Difrakcijske metode određivanja kristalnih struktura
(kristalnih i molekulskih!)

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small molecule crystallography \rightarrow protein crystallography
Number of solved structures

- 1912 – 1970 cca 4,000
- 1970 – 1980 cca 40,000
- 1980 – 2000 cca 200,000

15 NOBEL LAUREATS HAVE BEEN RECOGNIZED IN THE FIELD OF DIFFRACTION STRUCTURE ANALYSIS, INCLUDING Roentgen and Laue
• What is it what makes crystal structure analysis so powerful method in structure determination?

• What is the physical phenomenon that makes us possible to obtain so accurate results?

• What are the data to be observed in order to solve a structure?

• What is the mathematical approach which ensures the reliability of the results?
Crystal is regularly repeated arrangement of atoms represented by unit cell.

Symmetry is one of the main properties of crystals.

Miller indices are used to describe crystal faces.

Angles between the faces are constant.
Crystalline and amorphous SiO₂

- Unit cell is repeated in 3 dimensions
  - good diffraction expected
- No unit cell can be defined
  - very poor or no diffraction expected
Diffraction data collection

X-rays \hspace{1cm} \textbf{diffraction on a crystal} \hspace{1cm} \textbf{diffraction data}

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Bragg’s approach to the diffraction condition

Path difference: \( AB + BC = \delta \)  \( AB = \delta \)
\[
\sin \theta = \frac{AB}{d} = \frac{\delta}{2d}
\]

Bragg’ law:
\[
2d \sin \theta = n\lambda
\]
Data collection by automatic diffractometer
Diffraction image on a CCD or imaging plate

Information obtained

1. unit cell dimensions

2. set of reflections $hkl$ and their intensities from systematically absent reflections the space group and symmetry can be determined
Small molecule in the real space cell

Dodaj info o simetriji
Representation of the atoms in a small molecule of \((C_5H_5)_3Sb\)
Hexamer of 2-Zn insulin type in the rhombohedral crystal
**Chemical synthesis**

\[ \text{COSHg} \]

**Diffraction power**

\[ f_a \]

\[ hkl \]

\[ I \]

\[ \phi \]

\[ F \]

\[ \rho \]

**Crystal**

**Diffraction wave**

**To observe**

**Wave function**

**To calculate**

**Electron density map**

**Complete picture in REAL SPACE**

**FOURIER TRANSFORMATION**

**PHASE PROBLEM**

**Patterson function**

**Direct methods**

**List of atoms**

**Atomic scattering factors**

**Incomplete picture in reciprocal space**

**Impossible to record**

**Structure factor**

**Complete picture in reciprocal space**

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HOW TO PRESENT THE PHENOMENON OF DIFFRACTION?

\[ \bar{F}(\bar{S}(hkl)) = f(I, \varphi) \]

\[ I(\bar{S}(hkl)) = \bar{F}(\bar{S}) \cdot \bar{F}(\bar{S}) = F^2 \]

\[ \varphi(\bar{S}) = 2\pi \cdot \bar{S}(hkl) \cdot \bar{r}(xyz) \]

How many data can be observed?

\[ \bar{F}_o(\bar{S}(hkl)) = \sqrt{C \cdot I(\bar{S}(hkl))} \cdot \sum_{j=1}^{N} \exp(2\pi i (hx_j + ky_j + lz_j)) \]

\[ \bar{F}_c(\bar{S}(hkl)) = \sum_{j=1}^{N} f_j(\bar{S}(hkl)) \cdot \exp(2\pi i \cdot \bar{S} \cdot \bar{r}_j) \]
\[ \tilde{F}_c(\tilde{S}(hkl)) = \sum_{j=1}^{N} f_j(\tilde{S}(hkl)) \cdot \exp(2\pi i \cdot \tilde{S} \cdot \vec{r}_j) \]

or

\[ \tilde{F}(\tilde{S}) = \int_{V} \rho(\vec{r}(xyz)) \cdot \exp(2\pi i \cdot \tilde{S} \cdot \vec{r}) dV \]
\[
\tilde{F}(\vec{S}) = \int_V \rho(\vec{r}(xyz)) \cdot \exp(2\pi i \cdot \vec{S} \cdot \vec{r}) dV
\]

\[
\rho(\vec{r}) = \int_{V^*} \tilde{F}(\tilde{S}(hkl)) \cdot \exp(-2\pi i \cdot \vec{S} \cdot \vec{r}) dV^*
\]

\[
\rho(\vec{r}) \iff \tilde{F}(\vec{S})
\]

A pair of Fourier transforms represents the same phenomenon in two different spaces
Fourier transformation

\[ \rho(r) \Leftrightarrow F(S) \]

The maximums in the electron density map are interpreted as coordinates of atoms in the cell.
Electron density map in the real space can not be calculated without concept of the reciprocal space.
From direct to reciprocal lattice

In the reciprocal lattice the point $hkl$ is drawn

- at a distance $1/d_{hkl}$ from the origin 000
- in direction of the normal to the set of planes $(hkl)$ in the real space.
Laue’s approach to the diffraction condition

Constructive interference on a row of atoms

\[ a \sin \phi = n \lambda \]
Bragg’s approach to the diffraction condition

Path difference: \( AB + BC = \delta \)

\[ AB = \delta \]

\[ \sin \theta = AB / d \]

\[ \sin \theta = \delta / 2d \]

Bragg’ law:

\[ 2d \sin \theta = n \lambda \]
Ewald’s approach to the diffraction condition

![Diagram showing Ewald’s approach to diffraction condition]

- The diffraction will occur at a node of the reciprocal lattice when the Ewald sphere touches that node.

- Vectors in the reciprocal space are related to the incident and diffracted beams: \( S(hk\ell) = s_0 - s = d^* (hk\ell) \)
The application of the concept of reciprocal space

1. Indexing of diffraction maxima (in the early days)

Bernall chart for determination of Miller indices on a photodiffractogram

Weissenberg chart for determination of Miller indices on a photodiffractogram
2. Data collection in reciprocal space visualised by Ewald sphere

Ewald sphere, $r=1/\lambda$

X-ray source

Rotating reciprocal cell

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3. Data collection and structure solving

- To determine the unit cell in the real space and to precalculate all possible directions in which the diffraction beams can be expected.

\[ \bar{a}, \bar{b}, \bar{c}, \alpha, \beta, \gamma, \text{ set of } hkl \]

- To calculate electron density map as Fourier transform of structure factors, and data processing.

\[ \rho(\vec{r}) \Leftrightarrow \tilde{F}(\vec{S}) \]
Sommerfeld's Institute for theoretical physics, München 1912

A. Sommerfeld

W. Friedrich

M. von Laue

P. Ewald

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Roentgen’s and Sommerfeld’s group in Cafe Lutz
Active social life in the team
1910 - Sommerfeld: “...to find out the optical characteristics of anizotropic distribution of isotropic rezonators distributed statistically”
Ewald’s assumption: atoms in crystals are regularly distributed rezonators

1911 Christmas: all calculations done

1912 January: dinner with M. von Laue, discussion between colleagues:

• von Laue hesitates both the assumption and the results in the case of crystals

• Ewald ensures the generality of the results

PAUL EWALD:
Disertation submitted: February 16. 1912.,
Thesis defended: March 5, 1912.
Easter holidays: von Laue, Friedrich and Knipping are ready to prove that crystals can reflect but can not diffract x-rays since the atoms are distributed statistically.
MAX von LAUE:
June 8, 1912:
• Friedrich, Knipping & Laue: “Interferenz-erscheinungen bei Röntgenstrahlen”, *Sitzungsberichte*, pp. 303-322

PAUL EWALD:
• 1917: “On the Foundations of Crystal Optics”
Fast development 1914/1915

W. L. Bragg «The structure of some crystals as indicated by their diffraction of X-rays»,

W. L. Bragg & W. H. Bragg «The structure of diamond»

W. L. Bragg «The analysis of crystal by X-ray spectrometer».

First solved structures: KCl, KBr, KI, ZnS, NaCl, CaF₂, CaCO₃, i FeS.
Ewald explained the first dynamic theory of diffraction on crystals in the Thesis 1912 before diffraction device had been made and regular arrangement of atoms in crystals had been recognized.

Question: Where is the Ewald’s place?

-Wilhem Conrad Röntgen, Max von Laue, William H. Bragg, William L. Bragg

Paul Ewald