranged in 3-dimensional periodic lattices (crystal)

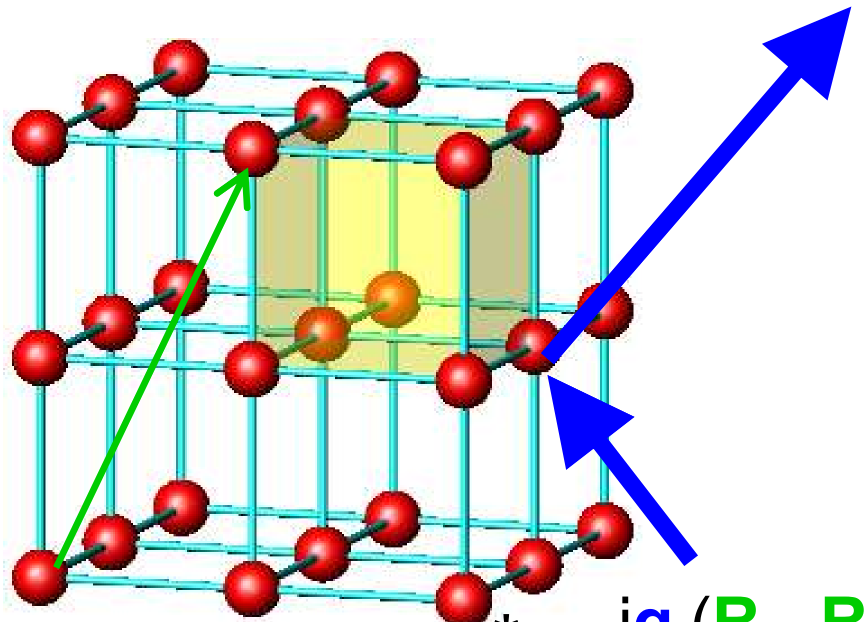


Simple-cubic lattice
(a=b=c)

Crystal is natural 3D diffraction grating

Crystalline Matter

Atoms in matter usually arranged in 3-dimensional periodic lattices (crystal)



$$I(\mathbf{q}) = \sum_{i,j} f_i f_j^* e^{i\mathbf{q}\cdot(\mathbf{R}_i - \mathbf{R}_j)}$$

Atoms identical

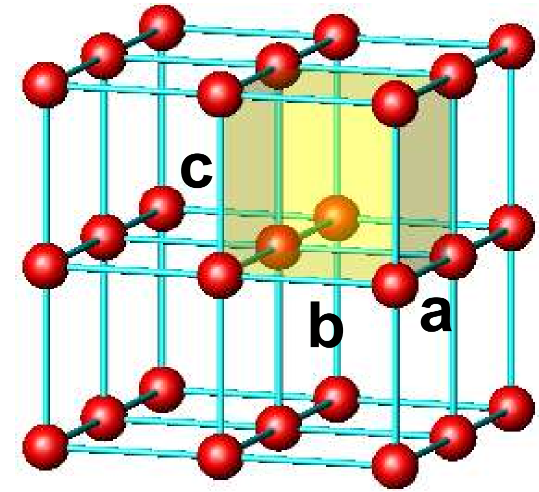
$$= f f^* \sum_{i,j} e^{i\mathbf{q}\cdot(\mathbf{R}_i - \mathbf{R}_j)} = I_{atom} \left|\sum_i e^{i\mathbf{q}\cdot\boldsymbol{R}_i}\right|^2$$

$f f^* = I_{atom}$

Math: $|\Sigma_i C_i|^2 = \Sigma_{ij} C_i C_j^*$

How to maximize

$$I(\mathbf{q}) = I_{atom} \left|\sum_i e^{i\mathbf{q}\cdot\mathbf{R}_i}\right|^2$$



Guess : choose q so that for all i $e^{i\mathbf{q}\cdot\mathbf{R}_i}$ is 1

$\rightarrow$ $\mathbf{q}\cdot\mathbf{R} = 2\pi n$ with n integer,
for **all** lattice vectors **R**

Otherwise destructive Interference !

$\Updownarrow$

$q_x a = 2\pi l$
$q_y b = 2\pi m$
$q_z c = 2\pi n$

Laue equations

l,*m*,*n* integer

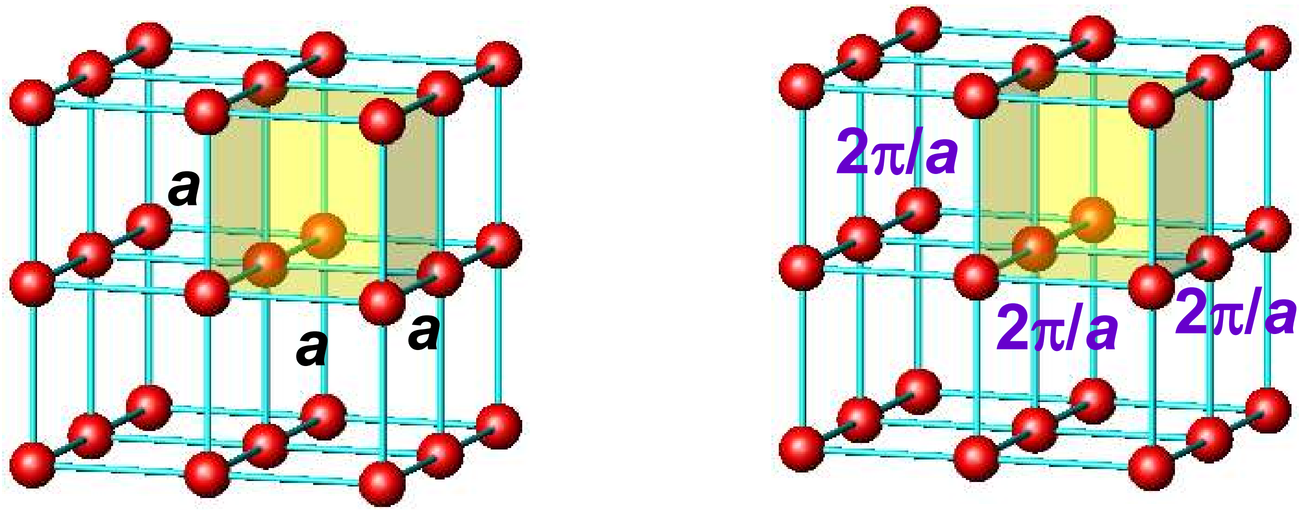
fulfilled $\longrightarrow$ **Bragg peaks**

The set of vectors **q** fullfilling the condition

> $\mathbf{q}\cdot\mathbf{R} = 2\pi n$ with n integer,
> for **all** lattice vectors **R**

is also a lattice, the ***reciprocal lattice*** to R.

The reciprocal lattice of a simple-cubic lattice with lattice constant *a* is also a simple-cubic lattice, with lattice constant **$2\pi/a$**



Coordinates usually given in units of reciprocal lattice constants, (h,k,l)

Ewald construction

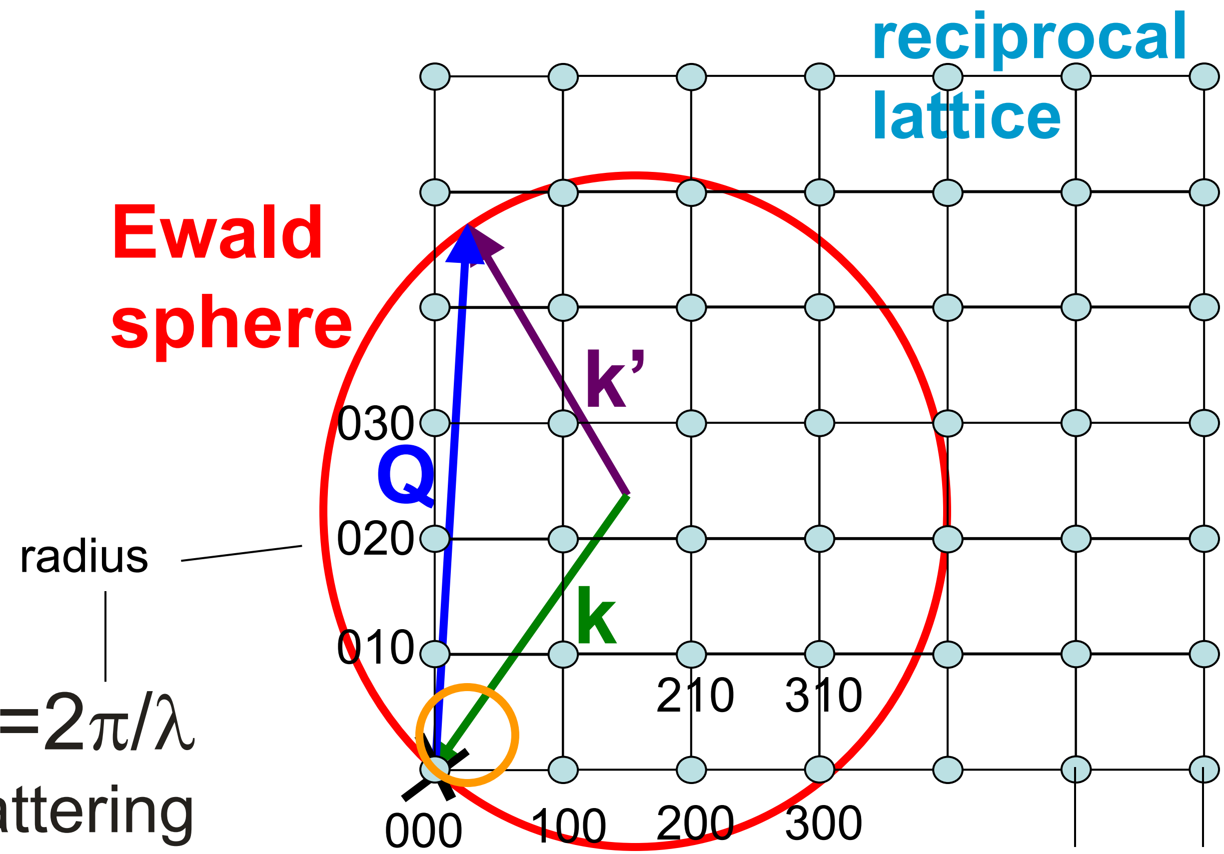
We have

$\mathbf{Q} = \mathbf{k'} - \mathbf{k}$

and

$|\mathbf{k'}| = |\mathbf{k}| = 2\pi/\lambda$

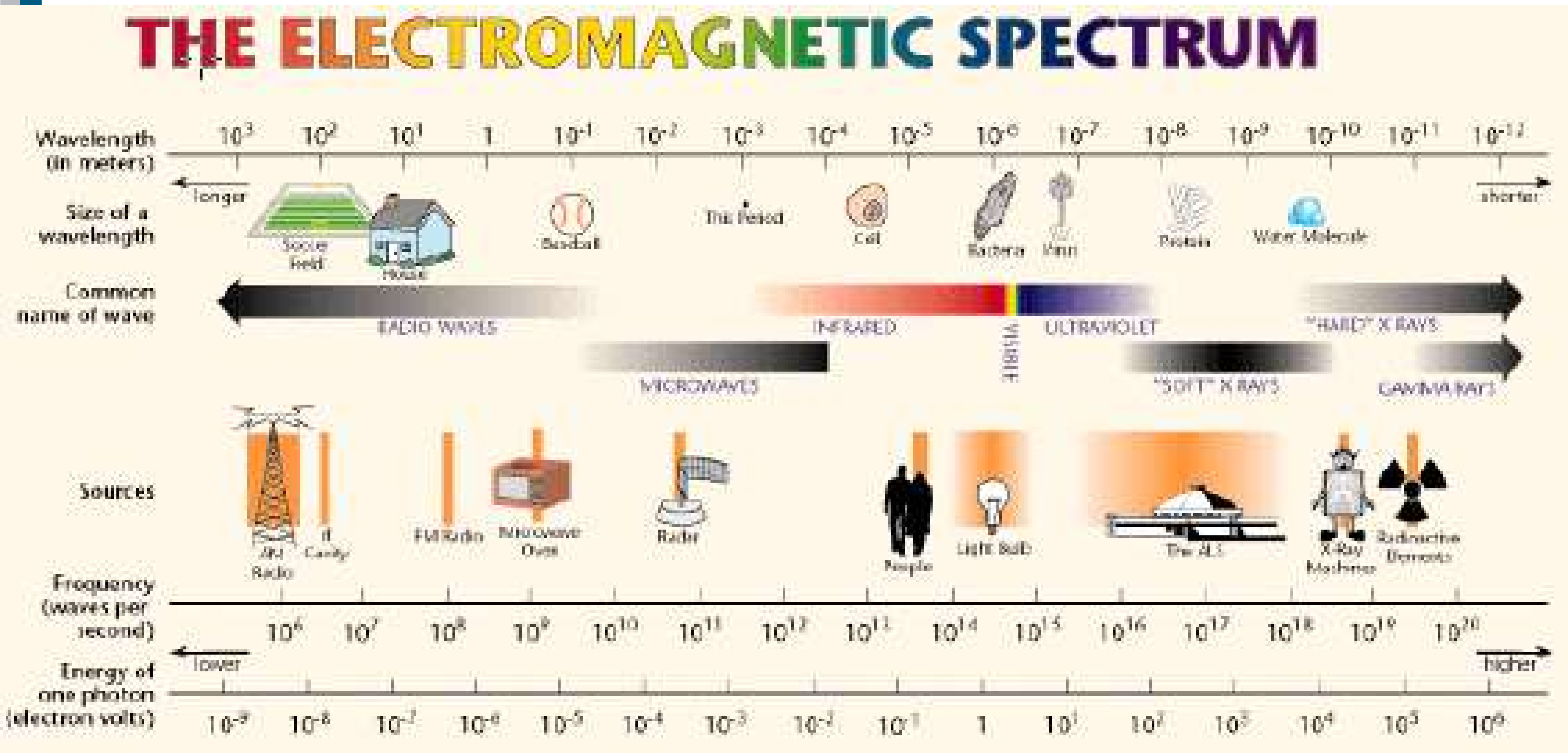
for elastic scattering



$Q_{max} = 4\pi/\lambda$.

Condition for diffraction: $\lambda < 2a$

Bragg conditions may be achieved by scanning the wave length or by „rocking“ the crystal
= rolling the reciprocal lattice relative to the Ewald sphere



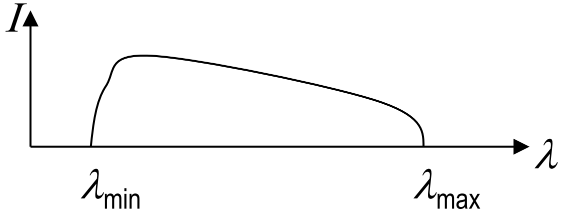
for elastic scattering

$Q_{max} = 4\pi/\lambda$.

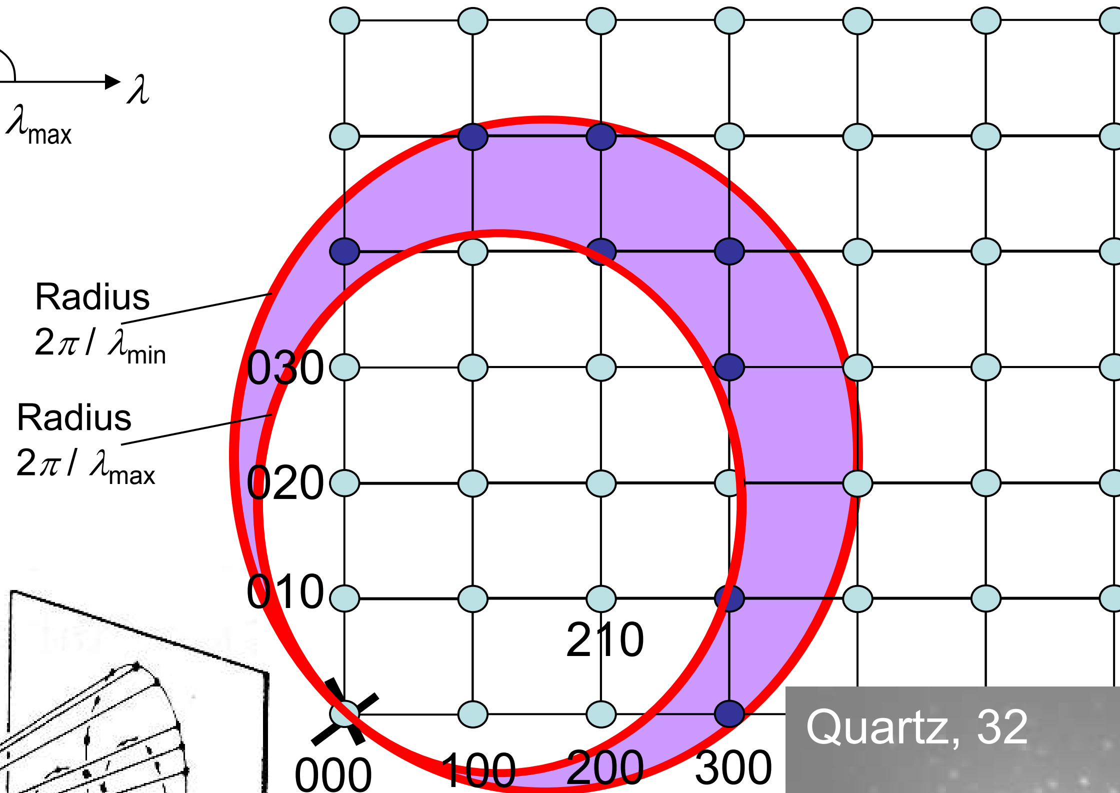
Condition for diffraction: $\lambda < 2a$

Bragg conditions may be achieved by scanning the wave length or by „rocking“ the crystal
= rolling the reciprocal lattice relative to the Ewald sphere

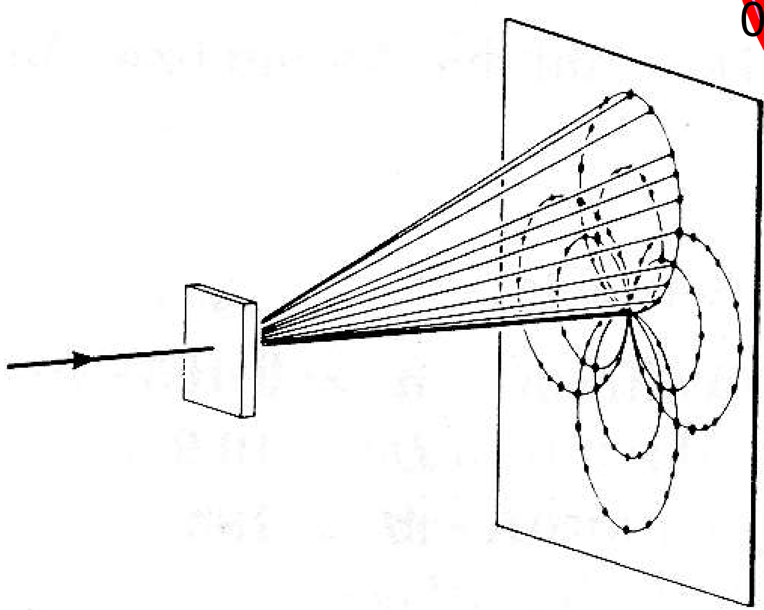
Laue method

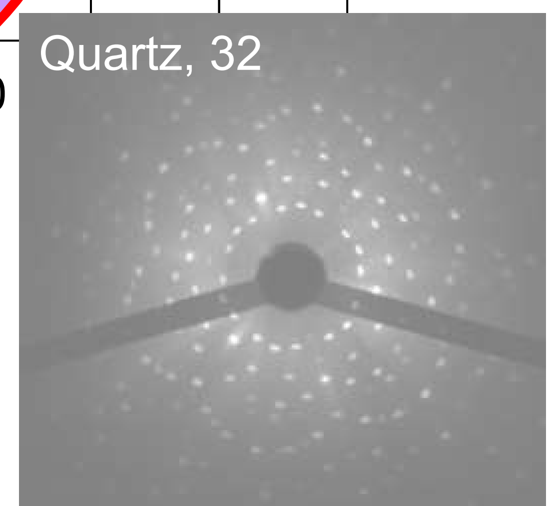


I
λ
λ_{min}
λ_{max}



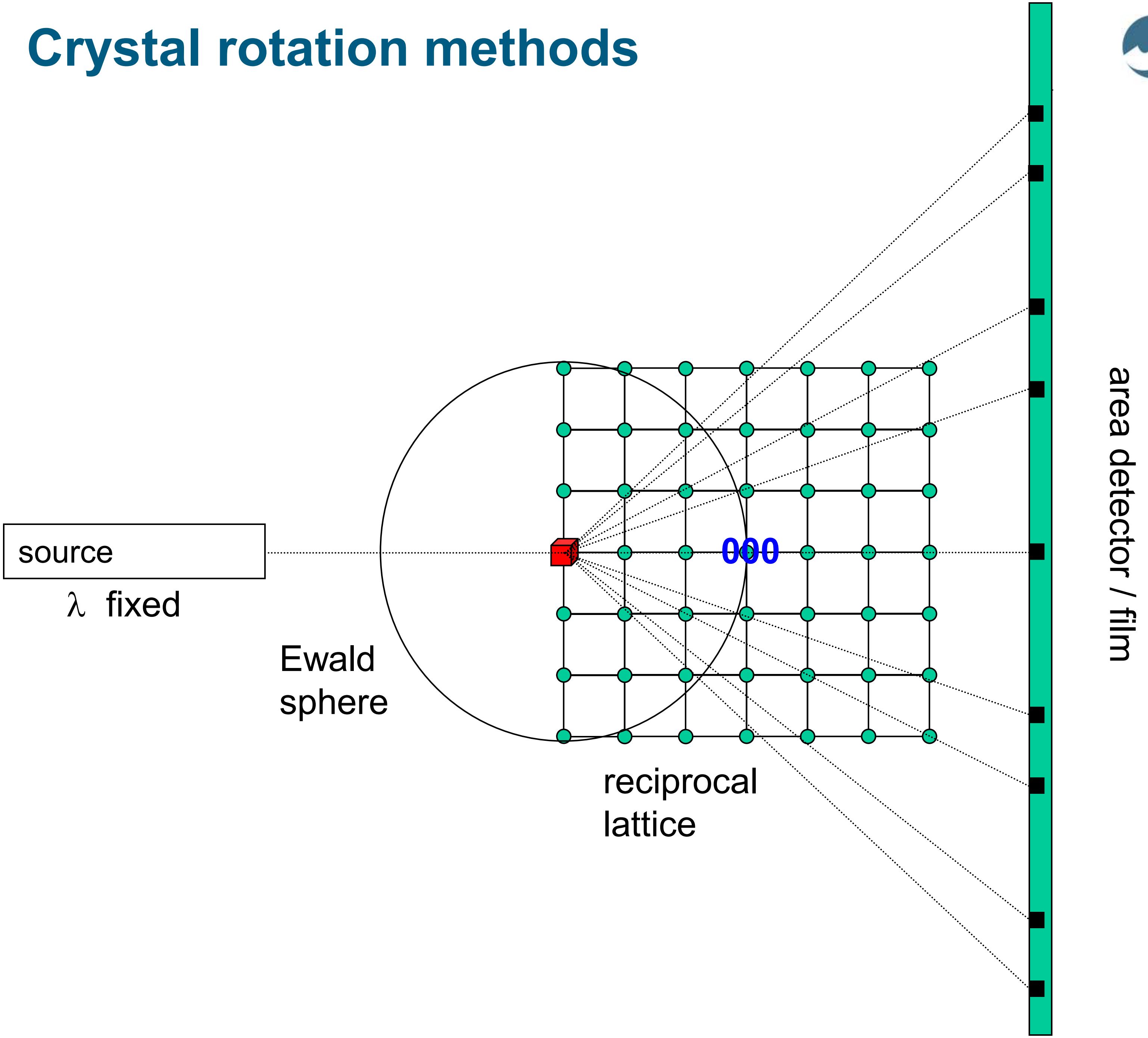
Radius $2\pi / \lambda_{min}$
Radius $2\pi / \lambda_{max}$
030
020
010
210
000
100
200
300



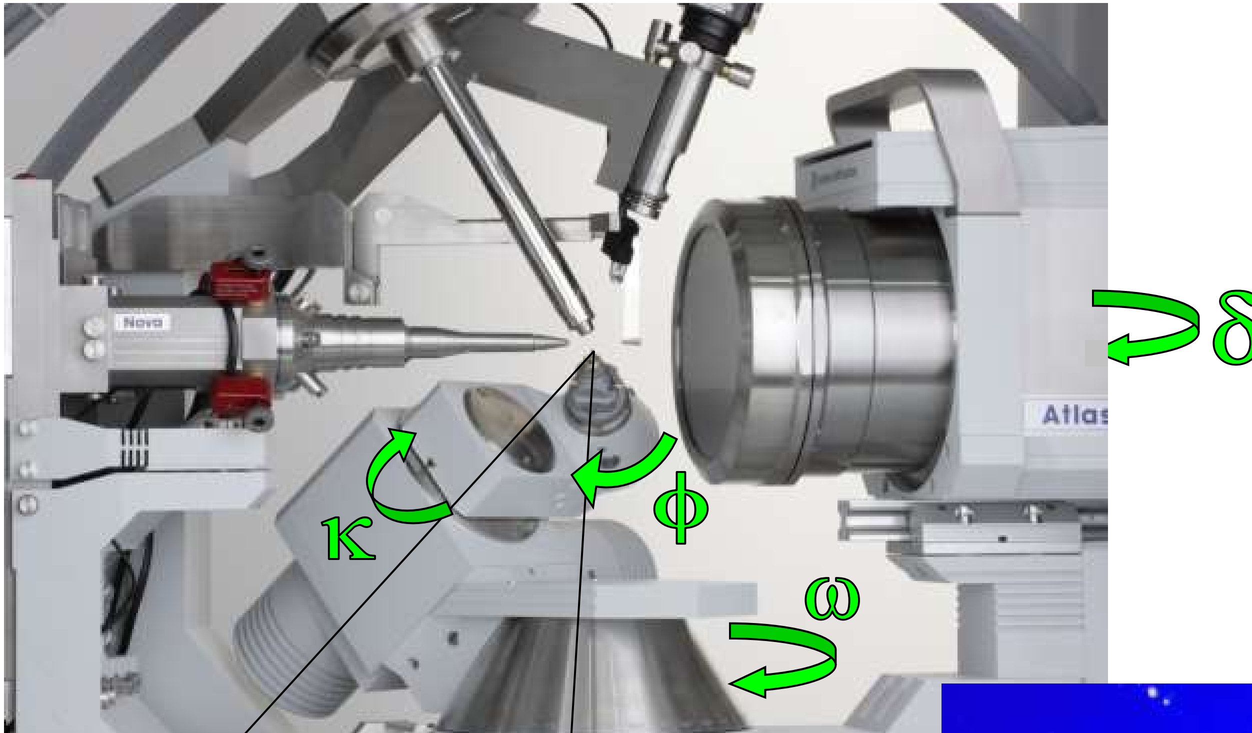


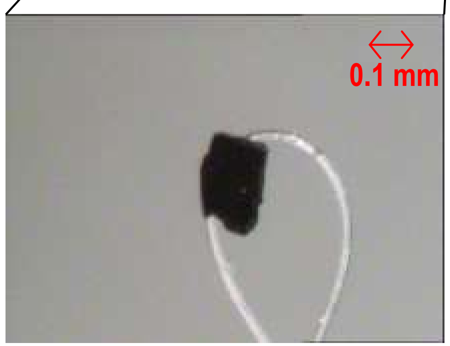
Quartz, 32

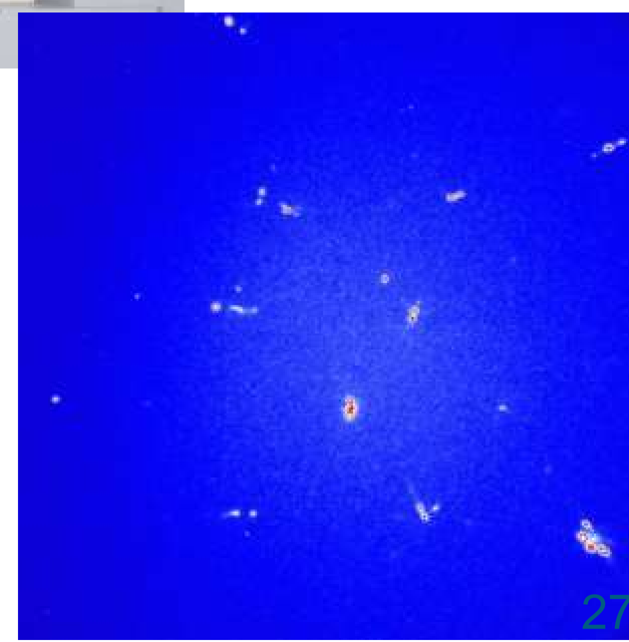
Crystal rotation methods



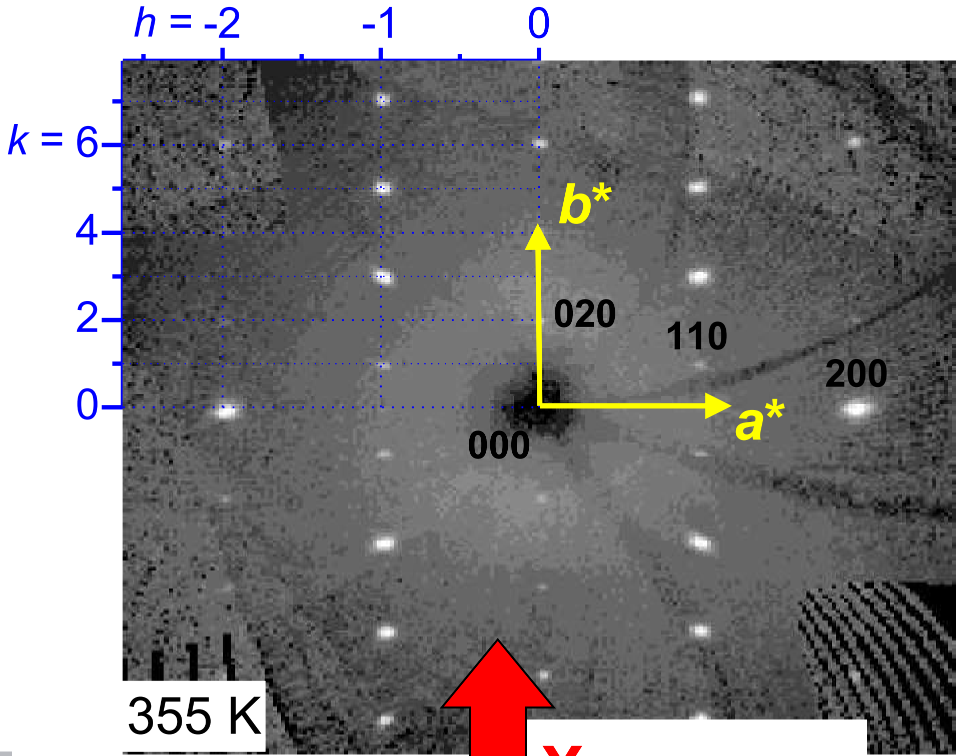
Single crystal diffractometry



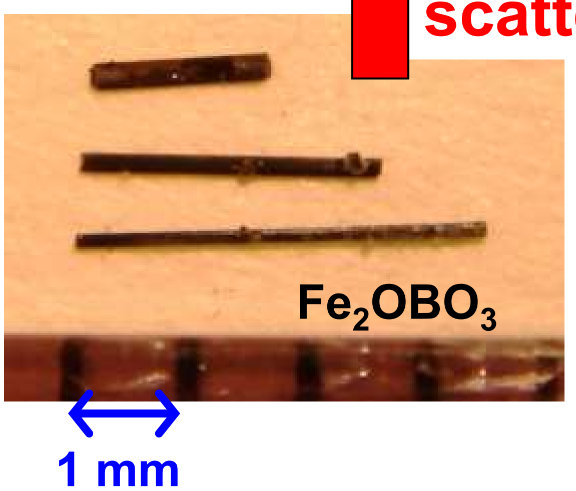




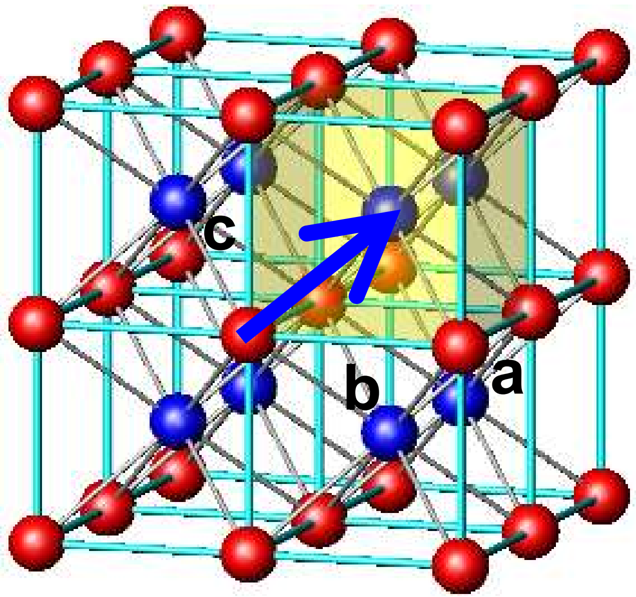
Agilent Supernova – dual (Cu Kα/Mo Kα) microfocus source / CCD det.



X-ray scattering



Structure factor



A second atom type:
lattice with basis

Every atom position **R** is sum of **V+u** where **V** is a lattice vector and **u** is in the unit cell

$\mathbf{u}_1 = 0$

$\mathbf{u}_2 = (1/2a, 1/2b, 1/2c)$

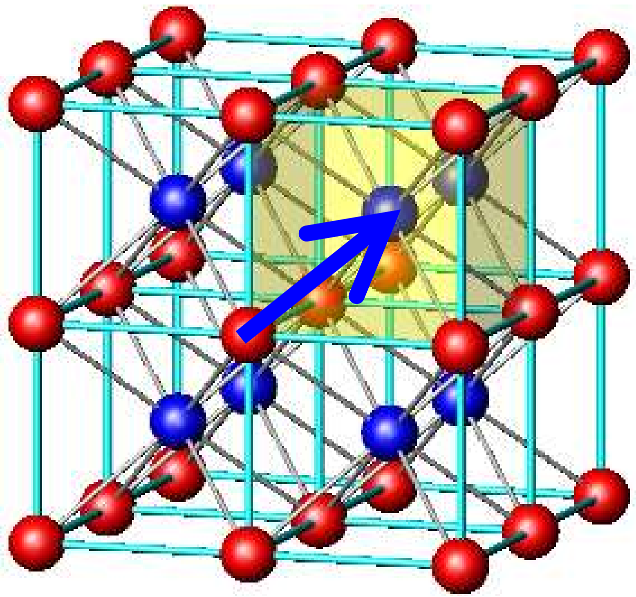
General scattered intensity (without proof)

$$I(\mathbf{q}) = \Big|\sum_i e^{i\mathbf{q}\cdot\mathbf{V}_i}\Big|^2 \bullet \Big|\sum_{j=1}^{n} f_j\, e^{i\mathbf{q}\cdot\mathbf{u}_j}\Big|^2$$

→ Laue condition as before

≡ F_{hkl} , **structure factor**

Structure factor



A second atom type:
lattice with basis

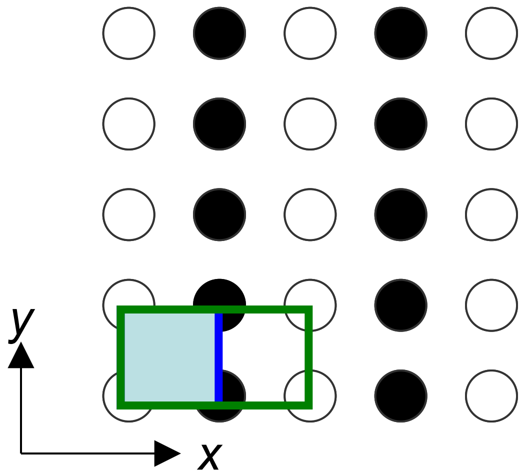
Every atom position **R** is sum of **V+u** where **V** is a lattice vector and **u** is in the unit cell

If $f_1 = f_2$
half the reflections are extinct

$$F_{hkl} = \sum_{j=1}^{n} f_j\, e^{i\mathbf{q}\cdot\mathbf{u}_i}$$

$$= f_1 \underbrace{e^{2\pi i\mathbf{q}\cdot\mathbf{0}}}_{1} + f_2 \underbrace{e^{2\pi i\,(h/2+k/2+l/2)}}_{\substack{1 \text{ if } h+k+l \text{ even} \\ -1 \text{ if } h+k+l \text{ odd}}}$$

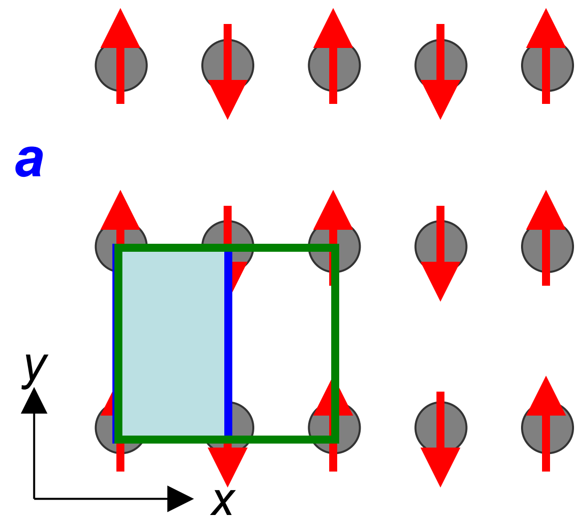
Super structures



unit cells:

crystallographic cell : *a*

"super-cell" : 2*a*

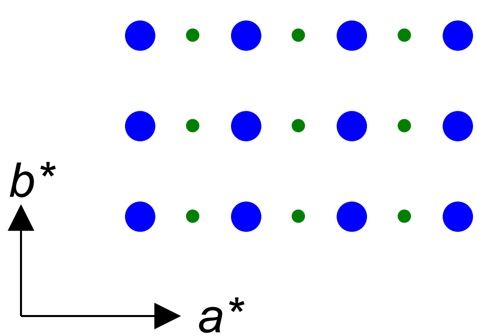


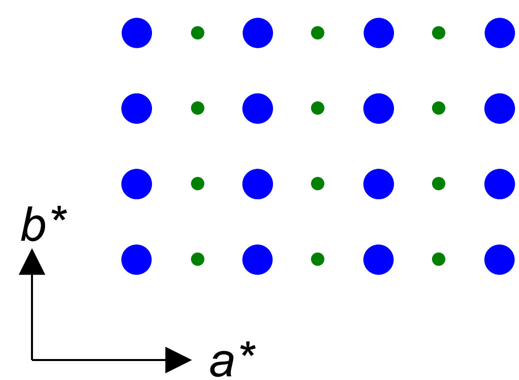
e.g. valence 2+ 3+

magnetic moment

How will the superstructure affect scattering on the sample ?

reciprocal lattice :



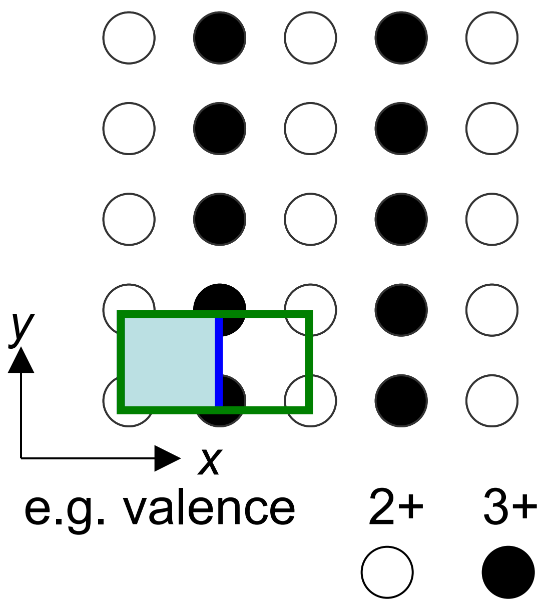


Super structures

unit cells:

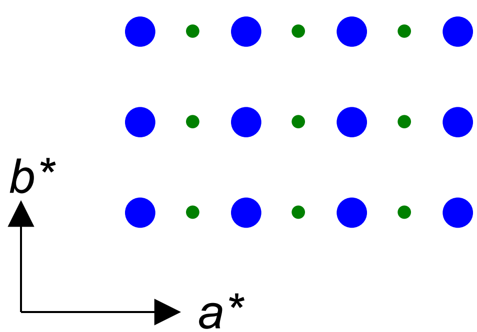
crystallog

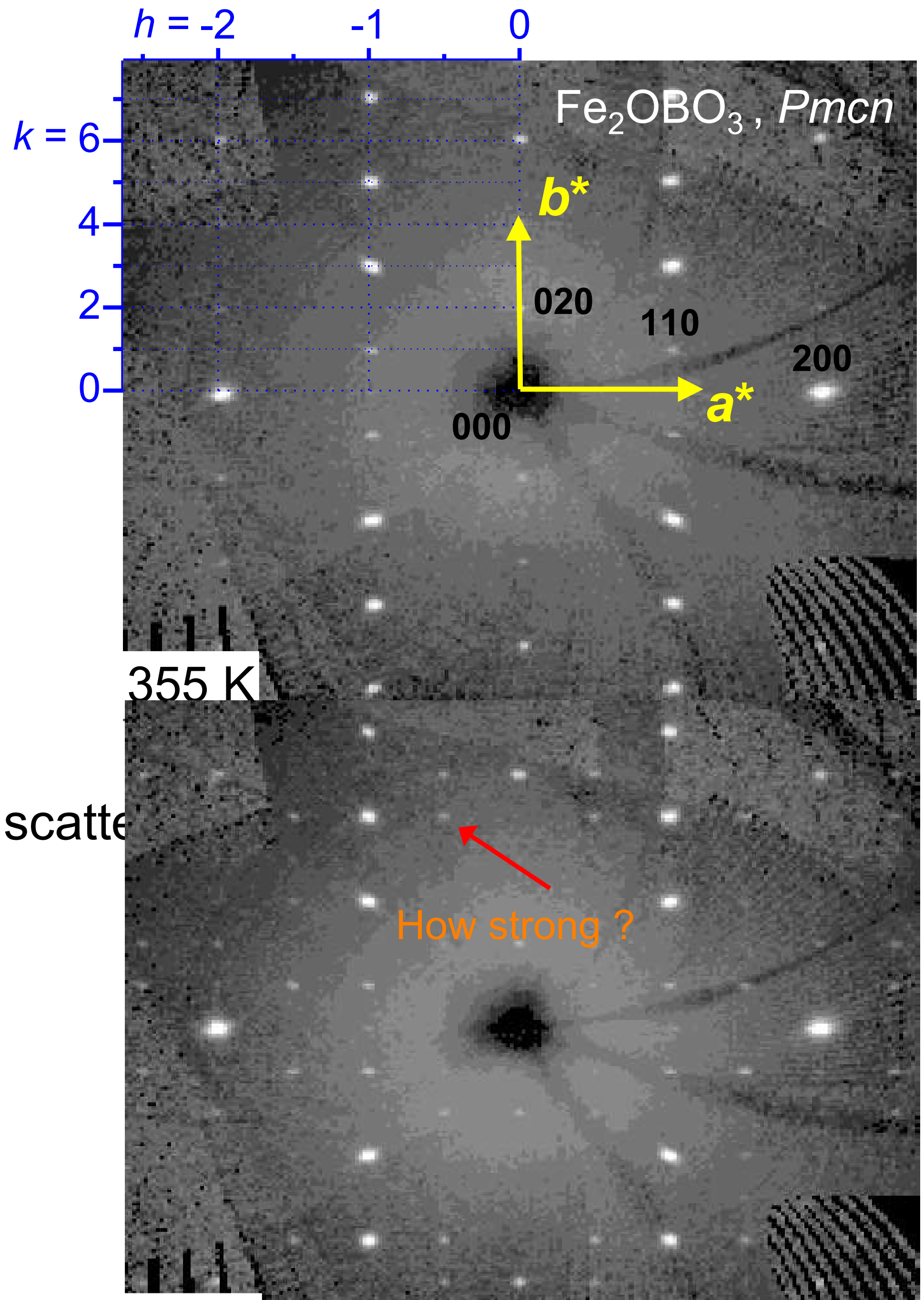
“super-cel



How will the superstructure affect scatte

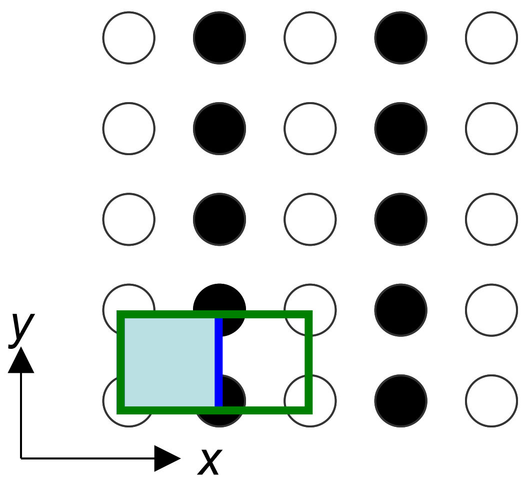
reciprocal lattice :





[MA *et al.*, PRL **99**, 086403 (2007)]

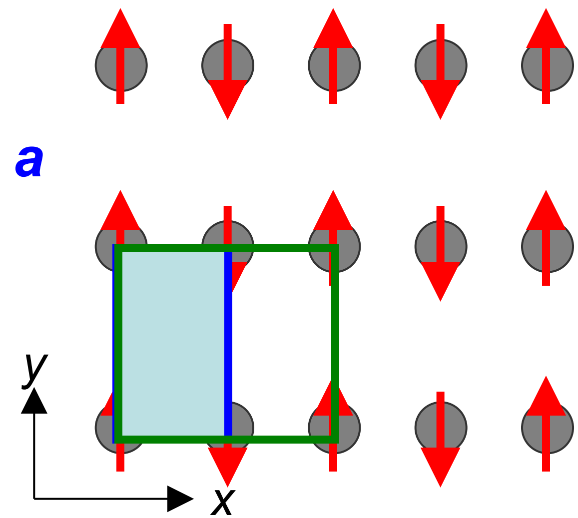
Super structures



unit cells:

crystallographic cell : *a*

“super-cell” : 2*a*



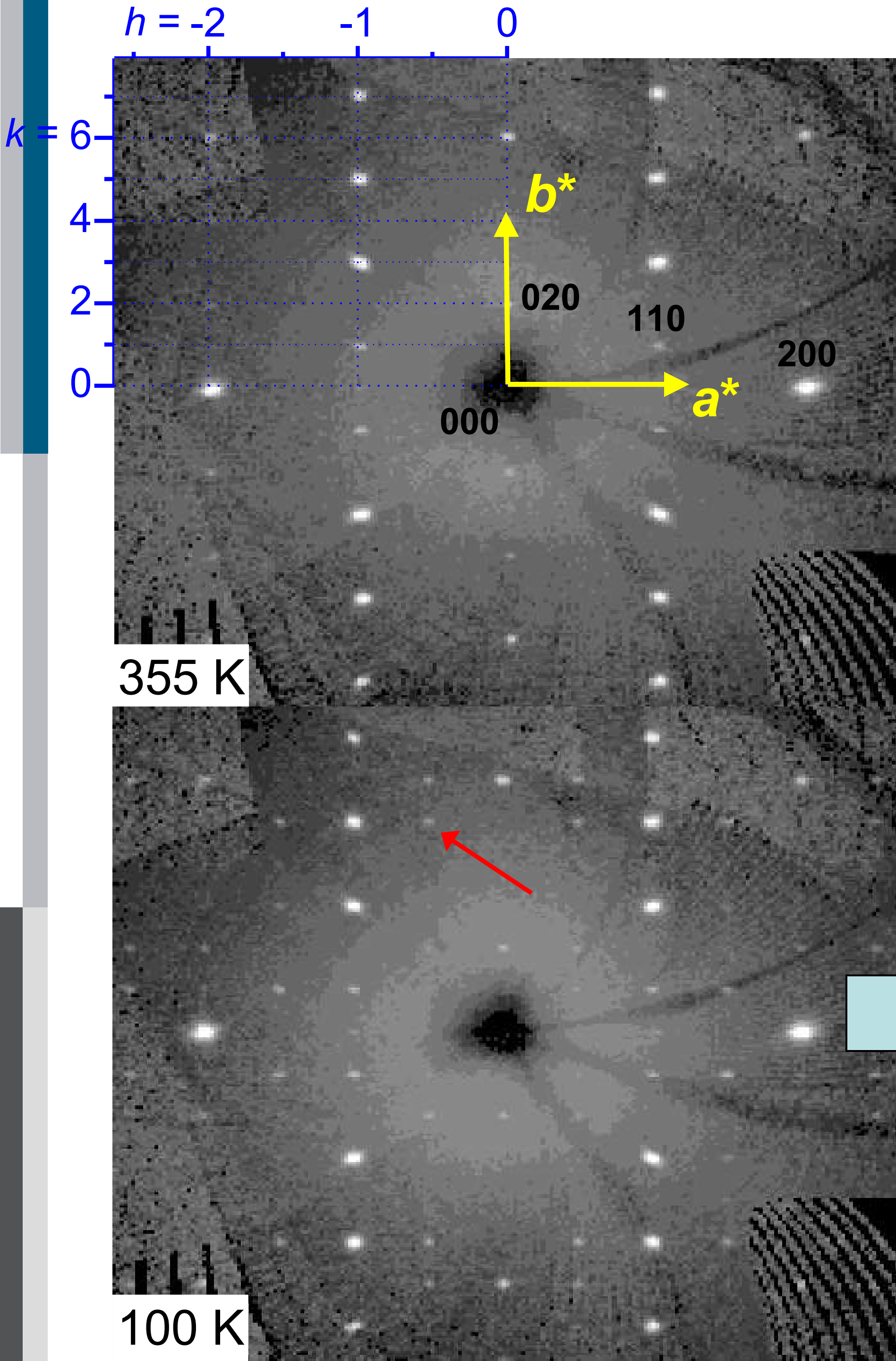
e.g. valence 2+ 3+

magnetic moment

$$F_{h,k,l} = f_1 + f_2\, e^{2\pi i\,(h/2+k+l)} = f_1 - f_2$$

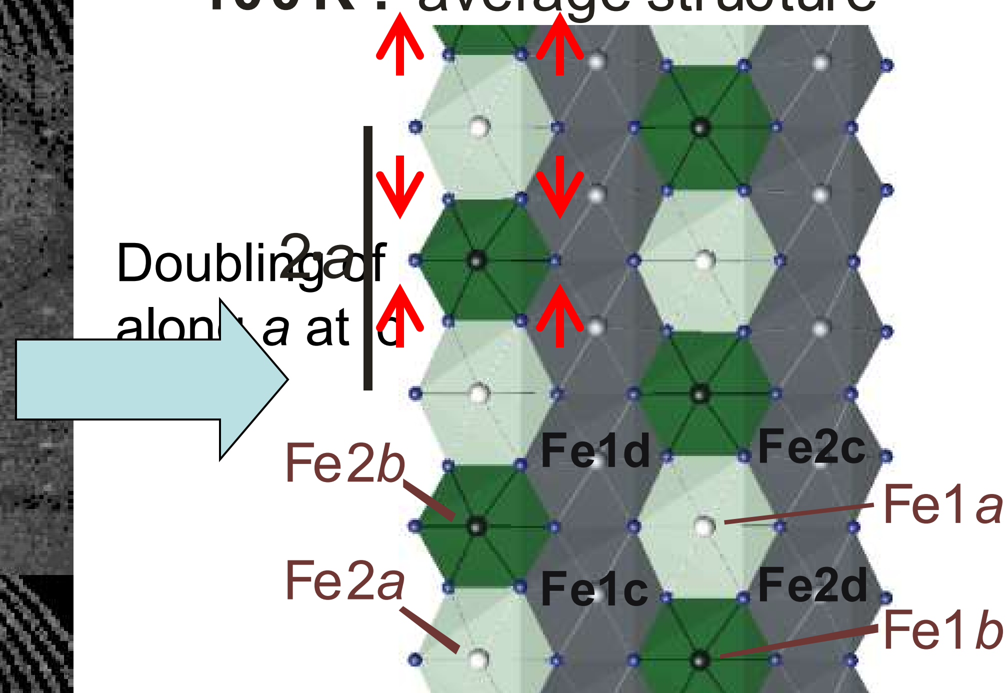
for h odd (superstructure reflections)

Supercell basis, i.e. super-peaks are those with h odd



X-ray diffraction:
Laboratory source
(Mo Kα)

100 K : average structure



Summary of concepts

Scattering can see directly microscopics underlying various phenomena

Particles used in scattering: neutrons (including magnetic), x-ray, electrons (surface)

Diffraction: Interference as in optics, crystals as 3D diffraction gratings

Laue condition and Bragg peaks, reciprocal lattice, Ewald sphere

Maximum wavelength useful for diffraction

Atomic form factor, structure factor

Superstructure reflections and cells