Scientific Problem:
How can we determine the electron density $\rho(\mathbf{r})$ within the unit cell and, thus, the crystal structure by means of X-ray diffraction?

Intensity of a Bragg reflection:

$$I = r_0^2 \cdot P^2 \cdot |G|^2 \cdot |S_{hkl}|^2$$

Structure factor

$$S_{\mathbf{G}} = S_{hkl} = \sum_j f_j(\mathbf{G}) \cdot e^{-i\mathbf{G} \cdot \mathbf{r}_j} = \sum_j f_j(\mathbf{G}) \cdot e^{-2\pi i (hx_j + ky_j + lz_j)}$$

Electron density

$$\rho(\mathbf{r}) = \frac{1}{V} \sum_{hkl} S_{hkl} \cdot e^{-i\mathbf{G} \cdot \mathbf{r}}$$

Answer:
Through measurement of the structure factors $S_{hkl}$ of all Bragg reflections!
• Determine both position and intensity of many (all!) Bragg reflections

• The structure factor (amplitude) \( S_{hkl} \) is a complex number

• We measure the diffracted intensity \( |S_{hkl}|^2 \)

• The complex phases of \( S_{hkl} \) have to be determined (\( \rightarrow \) this will be explained in more detail later in this lecture)

\[
\rho(x, y, z) = \frac{1}{V} \sum_{h,k,l} S_{hkl} e^{-2\pi i (hx + ky + lz)}
\]
Of course, we are not able to measure all Bragg reflections \( \rightarrow \) We should measure as many as possible

\[
\rho(x, y, z) = \frac{1}{V} \sum_{hkl} S_{hkl} e^{-2\pi i (hx+ky+lz)} \approx \frac{1}{V} \sum_{hkl}^{hkl(\text{max})} S_{hkl} e^{-2\pi i (hx+ky+lz)}
\]

We measure Bragg reflections (Fourier components) up to a maximum \((hkl)\)
\( \rightarrow \) Cut off of large spatial frequencies \(G_{\text{max}}\).

Resolution in real space \(\Delta r\) \(\quad \Longleftrightarrow \quad \) \(G_{\text{max}} \approx \pi/\Delta r\)

A sphere with radius \(G_{\text{max}}\) exhibits a volume of \(V = \frac{4\pi}{3} \cdot \left(\frac{\pi}{\Delta r}\right)^3\)

A single Bragg reflection ‘requires’ a volume of \(v = \left(\frac{2\pi}{a}\right)^3\)

The approximate number of Bragg reflections within \(V\) is given by \(N = V/v = \pi/6 \cdot (a/\Delta r)^3\)

Example: \(a = 5\ \text{Å}, \ \Delta r = 0.25\ \text{Å} \rightarrow N = 4188\)
Ewald Sphere and Ewald Construction

\[ \vec{G} = \vec{k}_f - \vec{k}_i \]

- \( |\vec{k}_i| = |\vec{k}_f| = k = 2\pi/\lambda \)
- Multitude of all possible incoming and outgoing directions of the x-ray beam defines a sphere with radius \( r = k = 2\pi/\lambda \) \( \rightarrow \) Ewald Sphere
- The origin of the incoming wave vector \( \vec{k}_i \) represents the center of the Ewald Sphere
- The head of the incoming wave vector \( \vec{k}_i \) is the origin of reciprocal space

Determination of Crystal Structure

\[ \text{G}_{hkl} \]
• If surface of Ewald Sphere comprises a reciprocal lattice point $\iff$ Bragg condition is fulfilled

• **Limiting sphere** (in German: “Ausbreitungskugel”) contains achievable reciprocal lattice points at a given X-ray wavelength

• Radius of limiting sphere: $r = 2k = \frac{4\pi}{\lambda}$

• Number of Bragg reflections within sphere:

$$N \approx \frac{4\pi}{3} \left(\frac{4\pi}{\lambda}\right)^3 = \frac{32}{3} \pi \cdot \frac{a^3}{\lambda^3}$$

• We can reach **eight times** more Bragg reflections when the wavelength is reduced by a **factor of two**

• $a = 5 \text{ Å}, \lambda = 0.7 \text{ Å}, N = 12000$
How can we reach as many Bragg reflections as possible?

- Use of **polychromatic (‘white’)** radiation

  - Set of Ewald spheres of with varying radii
  - We always find Ewald spheres which intersect with a reciprocal lattice point \( \mathbf{G} \)
  - Basis of the **Laue technique**

- Use of **monochromatic** radiation

  - Variation of direction of incoming wave
  - Ewald sphere is rotating inside limiting sphere
  - Basis of **rotating crystal method**

**Ewald Sphere and Ewald Construction**

**Determination of Crystal Structure**
The Laue Technique

- Oldest (1912)
- Simplest Technique

Experimental setup for X-Ray diffraction
W. Friedrich, P. Knipping und Max von Laue, 1912, Deutsches Museum

- Each net plane is selecting the suitable x-ray wavelength for which the Bragg condition is fulfilled.

- The angle of the diffracted beam relative to the incoming beam is then two times the Bragg angle (which is the angle of the incoming beam relative to the net plane).

Determination of Crystal Structure
The Laue Technique

Direction of incoming beam is collinear with a symmetry axis of the crystal

\[ \text{Al}_2\text{O}_3 \]
hexagonal c-plane

Simulation

11\bar{2}0

reciprocal directions

1\bar{1}00

\text{Experiment (Backscattering Geometry)}

- Laue Image contains \textit{symmetry of the crystal} (here: \(\rightarrow\) three-fold rotational symmetry)
- Laue Image contains \textit{additional inversion center} (\(\rightarrow\) six-fold rotational symmetry)
  \(\rightarrow\) Laue symmetries, Laue classes

Be aware: \textit{Crystal Twins} can fake false symmetries

Determination of Crystal Structure
The Laue Technique

Why does the Laue image always contain an inversion center?

Friedel's Rule

32 crystal classes / point groups

11 Laue classes / Laue groups

For real atomic scattering factors

\[ |S(\mathbf{Q})|^2 = \left| \sum_j f_j(\mathbf{Q}) e^{-i\mathbf{Q} \cdot \mathbf{r}_j} \right|^2 = \sum_j f_j(\mathbf{Q}) e^{-i\mathbf{Q} \cdot \mathbf{r}_j} \sum_k f_k^*(\mathbf{Q}) e^{i\mathbf{Q} \cdot \mathbf{r}_k} = \sum_j \sum_k f_j(\mathbf{Q}) f_k^*(\mathbf{Q}) e^{-i\mathbf{Q} \cdot (\mathbf{r}_j - \mathbf{r}_k)} = |S(-\mathbf{Q})|^2 \]

George Friedel

Home work:
(a) Are atomic scattering factors real or complex numbers? What does the imaginary part describe?
(b) Proof of Friedel's rule (for real atomic scattering factors)
(c) Validity with centrosymmetric crystals also for complex atomic scattering factors
Kristallstrukturbestimmung
Laue camera
with Polaroid film
(Backscattering geometry)
The Laue Technique

**Limitations of Laue technique for home lab X-ray sources**

- Complex spectral distribution from X-ray tube
  - characteristic lines (these wavelengths should be avoided)
  - modification of Bremsstrahlung through absorption inside anode
  - normalization of intensity is very difficult

- Application of Laue technique for crystal orientation

**Renaissance of Laue technique at synchrotron radiation facilities**

- continuous and predictable emission spectrum
- high photon flux, small divergence (→ high brilliance)

**Advantages:**
- fast (→ biological systems)
- time resolved (< 50 ps)
- use of area detectors (Image-Plates, CCD, CMOS)

**Drawbacks:**
- each Bragg reflection is created by a different X-ray wavelength (Assignment !)
- problems with higher harmonics (e.g. 002 (λ) und 004 (λ/2) appear at the same position on the detector)

---

**Determination of Crystal Structure**
Rotating Crystal Methods

Use of **collimated monochromatic** radiation

- Arbitrary crystal orientation → Bragg condition not fulfilled
- Change of direction of incoming beam
- Ewald sphere is rotating inside limiting sphere
- Basis of rotating crystal method

Basics:

- Orthogonality between real $\Leftrightarrow$ reciprocal space: $b_i \cdot a_j = \delta_{ij}$
- Choose rotation axis of crystal perpendicular to direction of incoming beam
- Orientation of crystal such that $a_3$ is parallel to rotation axis
- Within equatorial plane of limiting sphere: reflections appear as $(\text{hk}0)$ (zeroth reciprocal lattice plane, RELP)
- Adjacent RELPs: $(\text{hk}-1)$ and $(\text{hk}1)$, below and above zeroth RELP, respectively

Determination of Crystal Structure
Rotating Crystal Methods

- RELPs of reciprocal lattice intersect with the Ewald sphere kugel at a particular degree of latitude
- The corresponding Bragg reflections of a particular RELP appear on the film at identical heights

Determination of Crystal Structure
Rotating Crystal Methods

Example of a rotating crystal image of Turmalin (rotation axis [0001])

- All reflections of a RELP appear on a horizontal line on the film
- Problems with experimental resolution for more complex crystal structures
- Nowadays this technique plays no practical role anymore
Weißenberg-Technique

Weißenberg Camera

K: Crystal
R: X-Ray beam
B: Slit
F: Cylindric Film
S: Carriage

- Variant of rotating crystal technique
- **Selection of a particular RELP** through a ring shaped slit
- Simultaneous rotation of the crystal and translation of the cylindric film
- The Bragg reflections of the selected RELP are distributed across the entire film
Weißenberg-Technique

From catalogue “Huber Diffraktionstechnik”

Determination of Crystal Structure
Buerger Precession Technique

- Refined rotating crystal technique
- Adjustment of crystal similar to rotating crystal / Weißenberg technique
- Direction of incoming beam is parallel to rotation axis of the crystal ($\mu = 90^\circ$)
- The 0th RELP is just touching the Ewald sphere in one point and thus no Bragg reflections are excited from the 0th RELP.
Buerger Precession Technique

- $\mu = 90^\circ$: No reflections accessible

- $\mu = 90^\circ - \mu'$: All accessible reflections are located on cones with opening angle $2\mu'$

  - The intersection of the Ewald sphere with the RELP is a circular trajectory.

  - Projection of circular trajectory of a RELP onto a film

  - Precession (movement of cone surface) of the crystal and the film around incoming beam → Detection of a variety of Bragg reflections on the 0th RELP

  - Selection of a particular RELP through a ring shaped slit

Determination of Crystal Structure
Buerger Precession Technique

Angle preserving image of reciprocal space

→ Symmetries can be easily identified

Determination of Crystal Structure
**Buerger Precession Technique**


**Determinations of Crystal Structure**

1. Mo-Anode with collimator and filter: 0 or Zr
2. Goniometer head
3. Handrad (Dial)
4. Primary ray interceptors
5. Microscope-telescope system
6. Blende: Selection of a reciprocal layer
7. Film: Eu²⁺-doped BaBrF coated plate
8. Circular arc: $\mu = 10 - 30^\circ$
9. Motor
Diffractometric Techniques

Drawback of film methods: Quantitative evaluation of intensity is difficult

↓

Use of Diffractometers equipped with “linear” detectors

4 Circle Diffractometer
(Euler geometry)

Kappa Diffractometer

Advantages:
Movements can be easily followed
full $\chi$ range of 0 .. 180° accessible

Drawback:
Shadowing by Eulerian cradle

Advantage:
No shadowing effects

Drawbacks:
Restricted $\chi$ range of 0 .. 100°
Movements are not easy to follow

Determination of Crystal Structure
Diffractometric Techniques

Sample adjustment

• Precise positioning of the sample with respect to the center of rotation of the diffractometer is required

Determination of the crystal unit cell dimension \( \rightarrow (a_1, a_2, a_3) \)

• “Peak Hunting”: Find some (20 ..50) strong Bragg reflections
• Determination of so-called “orientation matrix”
• Now, every Bragg reflection can be found by just typing in the Miller indices (hkl)

Automatic measurement of a large variety of Bragg reflections

• Systematic search and measurement of Bragg reflections in reciprocal space
• Continued measurement of intense reference Bragg reflections

  ➢ Checking constant power of x-ray source
  ➢ Checking the state of the crystal (stability, radiation damage, …)

• Procedure may take about one day for 500-1000 reflections for a point detector
Diffractometric Techniques

• Use of area detectors
  - CCD detectors
  - Image plates
  - Wire detectors
  - CMOS detectors

• Identification von
  - Crystal Twins
  - Incommensurable Phases
  - Super structures (e.g. crystals with doubled unit cell) → Surfaces

• Strongly reduced data acquisition times

• Drawback: limited range of accepted 2θ range
Diffractometric Techniques

Evaluation of Intensities

\[ I = r_o^2 \cdot P^2 \cdot |G|^2 \cdot |S_{hkl}|^2 \]

Polarization correction

\[ P' = P^2 = \frac{1 + \cos^2 2\theta}{2} \]

for unpolarized light (x-ray tube)

\[ \theta : \text{scattering angle} \]

\[ P' = \left(1 + K \cos^2 2\theta\right) / (1 + K) \]

for additional correction when using a crystal monochromator or a mirror; \( K < 1\% \)

Lorentz factor

\[ L = \frac{1}{\sin 2\theta} \]

For continuous scans with constant angular velocity: different reflections are in Bragg condition for different lengths of time

Absorption correction

As a function of crystal shape and angle of incidence: x-ray beam ‘sees’ different lengths inside crystal

\[ \rightarrow \text{absorption loss of intensity is different for different directions of incidence} \]

\[ \rightarrow \text{for exact measurements: use of a crystal sphere} \]

Determination of Crystal Structure
Determination of Crystal Structure

\[ S(Q) = \sum_{j=1}^{k} f_j(Q) e^{-iQr_j} \]

Comment:

- Tabulated values for \( f_j(Q) \) → **spherical symmetry of electron density** of the atoms
- Neglection of **bonding orbitals**, which are located between the atoms
- However: This approximation does not severely influence the determination of crystal structure

\[ \rho(x, y, z) = \frac{1}{V} \sum_{h,k,l} S_{hkl} e^{-2\pi i (hx + ky + lz)} \]

Please remember:
- \( S_{hkl} \) is a complex number
- measured intensity \( I \propto |S_{hkl}|^2 \)
Direct methods: The Patterson Function

\[ P(\bar{u}) = \frac{1}{V} \sum_G S_G S_G^* e^{-i\bar{G}\bar{u}} \]

Lindo Patterson, 1934

Patterson Function = Fourier analysis of the intensity

Convolution theorem \( \Rightarrow \)

\[ P(\bar{u}) = \int \rho(\bar{r}) \rho(\bar{r} + \bar{u}) dV \]

\( \Rightarrow \) Pair correlation function

\( \Rightarrow \) Information about interatomic difference vectors

Home work: Derivation of 

\[ P(\bar{u}) = \int \rho(\bar{r}) \rho(\bar{r} + \bar{u}) dV \]

Determination of Crystal Structure
Properties of the Patterson Function

• Equivalent translational symmetry of $\rho(r)$ and $P(u)$

• Size of unit cells of electron density and of Patterson function are identical

• Atomic structure consists of $N$ atoms → Patterson function exhibits $N(N-1)+1$ Peaks

• Maximum of Patterson-Function appears at origin ($u = 0$)

• Patterson-Function is centrosymmetric even if electron density is not centrosymmetric.

• Reason: For each vector $u_{AB}$ pointing from atom A to atom B there exists the opposite vector $u_{BA} = -u_{AB}$ pointing from atom B to atom A

• Symmetry properties of Patterson function leads to the 24 Patterson groups
Advantages of Patterson Technique

- The Patterson function provides a ‘Map’ of interatomic distances in real space.
- Maxima of Patterson function appear at locations \( u \), which represent the distance vectors between two atoms.
- So we see interatomic distances.
- Implementation in many data evaluation programs (e.g. SHELXS-97:PATT).

V. Sasisekharan, 1956

"Typical" Patterson function (Patterson map)

Determination of Crystal Structure
Direct methods: The Patterson Function

Drawbacks of Patterson Technique

- Maxima of Patterson function always depend on the electron densities of two atoms.
- Peaks of Patterson function are thus broader than those of the electron density
- Particularly broad and intense maximum at $u = 0$
- The number of maxima amounts to $N(N-1)+1$

Application of Patterson Technique

- Simple structures (N small)
- Heavy atom structures – Determination of absolute positions of special heavy atoms
- Metal complexes, metal atoms inside protein crystals
- We can then make use of the positions of these heavy atoms for the determination of the positions of the other atoms

Determination of Crystal Structure
Determining the Crystal Structure

| \( S \) | \( \cdot \sin \phi \) |
| \( S \) | \( \cdot \cos \phi \) |

Length of the vector: \( |S| \)

- Imaginary numbers
- Real numbers

Phase angle \( \phi \)
**Direct Methods**

**Principle/Idea:**
- Direct determination of *phases* of the scattered waves directly (‘brute force’) from the experimental data set
- There is no common solution of this problem
- Helpful for finding a physical solution is:
  - Electron density \( \rho(r) \) is a positive number \( (\rho(r) > 0) \)
  - \( \rho(r) \) is concentrated at the atomic positions (discrete density)

- Direct methods are working since *many reflections* are at disposal for the determination of just a *small number of parameters*
  - Overdetermined system of equations
  - Statistical methods
For centrosymmetric crystals it becomes much easier.

\[
S_{\overline{G}} = \sum_{j=1}^{N/2} f_j(\overline{G}) \cdot \left[ e^{i\overline{G}r_j} + e^{-i\overline{G}r_j} \right] = 2 \sum_{j=1}^{N/2} f_j(\overline{G}) \cdot \cos(\overline{G}r_j)
\]

Identical atoms at \( r_j \) and \(-r_j\)

- Structure amplitudes \( S_G \) of all Bragg reflections are real numbers

- We just have to determine the Sign ( + or - ) of \( S_G \)
Apply the Cauchy-Schwartz **Inequality**

\[
\left( \sum_{n=1}^{\infty} a_n b_n \right)^2 \leq \sum_{n=1}^{\infty} a_n^2 \sum_{n=1}^{\infty} b_n^2
\]

to the Integral

\[
S_{h,k,l} = \iiint \rho(x, y, z) e^{-2\pi i (hx + ky + lz)} \, dx \, dy \, dz
\]

Then we can make **predictions** for the so-called **unitary structure factors**

\[
U_{hkl} = \frac{S_{hkl}}{Z}
\]

(Z is the number of electrons in unit cell)

**Concerning the probability of the sign** (phase) of the structure factor

**Determination of Crystal Structure**
• Information about sign of structure factor

• Large number of Inequalities for the symmetry elements

• However: Application for structures consisting of more than five atoms within unit cell is usually not possible

• Combination with other methods is necessary

---

Harker Kasper In-Equations (1948)

<table>
<thead>
<tr>
<th>Symmetrielement</th>
<th>Einschränkung</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$</td>
</tr>
<tr>
<td>3</td>
<td>$U_{41}^a \leq \frac{1}{3} + \frac{1}{3} U_{26} 26 26$</td>
</tr>
<tr>
<td>4</td>
<td>$</td>
</tr>
<tr>
<td>5</td>
<td>$</td>
</tr>
<tr>
<td>6</td>
<td>$</td>
</tr>
</tbody>
</table>

Liste der Harker-Kasper-Ungleichungen für verschiedene Symmetrielemente

Determination of Crystal Structure
\[ S_G = k \sum_{G'} S_{G'} S_{G-G'} \]

\( k > 0 \), Sayre Equation, 1953

- Normally the sum on the right side is dominated by a strong term, which then determines the sign of the total sum.

- Therefore, we can write for the sign (Signum \( s_G \)) of the structure factors in good approximation (triplet relationship):

\[
\begin{align*}
S_G &= S_{G'} \cdot S_{G-G'} \\
S_G \cdot S_{G'} \cdot S_{G-G'} &= +1
\end{align*}
\]

- Rule is fulfilled for strong Bragg reflections with approximately equal structure factors

- Rule allows for structure determination of (centrosymmetric) systems with about 50 .. 100 atom within unit cell

Nobel prize 1985: J. Karle, H. Hauptmann
So far we have focused on centrosymmetric structures.

Is there a way to gain access to non-centrosymmetric structures?
Brief Reminder: Atomic Form Factor

Electron density of a single atom: \( \rho_A(r) \)

\[
E_{\text{rad}}(\vec{R}, \vec{Q}) = r_0PE_0 \frac{e^{ikR}}{R} \int dV \rho_A(\vec{r}) e^{-i\vec{Q} \cdot \vec{r}} = r_0PE_0 \frac{e^{ikR}}{R} f(\vec{Q})
\]

atomic scattering factor (amplitude)
atomic form factor

\[
f(\vec{Q}) = \int dV \rho_A(\vec{r}) e^{-i\vec{Q} \cdot \vec{r}}
\]

experimental/calculated values are listed in:
International Tables of Crystallography
or
http://henke.lbl.gov/optical_constants/asf.html

Determination of Crystal Structure
Resonant Scattering (Anomalous Dispersion)

So far we have assumed that:

- all electrons are free and contribute equally to the total scattering process
- total scattering amplitude is the Fourier transform of the electron density $\rho(r)$ and is thus independent of the X-ray energy

More detailed description:

- The response of the electrons to the external time dependent electric field depends on the dynamic polarizability (dielectric susceptibility) $\chi(r, \omega)$

$$\chi(r, \omega) = \frac{\rho(r)e^2}{\varepsilon_0 m} \sum_j \frac{g_j}{\omega_j^2 - \omega^2 + i\omega\gamma_j}$$

- For a chemical element: $\chi(r, \omega) = \frac{\tau N_A}{\pi A} \chi^2 \rho_m(r) [f_0 + f'(\omega) + if''(\omega)]$

Hönl corrections

$N_A$: Avogadro's number  
$A$: molar mass  
$\rho_m(r)$: mass density

H. Hönl, Z. Phys. **84**, 1-16 (1933)
Resonant Scattering (Anomalous Dispersion)

\[ \chi(\mathbf{r}, \omega) = -\frac{r_0 N A}{\pi A} \lambda^2 \rho_m(\mathbf{r}) \left[ f_0 + f'(\omega) + i f''(\omega) \right] \]

\[ f_0 = Z \]

- Real part: \( f_0 + f'(\omega) \)
- Imaginary part: \( \mu \propto f''(\omega) \)

\[ f'(\omega) = \frac{2}{\pi} \cdot P \int_0^{\omega} \frac{\omega' f''(\omega')}{\omega^2 - \omega'^2} d\omega' \]

\[ f''(\omega) = \frac{2\omega}{\pi} \cdot P \int_0^{\infty} \frac{f'(\omega')}{\omega^2 - \omega'^2} d\omega' \]

\( \mu \): Linear Absorption Coefficient

- \( \Delta f/f \approx 20\% \)

Adapted from: H.-G. Haubold, Jülich

\( \triangleright \) We see a remarkable effect on \( \chi(\mathbf{r}, \omega) \) in the proximity of absorption edges only!

Determination of Crystal Structure
Resonant Scattering (Anomalous Dispersion)

\[
\chi(\vec{r}, \omega) = -\frac{r_0N_A}{\pi\lambda} \rho_m(\vec{r}) [f_0 + f'(\omega) + if''(\omega)]
\]

\[
f(Q,\omega) = f_0(Q) + f'(\omega) + if''(\omega)
\]

atomic scattering factor

Remarks:

- \(f'\) and \(f''\) are usually very small – except for the proximity of absorption edges
  \[\Longleftrightarrow\] Resonant (Anomalous) Scattering

- \(f''(\omega) > 0\) (\(\mu > 0\), attenuation of X-rays)

- \(f(Q,\omega) = f(-Q,\omega)\)

What is the impact of a complex atomic scattering factor \(f(Q,\omega)\) on the structure factor \(S(Q)\) and Friedel’s rule?

Determination of Crystal Structure
Resonant Scattering (Anomalous Dispersion)

What is the impact of a complex atomic scattering factor \( f(Q,\omega) \) on the structure factor \( S(Q) \) and Friedel's rule?

**Centrosymmetric Structures**

\[
S(\mathbf{Q},\omega) = \sum_{j=1}^{N} f_j(\mathbf{Q},\omega) e^{-i\mathbf{Q} \cdot \mathbf{r}_j} = \sum_{j=1}^{N/2} f_j(\mathbf{Q},\omega) \left[ e^{-i\mathbf{Q} \cdot \mathbf{r}_j} + e^{+i\mathbf{Q} \cdot \mathbf{r}_j} \right]
\]

\[
S(-\mathbf{Q},\omega) = \sum_{j=1}^{N} f_j(-\mathbf{Q},\omega) e^{+i\mathbf{Q} \cdot \mathbf{r}_j} = \sum_{j=1}^{N/2} f_j(-\mathbf{Q},\omega) \left[ e^{+i\mathbf{Q} \cdot \mathbf{r}_j} + e^{-i\mathbf{Q} \cdot \mathbf{r}_j} \right]
\]

and since \( f_j(Q,\omega) = f_j(-Q,\omega) \)

\[
S(-\mathbf{Q},\omega) = S(\mathbf{Q},\omega)
\]

For centrosymmetric structures Friedel's rule is still valid.

Determination of Crystal Structure
Resonant Scattering (Anomalous Dispersion)

Centrosymmetric Structures

\[ S(Q) = S(-Q) \]

\[ S(-\bar{Q}, \omega) = S(\bar{Q}, \omega) \]

Determination of Crystal Structure
Resonant Scattering (Anomalous Dispersion)

Non-Centrosymmetric Structures

\[
S(\vec{Q}, \omega) = \sum_{j=1}^{N} [f_{0j}(\vec{Q}) + f'_{j}(\omega)] e^{-i\vec{Q}\cdot\vec{r}_j} + i \sum_{j=1}^{N} f''_{j}(\omega) e^{-i\vec{Q}\cdot\vec{r}_j}
\]

\[
S(-\vec{Q}, \omega) = \sum_{j=1}^{N} [f_{0j}(-\vec{Q}) + f'_{j}(\omega)] e^{+i\vec{Q}\cdot\vec{r}_j} + i \sum_{j=1}^{N} f''_{j}(\omega) e^{+i\vec{Q}\cdot\vec{r}_j}
\]

If \( f''(\omega) \neq 0 \)

both, the real and the imaginary parts of \( S(\vec{Q},\omega) \) and \( S(-\vec{Q},\omega) \) are different

(although \( f_{0j}(\vec{Q}) = f_{0j}(-\vec{Q}) \))
Resonant Scattering (Anomalous Dispersion)

For non-centrosymmetric structures

\[ |S(-\vec{Q}, \omega)| = |S(\vec{Q}, \omega)| \]

For vanishing resonant scattering

\[ f', f'' = 0 \]

\[ \text{Re}[S(Q)] = \text{Re}[S(-Q)] \]

\[ \text{Im}[S(Q)] = -\text{Im}[S(-Q)] \]

Friedel’s rule is still valid
Resonant Scattering (Anomalous Dispersion)

Non-Centrosymmetric Structures

Appearance of resonant scattering

\[ f', f'' \neq 0 \]

\[ \text{Re}[S(Q)] \neq \text{Re}[S(-Q)] \]
\[ \text{Im}[S(Q)] \neq -\text{Im}[S(-Q)] \]

The modifications in \( S(Q) \) and \( S(-Q) \) are induced by atoms which experience resonant dispersion

\[ |S(-\tilde{Q}, \omega)| \neq |S(\tilde{Q}, \omega)| \]

For non-centrosymmetric structures
For non vanishing resonant scattering

Friedel's rule is broken
Resonant Scattering (Anomalous Dispersion)

![Graph showing the comparison between no anomalous dispersion and anomalous dispersion in the context of crystal structure determination.](image)

Determination of Crystal Structure
Resonant Scattering (Anomalous Dispersion)

Example: The absolute polar direction in ZnS

Zinc-blende: Atoms of Sort A at: \( \mathbf{r}_1 = (0,0,0), \mathbf{r}_2 = (0,1/2,1/2), \mathbf{r}_3 = (1/2,0,1/2), \mathbf{r}_4 = (1/2,1/2,0) \)
Atoms of Sort B at: \( \mathbf{r}_5 = (1/4,1/4,1/4), \mathbf{r}_6 = (1/4,3/4,3/4), \mathbf{r}_7 = (3/4,1/4,3/4), \mathbf{r}_8 = (3/4,3/4,1/4) \)

D. Coster, K.S. Knol, and J.A. Prins, Z.Phys 63, 345-369 (1930)
We make use of violation of Friedel’s Rule

- **Centrosymmetric structures**
  - Phases $\phi$ deviate from 0 or $\pi$
  - Friedel’s rule is still valid
  - Method is not applicable for structural analysis

- **Non-centrosymmetric structures**
  - Strong deviation from Friedel’s rule for heavy atoms (strong absorption)
  - Method is **applicable**

- Effect depends on number of contributing electrons (e.g. K shell, L shell, …)

- Elements of 3\textsuperscript{rd} column of the system of elements (e.g. S, Cl) show already a remarkable effect

Determination of Crystal Structure
Resonant Scattering (Anomalous Dispersion)

|S(111)|^2  | |S(-1-1-1)|^2

X-ray source Gold
Lα₁: 9.7133 keV
Lα₂: 9.6280 keV
K-edge of Zn: 9.6586 keV

D. Coster, K.S. Knol, and J.A. Prins, Z. Phys 63, 345-369 (1930)
Literature, Software, Databases

**Literature**

- W. Massa: Einführung in die Kristallstrukturanalyse, Teubner.
- Giacovazzo et al. (ed.): Fundamentals of Crystallography, Oxford.

**Software**

- z.B. SHELXS-97 (G. Sheldrick, Göttingen)

**Databases**

- ICSD (Inorganic Crystal Structure Database): Inorganics without intermetallic phases (expensive)
- Pearsons Crystal Data: Intermetallic Phases + Inorganics (very expensive)
- Pauling-File (Intermetallic Phases) (free registration)
- CSD (Cambridge Crystallographic Database) (Organics, Metal-Organics) (expensive)
- PDB (Protein Database) (freely available on the web)