

Crystal Structure Analysis

An Introduction

History & Overview

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Literature

C. Giacovazzo
Fundamentals of Crystallography (2011), Oxford University Press, 3rd Ed.

W. Massa
Kristallstrukturbestimmung (2007), Teubner 5. Aufl.

W. Clegg
Crystal structure analysis. Principles and practice (2009), Oxford University Press 2nd Ed.

E.R. Wölfel
Theorie und Praxis der Röntgenstrukturanalyse (198?), Vieweg 2. Aufl.

L.V. Azaroff
Elements of X-ray Crystallography (1968), McGraw-Hill

M. J. Buerger
Kristallographie (1968), DeGruyter

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Historical Notes I

Ca. 1890	230 Space groups A. Schoenflies (1891), E.S. Fedorov (1890), Barlow (1894)
1895	X-rays (W.C. Röntgen)
<u>1912 - 1922</u>	<u>Early beginnings of a new method</u>
05/1912	„Munich table“ (W.C. Röntgen, A. Sommerfeld, P.P. Ewald, M. von Laue, W. Friedrich, P. Knipping, P. von Groth) First X-ray diffraction on $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$
07/1912	Bavarian Academy of Sciences
11/1912	Bragg's Law Structures (mostly geometrical considerations): Alkalihalides, Fluorite, Calcite, Diamond (1913), Sanidine (1922)

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Historical Notes II

<u>1923 - 1932</u>	<u>Solution by space group and unit cell informations</u>
Ca. 1925	„Fourier methods“ (eg. Diopside 1929) trial and error refinement of ca. 20 free parameters
<u>1932 - 1942</u>	<u>Isomorphous replacement, Patterson methods</u>
1934	A.L. Patterson, F^2 as Fourier coefficients auto-correlation function of electron density
1936	Harker peaks/sections
<u>1942 - 1952</u>	<u>Heavy atom method</u>
1939	J.M. Robertson
1950	B_{12}
1950	Image seeking methods (Buerger)
1953	DNA (Crick, Watson, Franklin)
1954	First protein structure
1960	Haemoglobin

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Historical Notes III

1952 - 1962 **Direct methods**

1947 Harker-Kasper equations
 1947 Wilson statistics
 1950 Sayre, Zachariasen (Sayre equation)
 1952 Karle & Hauptmann (Triplet relations)

 1955 Anomalous dispersion (Okaia et al.)

1962 - 1972 **Development of computer programs**

1965 ORTEP (Stewart)
 1970 XRAY70 (Johnson)

1972 - today **„Faster, Higher, Wider...“**

Number of atoms, resolution
 Programs
 Synchrotron radiation
 Automatisation
 Black box (?)

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Historical Notes IV

1912 - today **Instrumentation and sources**

1912 Laue method
 1913 Bragg's X-ray spectrometer
 1913 Rotation method (deBroglie)
 1916 Debye-Scherrer
 1919 Seemann-Bohlin

 1924 Weissenberg (Sauter 1932, Schiebold 1934)
 1935 Straumanis
 1937 Guinier
 1938 DeJong-Bouman
 1942 Precession (Buerger)

1947 - 1950 First automatic 2-circle diffractometers

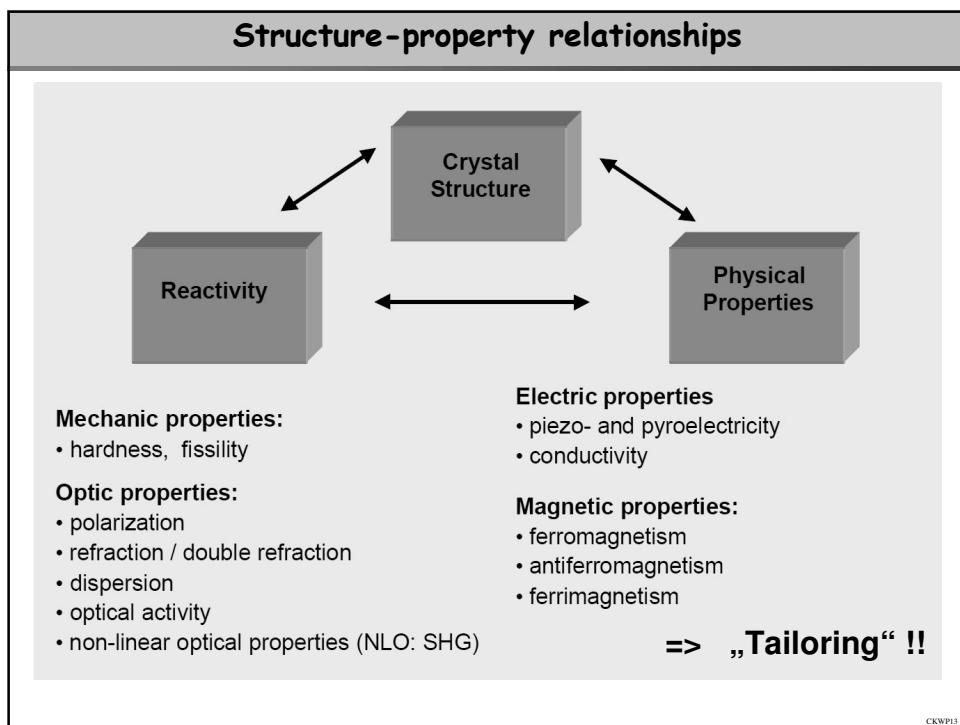
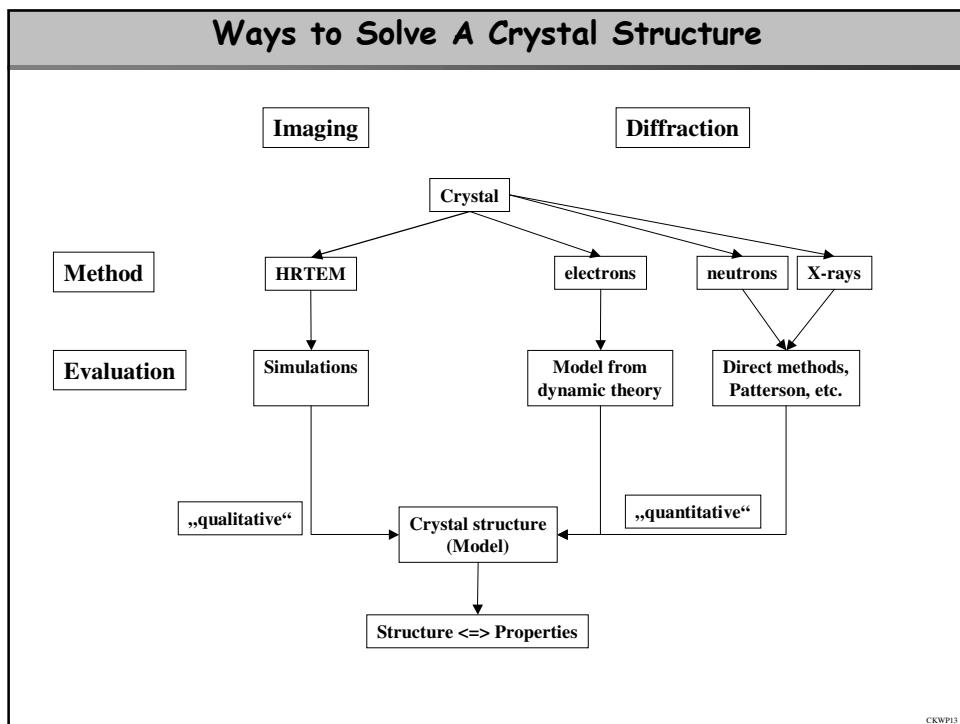
Ca. 1960 Automatic 4-circle diffractometers

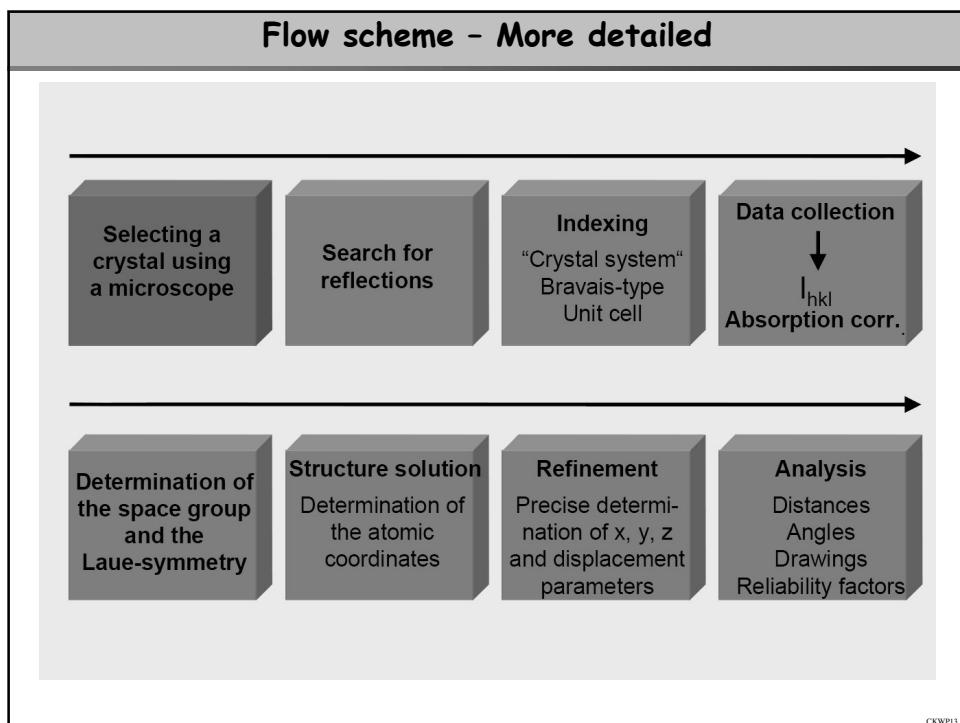
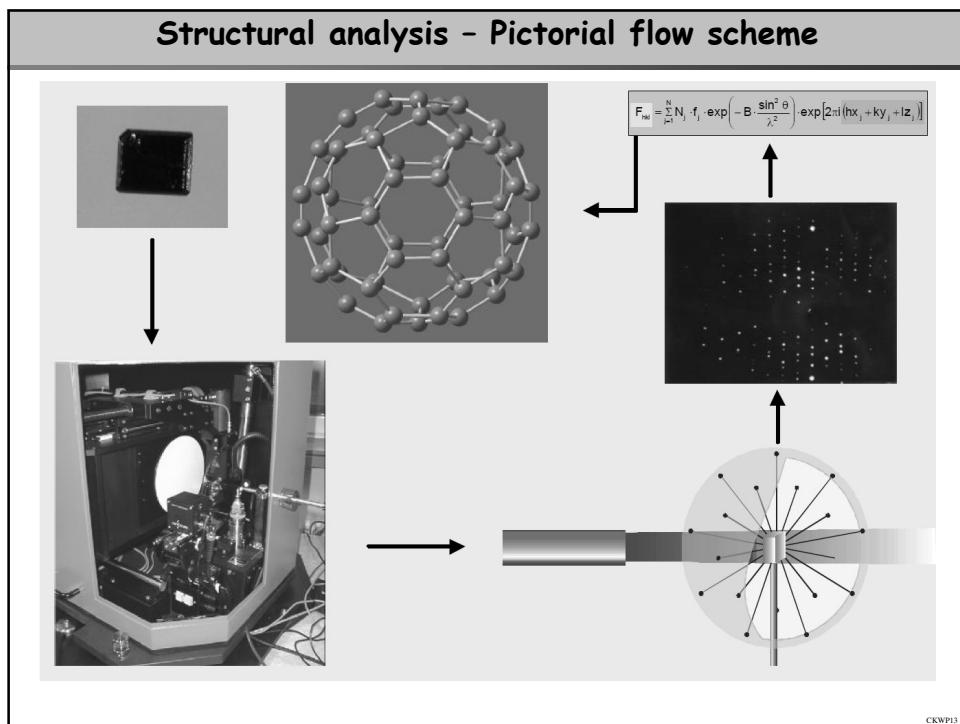
Ca. 1980 Rotating anodes
 Synchrotron radiation

Imaging plates

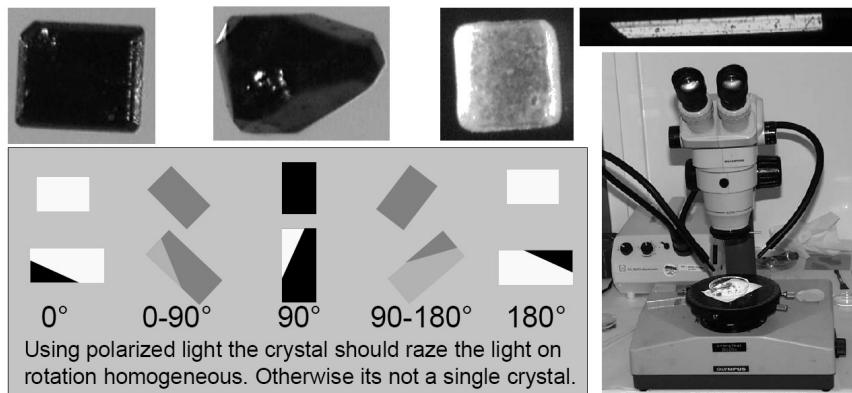
Ca. 1990 CCD-detectors

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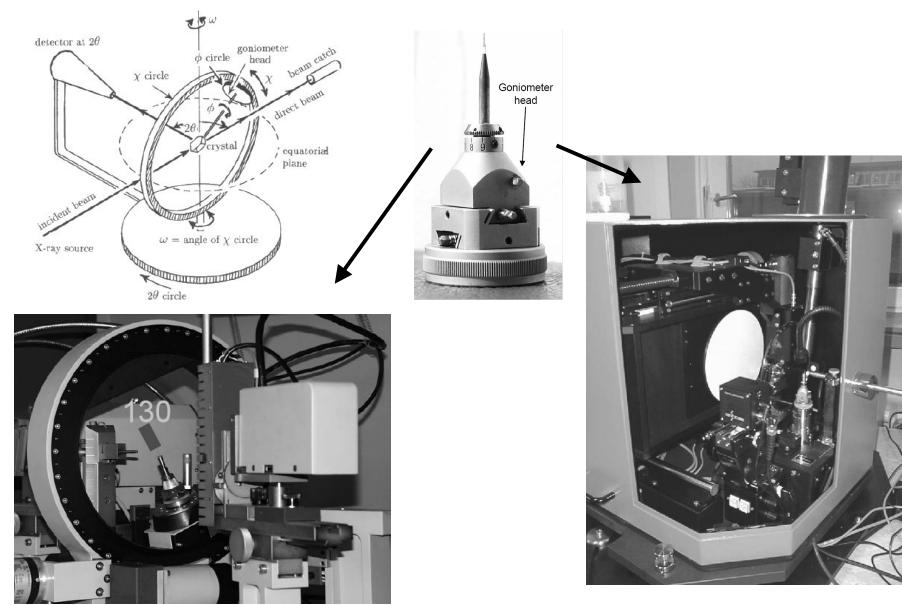
Sample selection



A real judgement of the crystal quality can only be performed using diffraction methods.

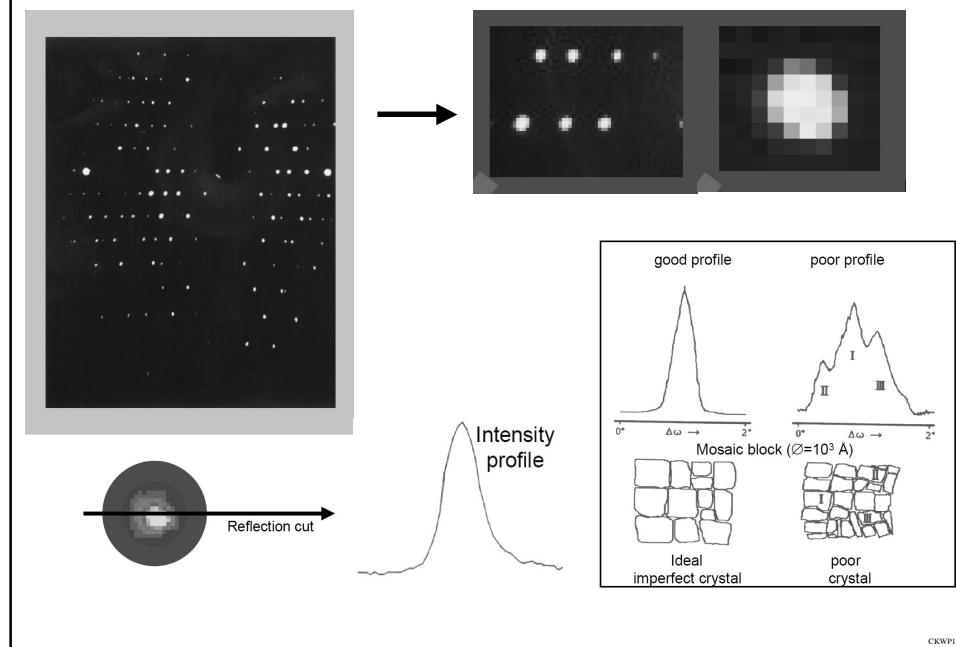
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Single-crystal diffractometers

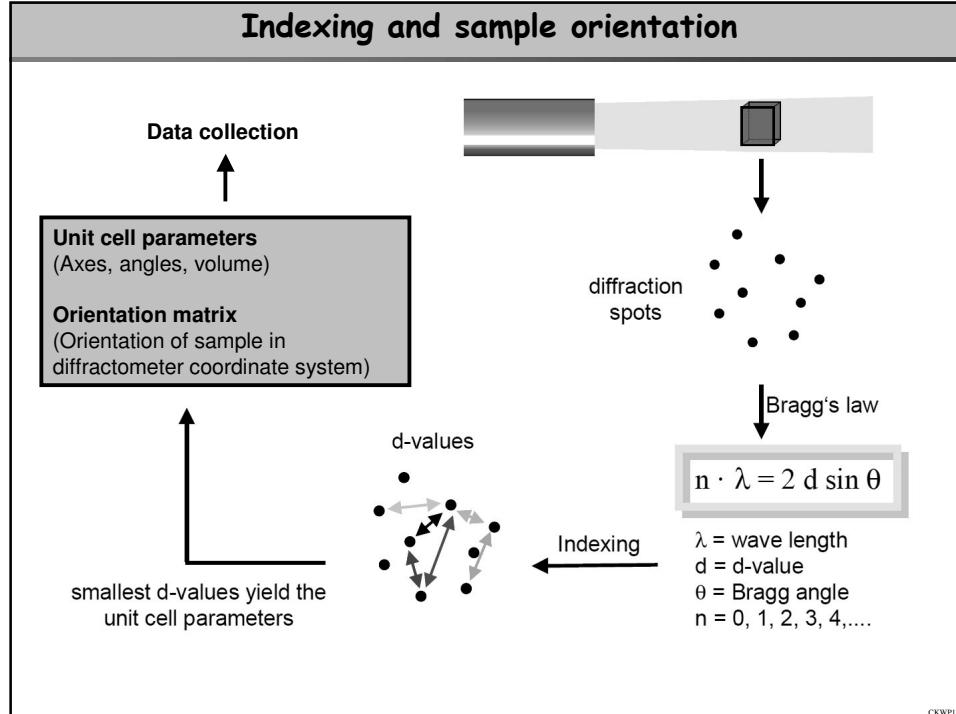


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Sample quality - Width and shape of reflections



Indexing and sample orientation



The result...

H	K	L	$I_{int.}$	σ	Batch-Nr.	Directional cosine
-10	3	-3	1.49	0.21	1	-0.70857-0.22509-0.69641 0.97050-0.11269-0.08746
-10	3	-2	1.12	0.20	1	-0.71032-0.22335-0.69927 0.97330-0.07926-0.05426
-10	3	-1	0.03	0.47	1	-0.71169-0.22198-0.70090 0.97486-0.04581-0.02107
-10	3	0	2.62	0.20	1	-0.71268-0.22099-0.70131 0.97521-0.01235 0.01210
-10	3	1	-0.78	0.47	1	-0.71330-0.22037-0.70050 0.97434 0.02113 0.04526
-10	3	2	1.12	0.20	1	-0.71353-0.22014-0.69848 0.97226 0.05462 0.07840
-10	3	3	1.42	0.21	1	-0.71338-0.22029-0.69524 0.96895 0.08812 0.11154
-10	2	4	0.38	0.21	1	-0.64057-0.29310-0.76034 0.94272 0.10782 0.15856
-10	2	3	0.37	0.17	1	-0.63977-0.29389-0.76501 0.94744 0.07406 0.12568
-10	2	2	2.14	0.20	1	-0.63866-0.29500-0.76842 0.95092 0.04033 0.09278
-10	2	1	4.89	0.23	1	-0.63725-0.29642-0.77059 0.95315 0.00663 0.05984
-10	2	0	1.14	0.19	1	-0.63554-0.29813-0.77152 0.95415-0.02704 0.02688
-10	2	-1	5.18	0.23	1	-0.63354-0.30013-0.77122 0.95391-0.06068-0.00612
-10	2	-2	1.68	0.20	1	-0.63125-0.30241-0.76968 0.95244-0.09429-0.03914
-10	2	-3	0.00	0.47	1	-0.62869-0.30497-0.76690 0.94971-0.12787-0.07220
-10	2	-4	0.72	0.17	1	-0.62585-0.30781-0.76285 0.94573-0.16141-0.10530
-10	1	-5	0.31	0.21	1	-0.53552-0.39813-0.81758 0.90925-0.21067-0.12259
-10	1	-4	4.65	0.24	1	-0.53928-0.39437-0.82309 0.91469-0.17706-0.08956
-10	1	-3	3.91	0.20	1	-0.54288-0.39077-0.82729 0.91883-0.14340-0.05658
-10	1	-2	9.43	0.26	1	-0.54632-0.38733-0.83021 0.92169-0.10968-0.02366
-10	1	-1	2.59	0.19	1	-0.54958-0.38407-0.83187 0.92328-0.07591 0.00920
-10	1	0	0.38	0.45	1	-0.55266-0.38100-0.83226 0.92361-0.04210 0.04202

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Absorption correction

Necessary for:

- Large crystals
- Anisotropic crystals
- High absorption coefficients μ (eg. Pb, ...)

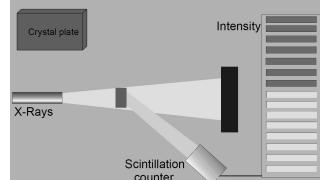
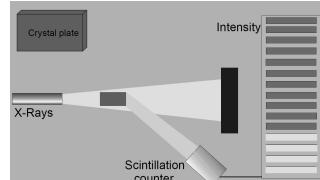
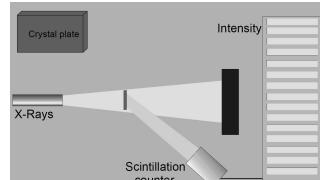
$$\begin{aligned} I(\text{CuK}\alpha) &\sim 8x I(\text{MoK}\alpha) \\ \text{Abs (CuK}\alpha) &\sim 10x \text{Abs(MoK}\alpha) \end{aligned}$$

To overcome restricted lab wavelengths:
=> Synchrotron radiation

„Optimal“ crystal size:

$$D = 2 / \mu$$

D = crystal size
 μ = absorption coefficient [cm^{-1}]



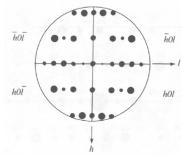
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Laue-symmetry

Friedel-Law: Diffraction patterns are centrosymmetric: $I(hkl) = I(-h-k-l)$

Any further symmetry: Laue-symmetry

=> Determines the crystal system (!)



Unit cell parameters normally do NOT allow a definite decision

Crystal system	Crystal class	Laue-group	Symmetry equivalent reflections
triclinic	1, -1	1	2: hkl, -h-k-l
monoclinic	2, m, 2/m	2/m	4: hkl, -h-k-l, h-kl, h-kl
orthorhombic	222, mm2, mmm	mmm	8: hkl, -h-k-l, h-kl, h-kl, -hkl, hk-l, -h-kl, h-k-l
tetragonal	4, -4, 4/m 422, -42m, 4mm, 4/mmm	4/m 4/mmm	8: hkl, -h-k-l, khl, -k-h-l hk-l, -h-kl, kh-l, -k-hl 16
trigonal	3, -3 321, 3m1, -3m1 312, 31m, -31m	3 -3m1 -31m	6 12 12
hexagonal	6, -6, 6/m 622, -62m, 6mm, 6/mmm	6/m 6/mmm	12 24
cubic	23, m-3 432, -43m, m-3m	m-3 m-3m	24 48

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Space group determination

Determination by analysis of systematic extinctions => Symmetry elements

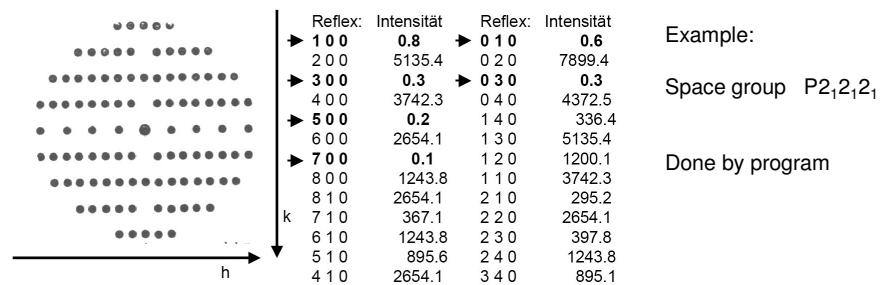
Extinctions by:

Centered lattices
Screw axes
Glide planes

No extinctions:

Rotation axes
Inversion axes => 50 unique space groups
Mirror planes

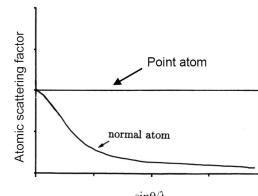
Possible pitfalls: Twinning, incorrect analysis of extinctions



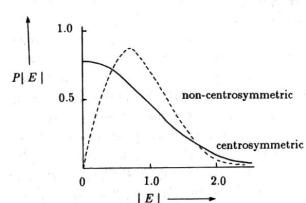
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Space group determination – Wilson statistics

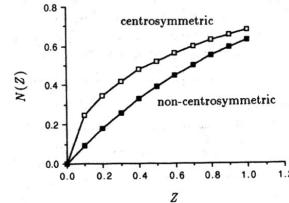
- A.J.C. Wilson: Average intensities only depend on unit cell content
Intensity distribution is different for centro- and non-centrosymmetric structures
- Problem: Intensities not directly comparable since $f_j = F(2\theta)$
- Solution: Definition of „normalized structure factors“
=> „point atom“
=> electron density map becomes sharper



Probability of the E-value distribution in a centrosymmetric and non-centrosymmetric structure



Distribution of the E-values in a centrosymmetric and a non-centrosymmetric structure
 $Z = |E|^2$ -values; $N(Z)$ Number of reflections

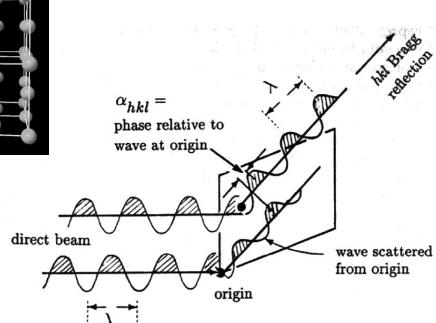
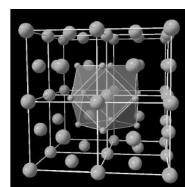


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Link between structure & intensity – The structure factor



$$I_{hkl} \sim |F_{hkl}|^2$$

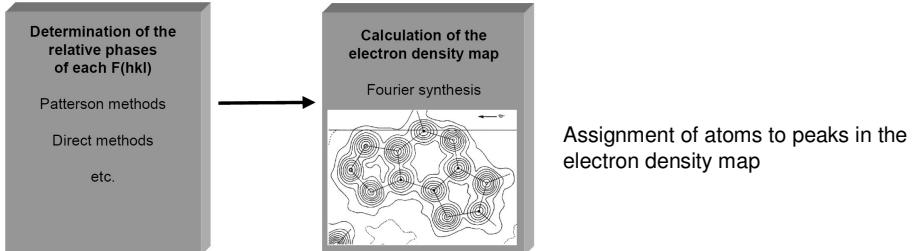


What is needed for a structure determination?

- Intensity of each reflection (measurement)
- Phase of each reflection
 - => Lost during measurement
 - => „Phase problem“

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Methods for the solution of structures



1. Trial and Error

- Take reasonable (physical, chemical) structure model to compute E-map

2. Patterson-method (Heavy-atom method)

- $|F|$ -values as coefficients for E-map => „E-map“ contains interatomic distances of all atoms
- Heavy atoms can be easily identified

3. Direct methods

- Statistical method for determination of phase angles (Intensity statistics)
- Works generally for all atoms
- Phase angles are estimated with some probability

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Calculation of electron density maps

X-rays are scattered by the electrons of the atoms; therefore, the result of a structure determination is the electron distribution in the crystal (asymmetric unit)

The electron density in a crystal is a periodically function

The electron density map is calculated by a Fourier synthesis:

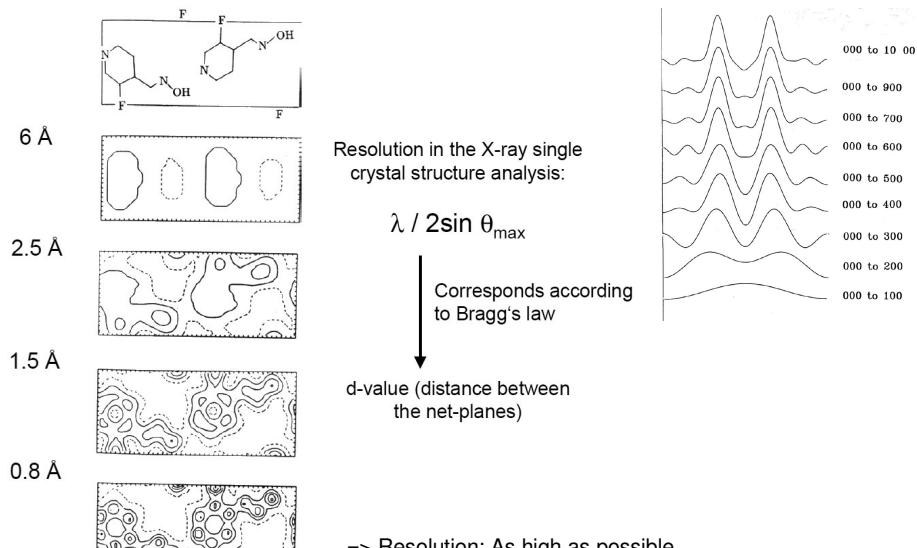
If the intensity and the phase angle of each reflection (structure factor) is known, the E-map which means the crystal structure can be calculated.

$$\rho(xyz) = \frac{1}{V} \sum_h \sum_k \sum_l |F(hkl)| \cos 2\pi(hx + ky + lz) - \alpha_{hkl}$$

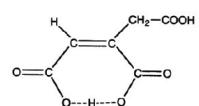
The electron density ($e/\text{\AA}^3$) can be calculated at each point in the asymmetric unit. Normally it is calculated at every 0.2 Å.

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The effect of resolution



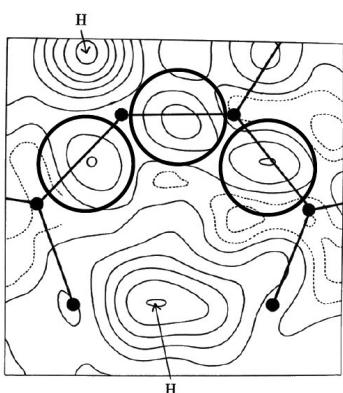
Electron density difference maps



Assumption:
Heavy atoms are all identified

=> $F(\text{obs}) - F(\text{calc})$ as coefficients for fourier synthesis

=> E-map contains residual electron density



Effects for structure solution:

- Identification of light atoms (eg. hydrogen)
- Covalent electron density between atoms

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Structure refinement

Problem:

Structure model from E-map still contains errors (coordinates)

Solution:

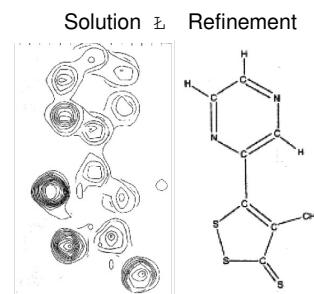
Variation of parameters to minimize $F_{\text{obs}} - F_{\text{calc}}$

Method:

Least-squares refinement

Parameters to be refined:

- Atomic coordinates x, y, z
- Isotropic and anisotropic displacement parameters
(Thermal motion, disorder, ...)



Judgement of model:

By „agreement factors“ (R-values)

Conventional R-value:

$R < 0.05 = 5\%$ for „good“ structures

$$R = \sum_{\text{all } hkl} \left| F(hkl)_{\text{o}} - F(hkl)_{\text{c}} \right| / \sum_{\text{all } hkl} |F(hkl)|_{\text{o}}$$

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Isotropic / anisotropic refinement

Non-static atoms:

$$F_{hkl} = \sum_{j=1}^N N_j \cdot f_j \cdot \exp\left(-B \cdot \frac{\sin^2 \theta}{\lambda^2}\right) \cdot \exp[2\pi i (hx_j + ky_j + lz_j)]$$

=> Intensity decrease

=> Broadening of E-map

=> Additional parameters in refinement

=> Only spherical motion in first step (isotropic)

„Temperature factor“
(Debye-Waller factor)

Amount of motion is anisotropic (ellipsoidal):

=> Introduction of anisotropic displacement parameters

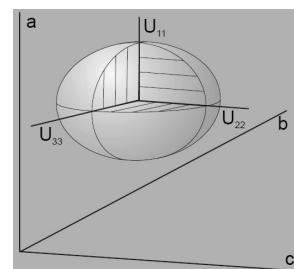
=> Size and orientation described by 6 parameters (U_{ij} -values)

U_{11}, U_{22}, U_{33} : Displacement along ellipsoidal axes

U_{12}, U_{13}, U_{23} : Orientation of ellipsoid relative to unit cell axes

Equivalent isotropic displacement parameters

$$U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i \cdot a_j$$



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Final considerations

- The model should be chemically correct and should correspond to what is expected by theory
- The agreement between observed and calculated structure factors should be as good as possible ($R_1 < 5\%$; $wR_2 < 15\%$)
If heavy atoms are present the R-values are frequently low but the position of the light atoms are mostly inaccurate determined
- The estimated standard deviation (e.s.d's) should be as low as possible
- The residual electron density should not contain any significant maxima or minima
- All anisotropic displacement parameters should be physically meaningful
- The relation between the observed reflections and the number of parameters refined should be at least 10 : 1

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