

# Crystal structure analysis/determination

Analysis/determination of the crystal/molecular structure of a solid with the help of X-rays or neutrons means (because of the 3D periodicity of crystals):

Determination of

- the **geometry** (lattice constants  $a, b, c, \alpha, \beta, \gamma$ )
- the **symmetry** (space group)
- the **content** (typ, site  $x_j, y_j, z_j$  and thermal parameters  $B_j$  of the atoms  $j$ )

of the **unit cell** of a crystalline compound and their **analysis/interpretation** with respect to chemical or physical problems or questions.

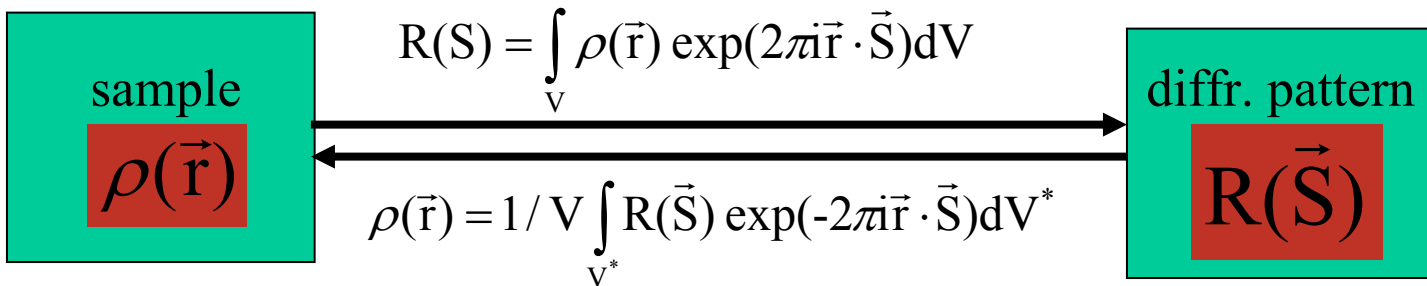
# Crystal structure analysis/determination

is based on diffraction of electromagnetic radiation or neutrons of suitable energies/wavelengths/velocities and one needs:

- a crystalline sample (powder or **single crystal**,  $V \sim 0.01 \text{ mm}^3$ )
- an adequate **electromagnetic radiation** ( $\lambda \sim 10^{-10} \text{ m}$ )
- some knowledge of properties and **diffraction of radiation**
- some knowledge of structure and **symmetry of crystals**
- a diffractometer (with point and/or area detector)
- a powerful computer with the required **programs for solution, refinement, analysis and visualization** of the crystal structure
- some chemical feeling for **interpretation** of the results

# Crystal structure analysis/determination

If a substance is irradiated by electromagn. Radiation or neutrons of suitable wavelength, a small part of the primary radiation ( $\sim 10^{-6}$ ) is scattered by the electrons or nuclei of the atoms /ions/molecules of the sample **elastically** ( $\Delta E = 0$ ) and **coherently** ( $\Delta\phi = \text{konstant}$ ) in all directions. The resulting **scattering/diffraction pattern** **R** is the **Fourier transform** of the **elektron/scattering distribution function**  $\rho$  of the sample and vice versa.

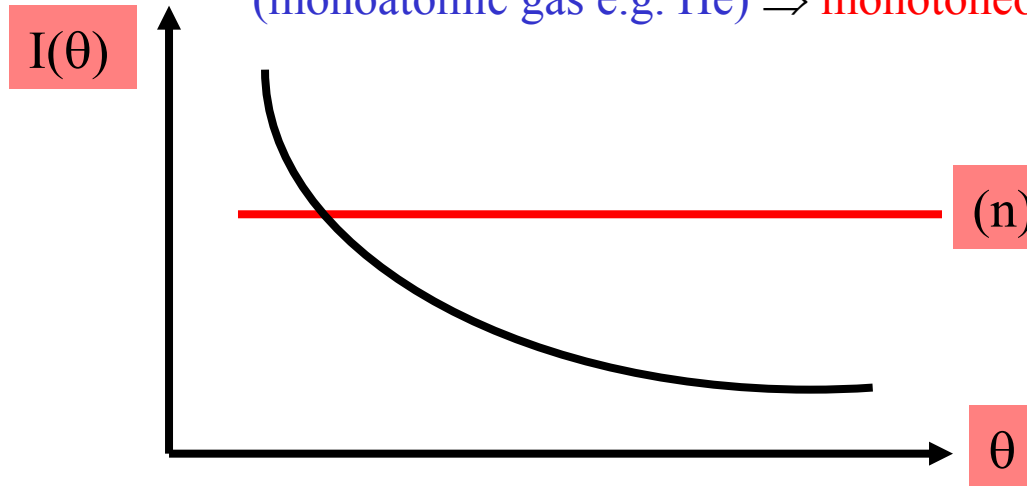


The shape of the resulting **scattering/diffraction pattern** depends on the **degree of order** of the sample.

# A. X-ray scattering diagram of an amorphous sample

no long-range order, no short range order

(monoatomic gas e.g. He)  $\Rightarrow$  monotoneous decrease



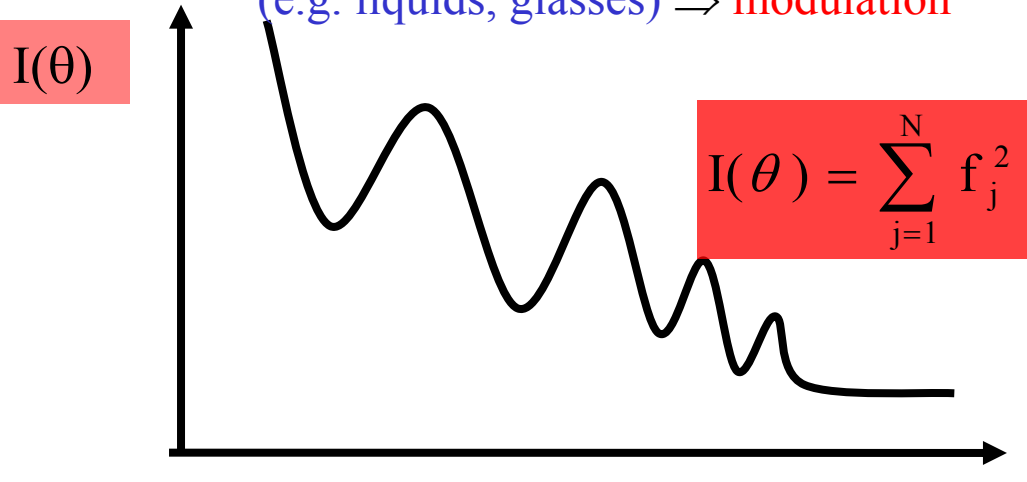
$$I(\theta) = N \cdot f^2$$

$f$  = scattering length of atoms  $N$

$\Rightarrow$  no information

no long-range, but short range order

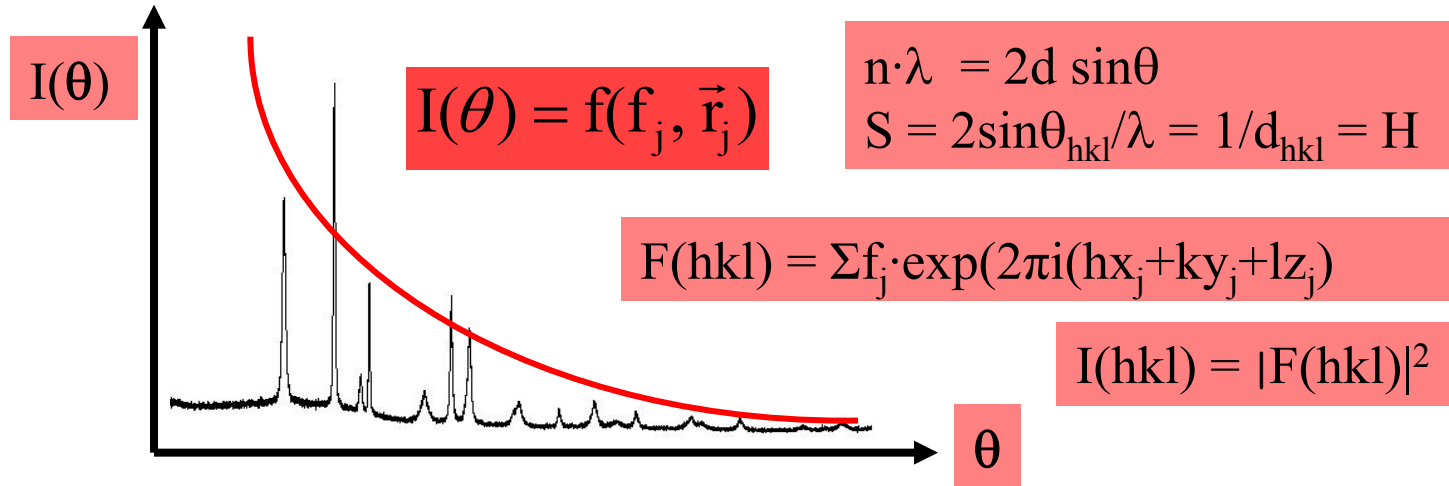
(e.g. liquids, glasses)  $\Rightarrow$  modulation



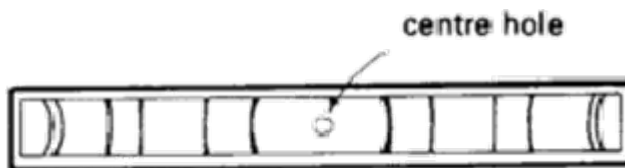
$$I(\theta) = \sum_{j=1}^N f_j^2 + 2 \sum_{j>} \sum_i f_j f_i \cos \left[ \pi (\vec{r}_j - \vec{r}_i) \vec{S} \right]$$

$\Rightarrow$  radial distribution function  
atomic distances

## B. X-ray scattering diagram of a crystalline sample

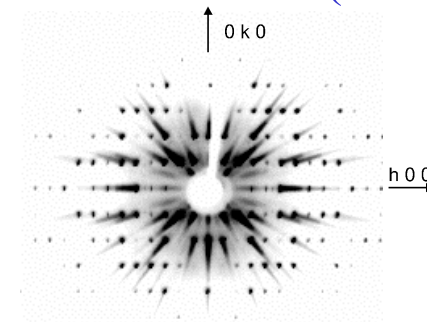


crystal powder  
 orientation statistical,  $\lambda$  fixed  
 $\Rightarrow$  cones of interference



Debye-Scherrer diagram

single crystal  
 orientation or  $\lambda$  variable  
 $\Rightarrow$  dots of interference (reflections)

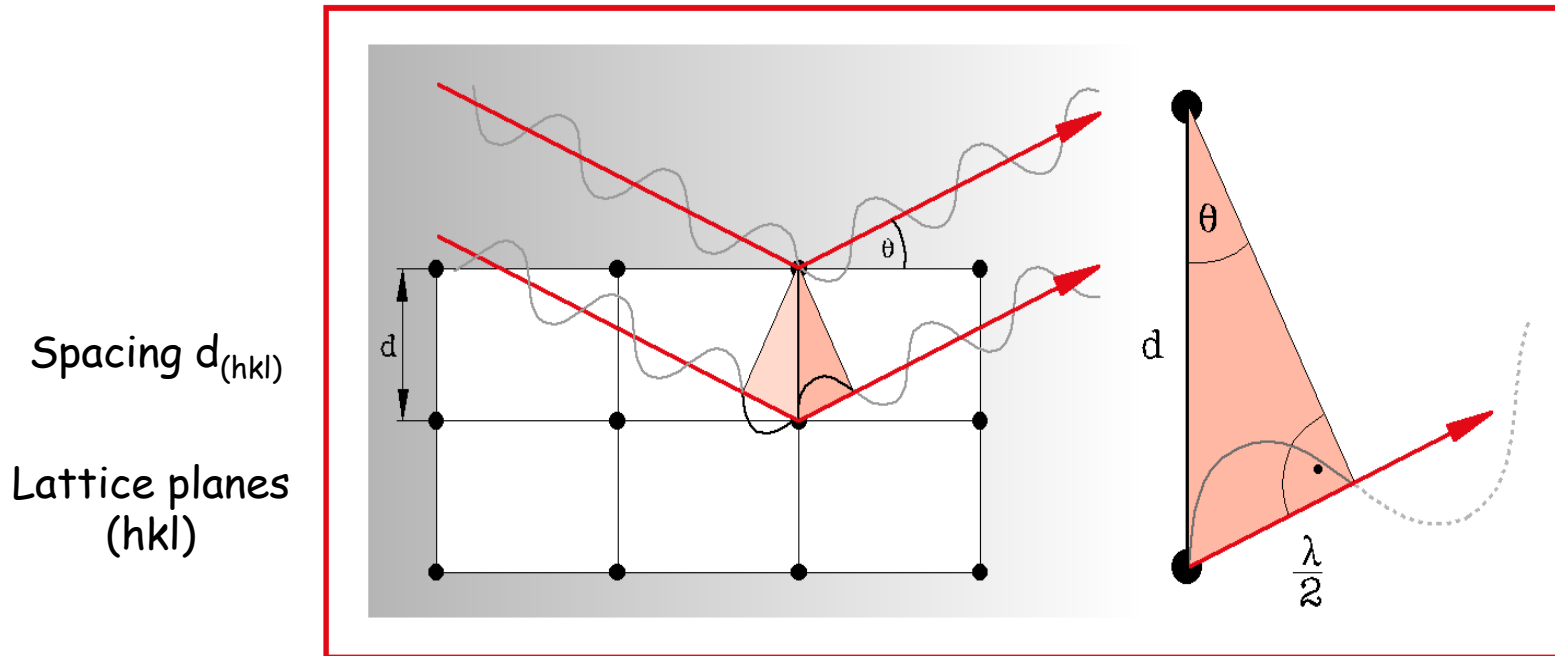


precession diagram

Why that?

# Diffraction of X-rays or neutrons at a crystalline sample (single crystal or crystal powder)

X-rays scattered from a crystalline sample are not totally extinct only for those directions, where the scattered rays are „in phase“.  
 $R(S)$  und  $I(\theta)$  therefore are periodic functions of „Bragg reflections“ .



Bragg equation:  $n \cdot \lambda = 2d \cdot \sin\theta$  or  $\lambda = 2d_{(hkl)} \cdot \sin\theta_{(hkl)}$  6

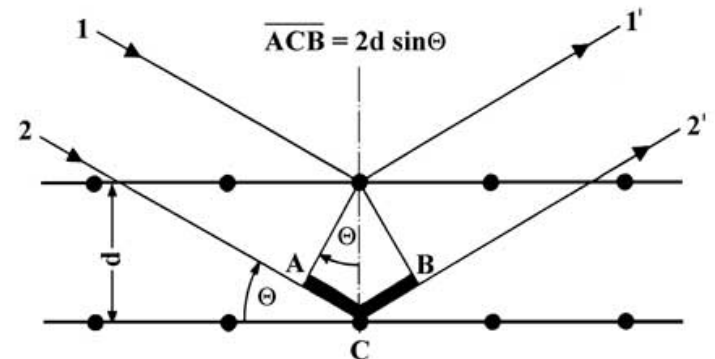
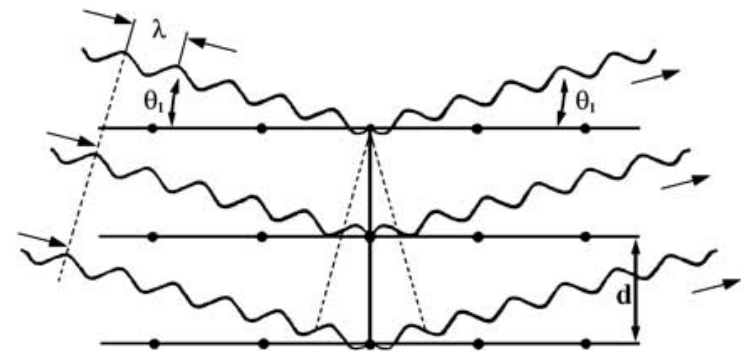
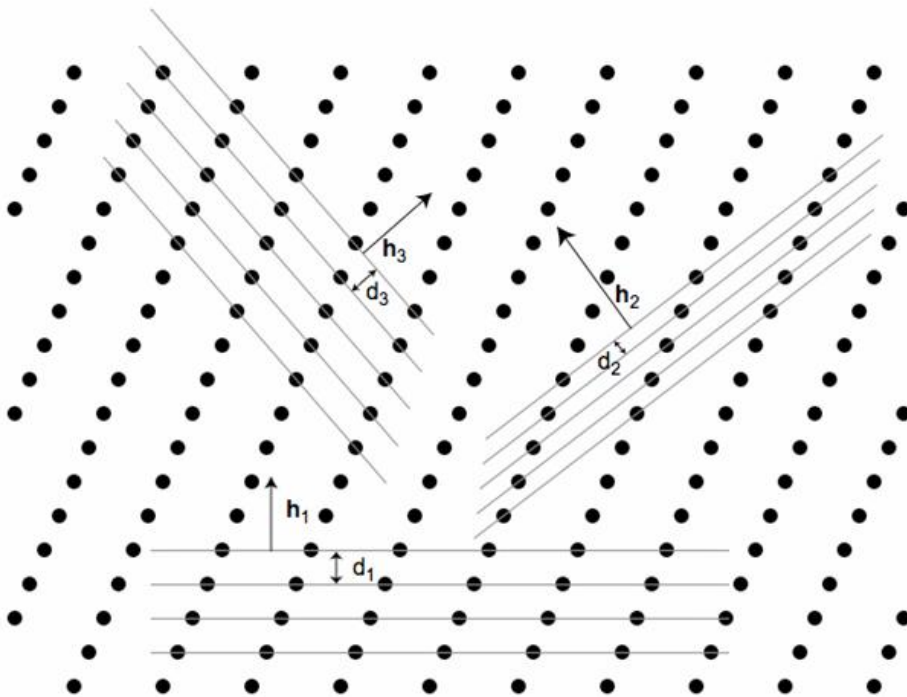
# Basic equation of X-ray analysis: Bragg equation

Lattice planes: Why are they important ?

Bragg equation:

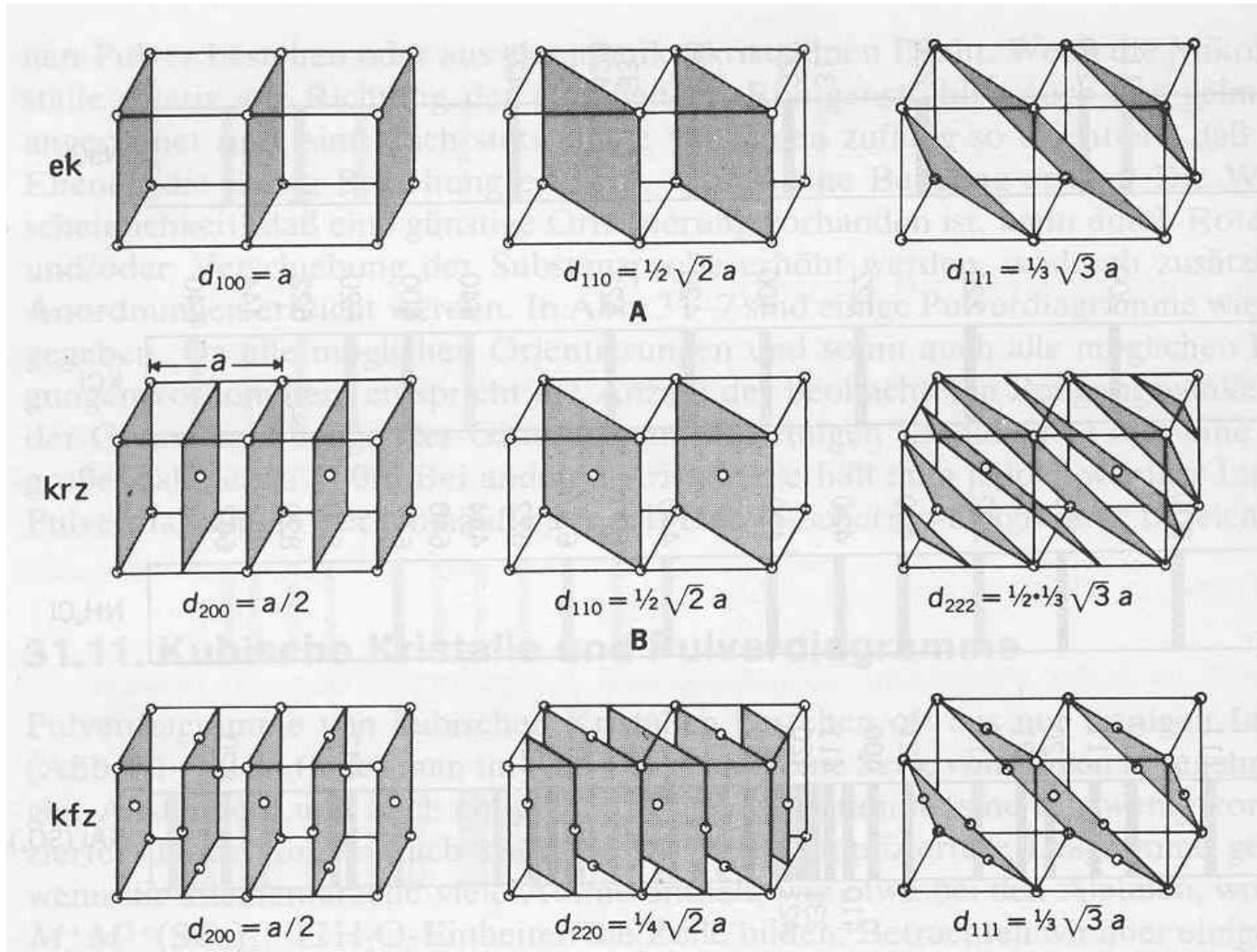
$$n\lambda = 2d \sin\theta$$

$$\lambda = 2d_{(hkl)} \sin\theta_{(hkl)}$$



Question: How are directions and planes in a regular lattice defined ?

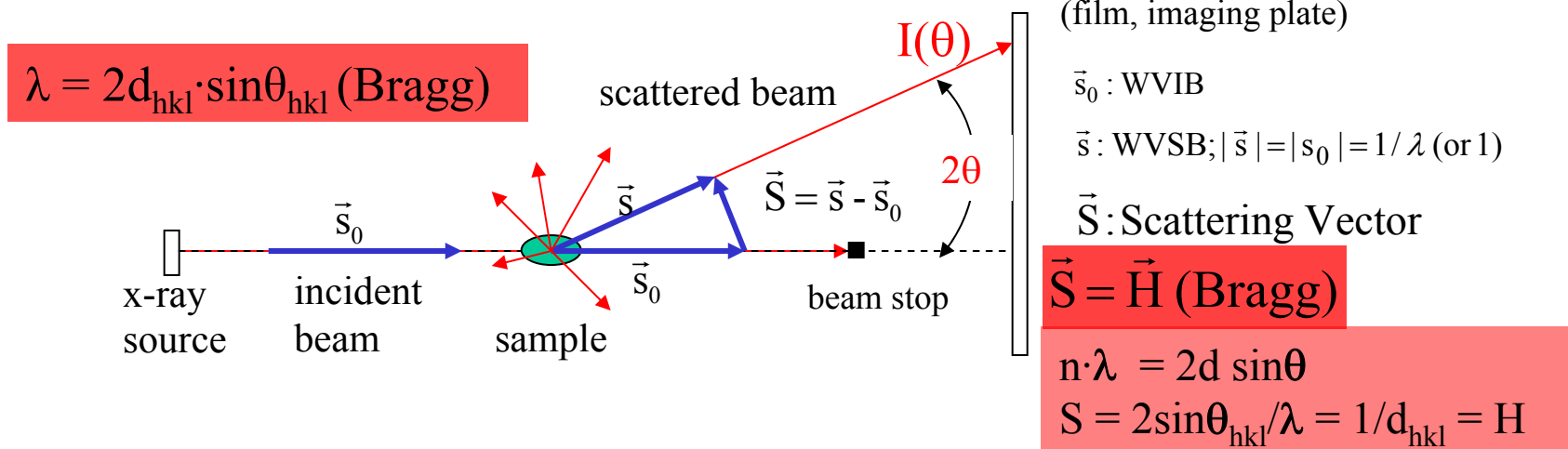
# Lattice plane series: Miller indices hkl, d values



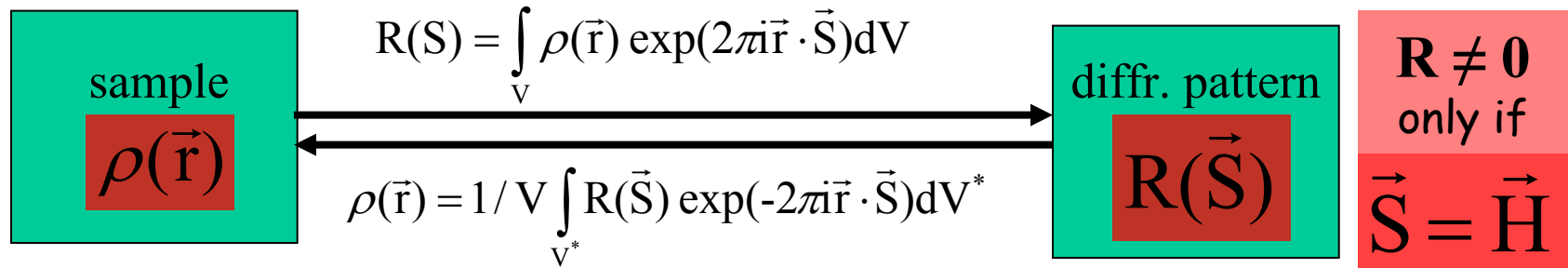


# (X-ray) diffraction of a crystalline sample

(single crystal or crystal powder)



Fourier transform of the electron density distribution



$V$  : volume of sample  $\vec{r}$  : vector in space  $R$  : scattering amplitude

$\vec{S}$  : scattering vector  $\equiv$  vector in Fourier (momentum) space

# Crystal structure analysis/determination

Analysis/determination of the crystal/molecular structure of a **crystalline solid** with the help of X-rays or neutrons therefore means:

Determination of

- the **geometry** (lattice constants  $a, b, c, \alpha, \beta, \gamma$ )
- the **symmetry** (space group)
- the **content** (type, site  $x_j, y_j, z_j$  and thermal parameters  $B_j$  of the atoms  $j$ )

**of the unit cell** of that crystalline compound from the scattering/diffraction pattern  **$R(S)$  or  $I(\theta)$  or  $I(hkl)$**

How does that work?

# Crystal structure analysis/determination

- The **geometry** (lattice constants  $a, b, c, \alpha, \beta, \gamma$ ) of the unit cell/ compound one can get from the **geometry of the diffraction pattern**, i.e. from the **site of the reflections** (diffraction angles  $\theta$  for a powder; „Euler angles“  $\theta, \omega, \varphi, \chi$  for a single crystal)
- The **symmetry** (space group) one can get from the **symmetry of the reflections** and the **systematically extinct reflections**,
- The **content** of the unit cell (typ, site  $x_j, y_j, z_j$  and thermal parameters  $B_j$  of the atoms  $j$ ) one can get from the **intensities  $I(hkl)$  of the reflections** and the respective **phases  $\alpha(hkl)$** .

$$|F_o(hkl)| \approx (I(hkl))^{1/2} \quad F_c(hkl) = \sum f_j \cdot \exp(2\pi i(hx_j + ky_j + lz_j))$$
$$\delta(xyz) = (1/V) \cdot \sum |F_o(hkl)| \cdot \exp(i\alpha(hkl)) \cdot \exp(-2\pi i(hx + ky + lz))$$

The structure factor is named  **$F_o(hkl)$** , if observed, i.e. derived from measured  $I(hkl)$  and  **$F_c(hkl)$**  if calculated from  $f_j, x_j, y_j, z_j$ . Note that  **$(hkl)$**  represent lattice planes and  **$hkl$**  reflections.

# Crystal structure analysis/determination

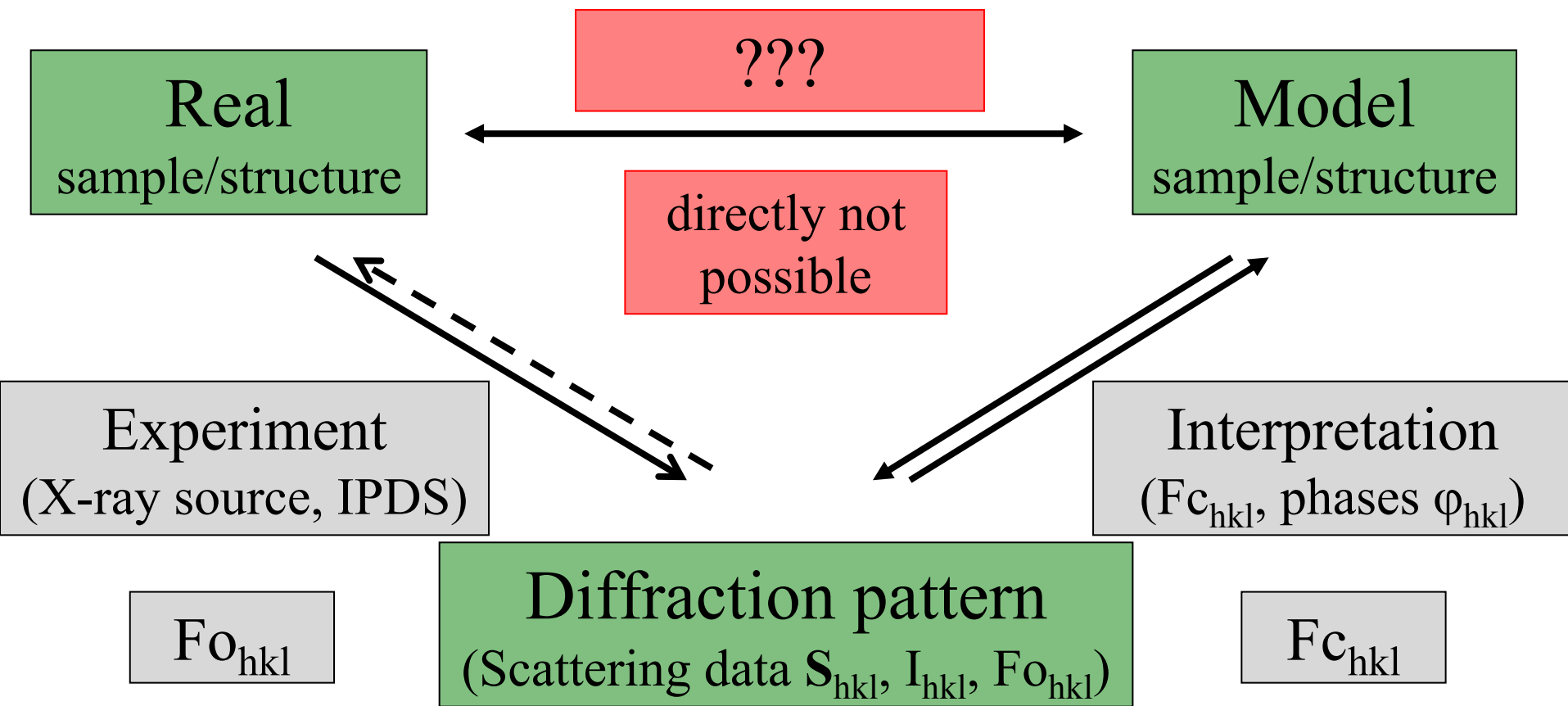
- The **intensities**  $I_{hkl}$  of the reflections (i.e. of the reciprocal lattice points) thus reflect the atomic arrangement of the **real crystal structure**.
- Each **intensity**  $I(hkl)$  or  $I_{hkl}$  is proportional to the **square** of a quantity called **structure factor**  $F(hkl)$  or  $F_{hkl}$  ( $F_o$  for observed,  $F_c$  for calculated).
- The structure factor  $F(hkl)$  is a **complex number** in general but becomes **real** in case of crystal structures with a **centre of symmetry**:

$$F(hkl) = F_{hkl} = \sum_j f_j \cos 2\pi(hx_j + ky_j + lz_j)$$

- In case of centrosymmetric crystal structures, the phases are 0 or  $\pi$ , i.e. „only“ the signs instead of the phases of the structure factors have to be determined.

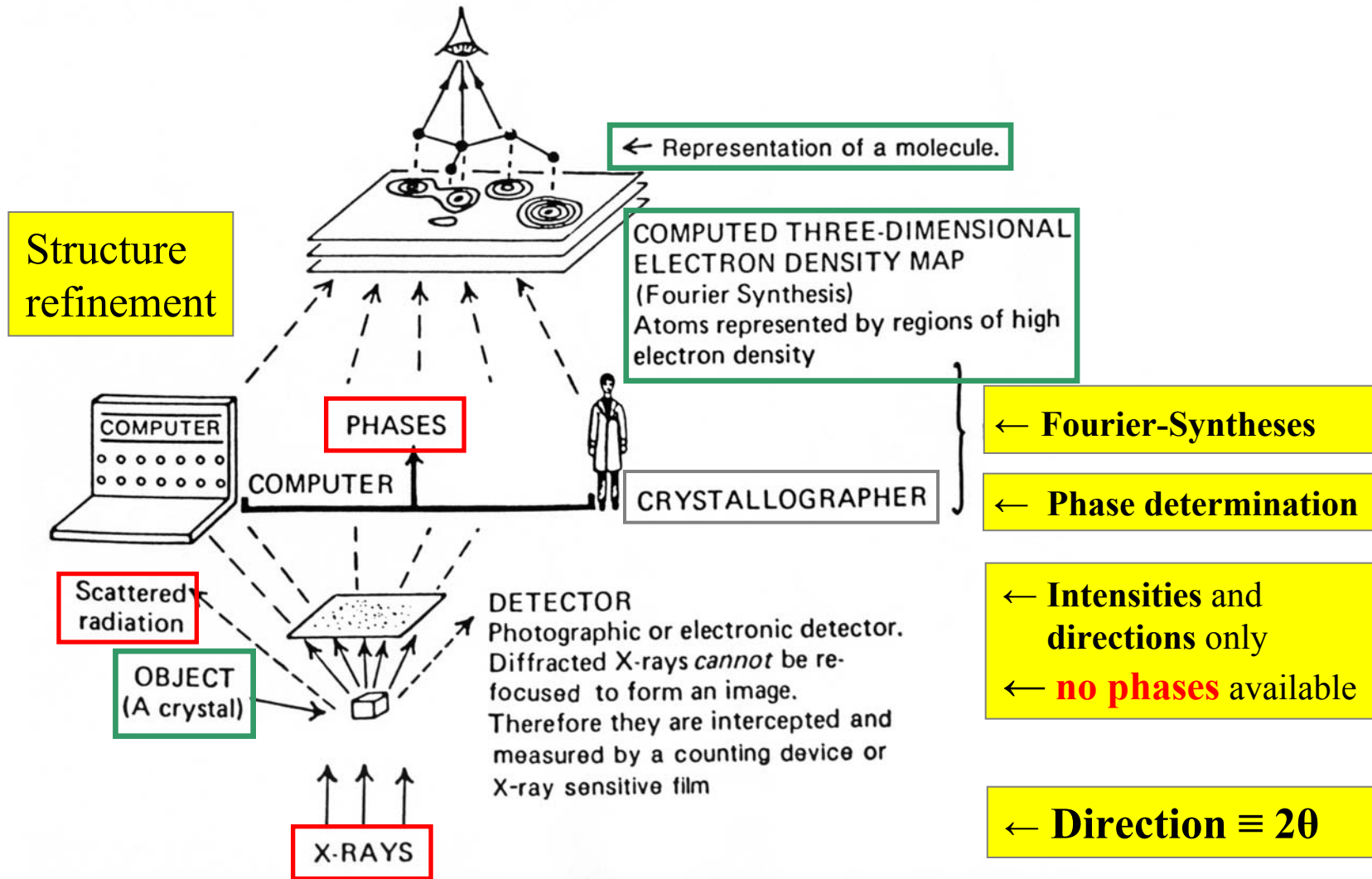
The problem is that the **phases/signs** are lost upon measurement of the intensities of the reflections (**phase problem** of crystal structure analysis/determination)

# Crystal structure analysis/determination



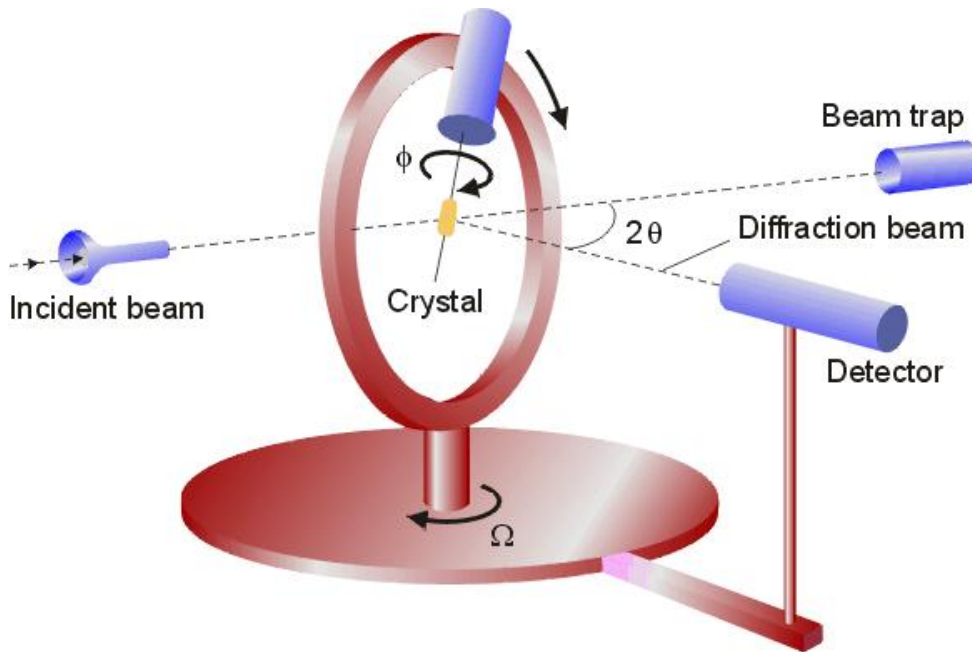
Structure determination only indirectly possible!

# Crystal structure analysis/determination



# Realisation of a crystal structure determination

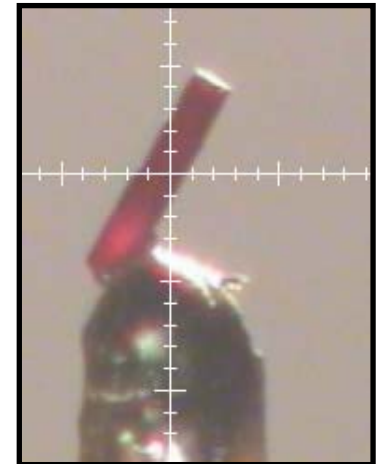
1. Fixing und centering of a crystal on a diffractometer and determination of the **orientaion matrix**  $M$  and the **lattice constants**  $a, b, c, \alpha, \beta, \gamma$  of the crystal from the Eulerian angles of the reflections  $(\theta, \omega, \phi, \chi)$  and of the **cell content number**  $Z$  (aus cell volume, density and formula),



Principle of a four-circle diffraktometer for single crystal stucture determination by use of X-ray or neutron diffraction

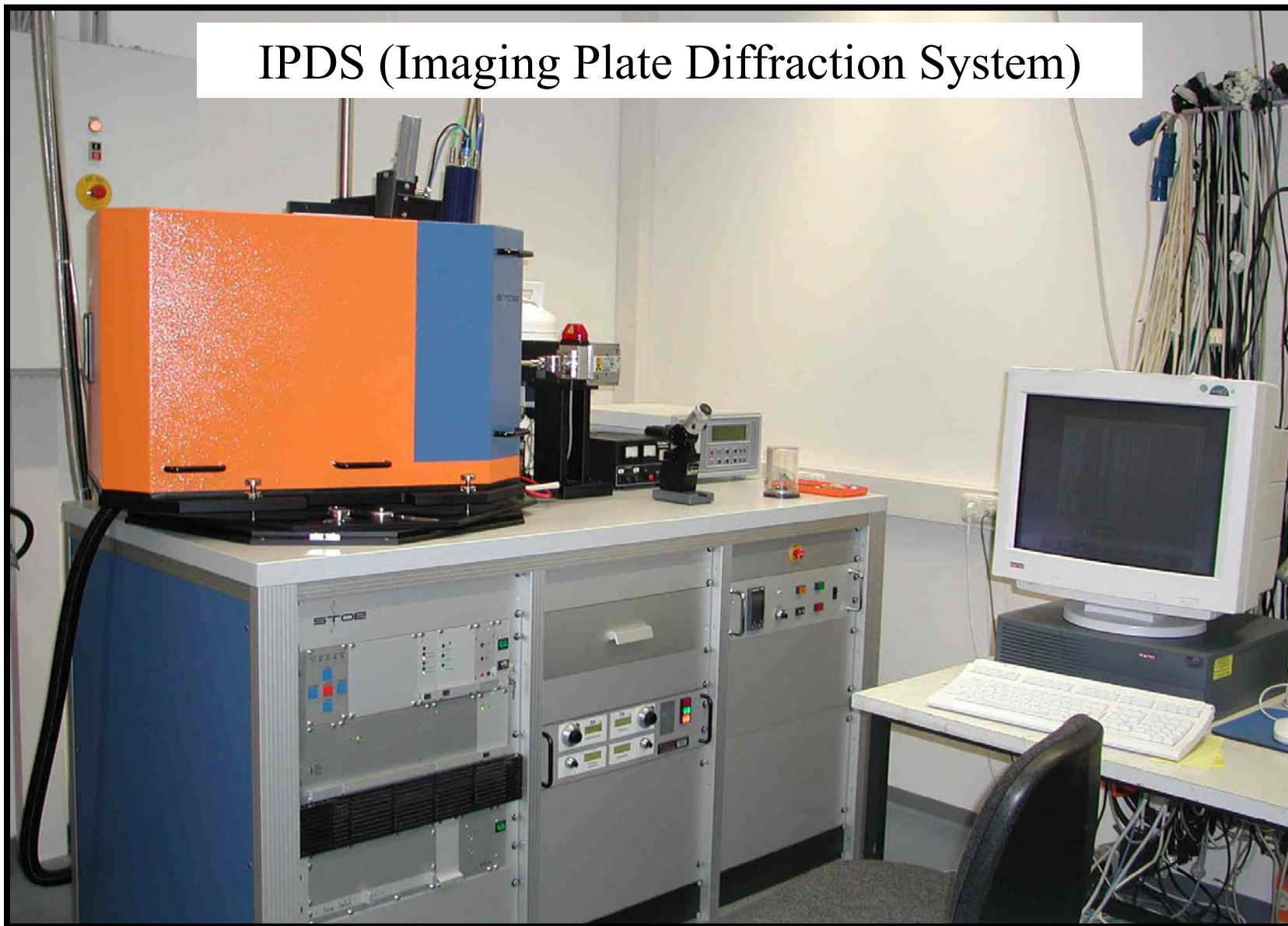


# CAD4 (Kappa-Axis-Diffraktometer)

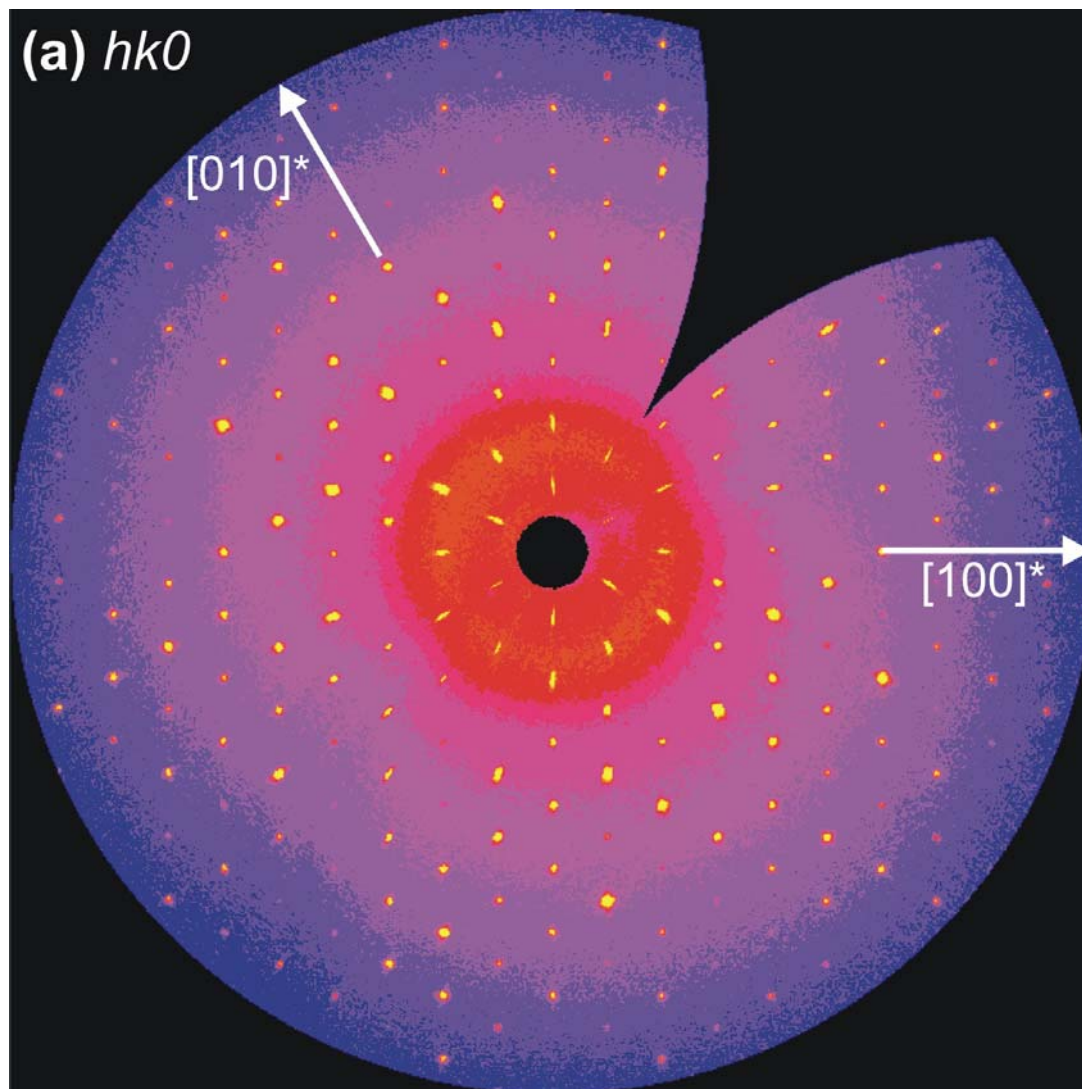




# IPDS (Imaging Plate Diffraction System)



# X-ray analysis with single crystals: Reciprocal lattice (calculated from an IPDS measurement)



# Realisation of a crystal structure determination

2. Determination of the space group (from symmetry and systematic extinctions of the reflections)
3. Measuring of the **intensities**  $I(hkl)$  of the reflections (asymmetric part of the reciprocal lattice up to  $0.5 \leq \sin\theta/\lambda \leq 1.1$  is sufficient)
4. Calculation of the **structure amplitudes**  $|F_{o_{hkl}}|$  from the  $I_{hkl}$  incl. absorption, extinction, LP correction → **data reduction**
5. Determination of the **scale factor**  $K$  and of the mean **temperature parameter**  $B$  for the compound under investigation from the mean  $|F_{o_{hkl}}|$  values for different small  $\theta$  ranges  $\theta_m$  according to  $\ln(|F_o|^2/\Sigma f_j^2) = \ln(1/K) - 2B(\sin^2\theta_m)/\lambda^2$  → **data skaling**

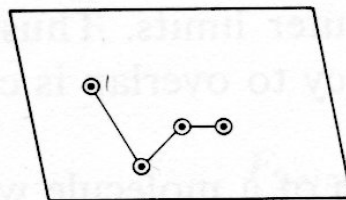
# Realisation of a crystal structure determination

6a. Determin. of the **phases**  $\alpha_{hkl}$  of the **structure amplitudes**  $|F_{0_{hkl}}|$   
→ **phase determination** (**phase problem of structure analysis**)

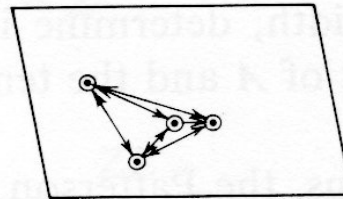
- trial and error (model, than proff of the scattering pattern)
- calculation of the **Patterson function**

$$P_{(uvw)} = (1/V) \cdot \sum |F_{hkl}|^2 \cos 2\pi(hu + kv + lw)$$

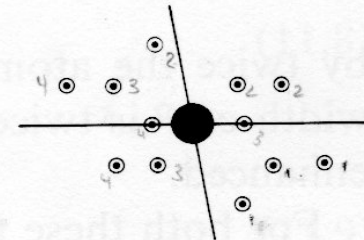
from the **structure amplitudes** resulting in **distance vectors**  
between all atoms of the unit cell



crystal



distance vectors



Patterson function

Points to the distribution and position of „heavy atoms“  
in the unit cell → **heavy atom method**

# Realisation of a crystal structure determination

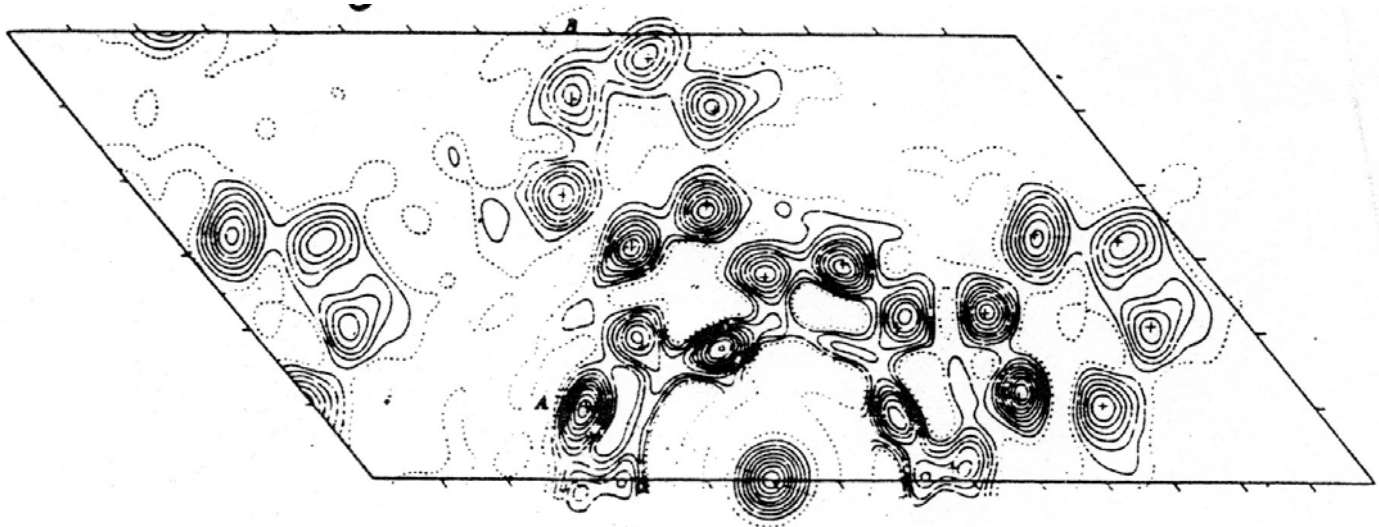
- 6b. Determin. of the **phases**  $\alpha_{hkl}$  of the **structure amplitudes**  $|F_{o_{hkl}}|$
- **direct methodes** for phase determination  
phases  $\alpha_{hkl}$  and intensity distribution are not independent from each other  $\rightarrow$  allows determination of the phases  $\alpha_{hkl}$   
e.g.  $F(hkl) \sim \sum \sum \sum F(h'k'l') \cdot F(h-h', k-k', l-l')$  (Sayre, 1952)  
oder  $S(F_{hkl}) \sim S(F_{h'k'l'}) \cdot S(F_{h-h', k-k', l-l'})$  ( $S = \text{sign of } F$ )  
direct methodes today are the most important methodes for the solving the phase problem of structure analysis/determination
  - anomalous dispersion methodes use the phase and intensity differences in the scattering near and far from absorption edges (measuring with X-rays of different wave lengths necessary)



# Realisation of a crystal structure determination

## 7. Calculation of the **electron density distribution function**

$\delta(xyz) = (1/V) \cdot \sum |F_{0_{hkl}}| \cdot \exp(i\alpha_{hkl}) \cdot \exp(-2\pi i(hx+ky+lz))$  of the unit cell from the **structure amplitudes**  $|F_{0_{hkl}}|$  and the **phases**  $\alpha_{hkl}$  of the reflections  $hkl$  (using B and K)  $\rightarrow$  **Fourier synthesis**



Platin-Phthalocyanin, PtC<sub>32</sub>H<sub>16</sub>N<sub>8</sub>: Elektronendichteprojektion  $\rho(xz)$ .

and determination of the elements and the atom sites  $x_j, y_j, z_j$

# Realisation of a crystal structure determination

8. Calculation of the **structure factors**  $F_{c_{hkl}}$  (c: calculated) by use of these atomic sites/coordinates  $x_j, y_j, z_j$  and the **atomic form factors** (atomic scattering factors)  $f_j$  according to

$$F_{c_{hkl}} = \sum f_j \cdot \exp(2\pi i(hx_j + ky_j + lz_j))$$

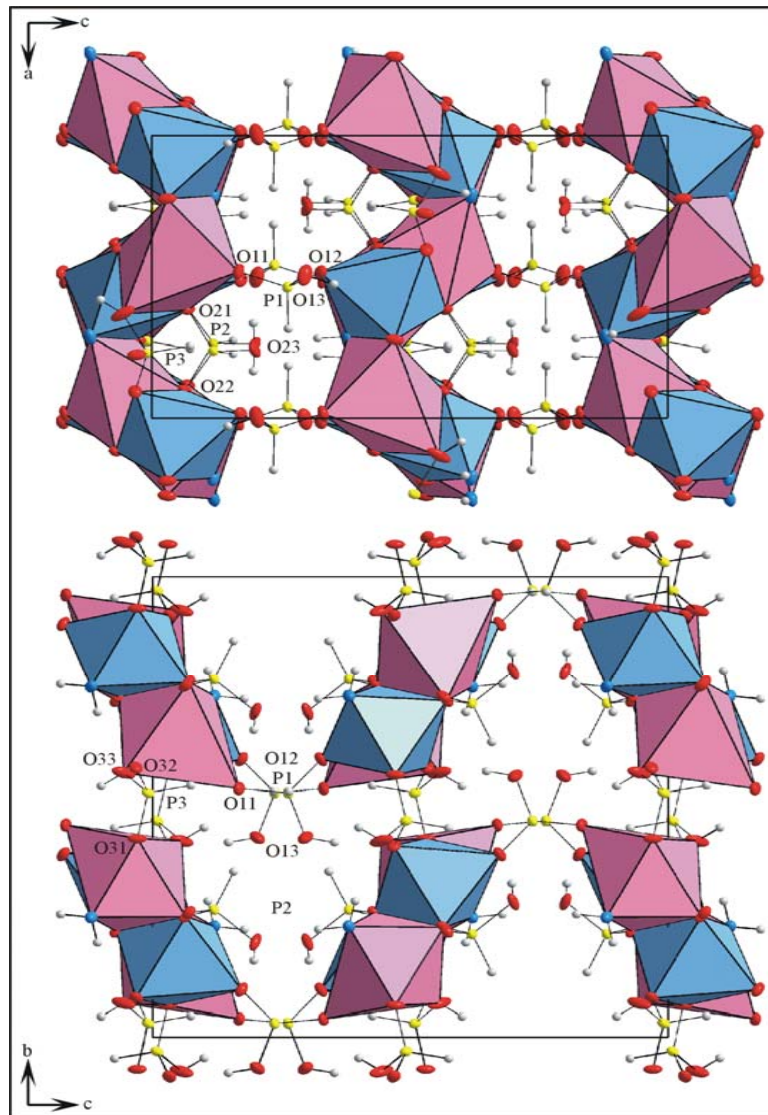
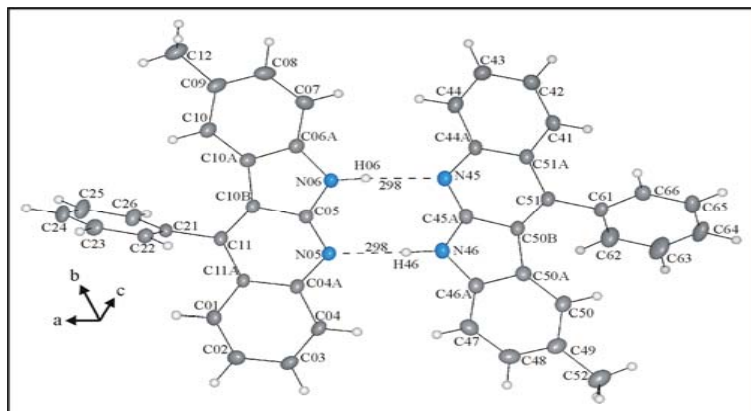
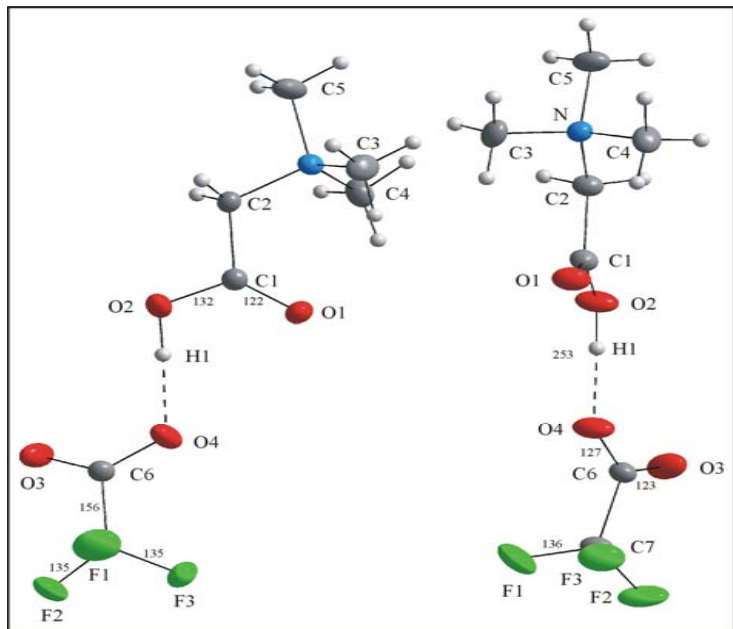
9. **Refinement** of the **scale factor**  $K$ , the **temperature parameter**  $B$  (or of the individual  $B_j$  of the atoms  $j$  of the unit cell) and of the **atomic coordinates**  $x_j, y_j, z_j$  by use of the least squares method, LSQ via minimising the function

$$(\Delta F)^2 = (|F_o| - |F_c|)^2 \text{ for all measured reflections } hkl$$

**agreement factor:**  $R = \sum (|F_o| - |F_c|) / \sum |F_o|$

10. Calculation of the **bond lengths and angles** etc. and graphical visualisation of the structure (structure plot)

# Results





# Results

## Crystallographic and structure refinement data of $\text{Cs}_2\text{Co}(\text{HSeO}_3)_4 \cdot 2\text{H}_2\text{O}$

Name	Figure		Name	Figure
Formula	$\text{Cs}_2\text{Co}(\text{HSeO}_3)_4 \cdot 2\text{H}_2\text{O}$		Diffractometer	IPDS (Stoe)
Temperature	293(2) K		Range for data collection	$3.1^\circ \leq \Theta \leq 30.4^\circ$
Formula weight	872.60 g/mol		<i>hkl</i> ranges	$-10 \leq h \leq 10$
Crystal system	Monoclinic			$-17 \leq k \leq 18$
Space group	$P 2_1/c$			$-10 \leq l \leq 9$
Unit cell dimensions	$a = 757.70(20)$ pm		Absorption coefficient	$\mu = 15.067$ mm <sup>-1</sup>
	$b = 1438.80(30)$ pm		No. of measured reflections	9177
	$c = 729.40(10)$ pm		No. of unique reflections	2190
	$\beta = 100.660(30)^\circ$		No. of reflections ( $I_0 \geq 2\sigma(I)$ )	1925
Volume	$781.45(45) \times 10^6$ pm <sup>3</sup>		Extinction coefficient	$\varepsilon = 0.0064$
Formula units per unit cell	$Z = 2$		$\Delta\rho_{\min} / \Delta\rho_{\max} / \text{e/pm}^3 \times 10^{-6}$	-2.128 / 1.424
Density (calculated)	3.71 g/cm <sup>3</sup>		$R_1 / wR_2 (I_0 \geq 2\sigma(I))$	0.034 / 0.081
Structure solution	SHELXS – 97		$R_1 / wR_2$ (all data)	0.039 / 0.083
Structure refinement	SHELXL – 97		Goodness-of-fit on $F^2$	1.045
Refinement method	Full matrix LSQ on $F^2$			

# Results

Positional and isotropic atomic displacement parameters of  $\text{Cs}_2\text{Co}(\text{HSeO}_3)_4 \cdot 2\text{H}_2\text{O}$

Atom	WP	x	y	z	$U_{\text{eq}}/\text{pm}^2$
Cs	4e	0.50028(3)	0.84864(2)	0.09093(4)	0.02950(11)
Co	2a	0.0000	1.0000	0.0000	0.01615(16)
Se1	4e	0.74422(5)	0.57877(3)	0.12509(5)	0.01947(12)
O11	4e	0.7585(4)	0.5043(3)	0.3029(4)	0.0278(7)
O12	4e	0.6986(4)	0.5119(3)	-0.0656(4)	0.0291(7)
O13	4e	0.5291(4)	0.6280(3)	0.1211(5)	0.0346(8)
H11	4e	0.460(9)	0.583(5)	0.085(9)	0.041
Se2	4e	0.04243(5)	0.67039(3)	-0.18486(5)	0.01892(12)
O21	4e	-0.0624(4)	0.6300(2)	-0.3942(4)	0.0229(6)
O22	4e	0.1834(4)	0.7494(3)	-0.2357(5)	0.0317(7)
O23	4e	-0.1440(4)	0.7389(2)	-0.1484(4)	0.0247(6)
H21	4e	-0.120(8)	0.772(5)	-0.062(9)	0.038
OW	4e	-0.1395(5)	1.0685(3)	0.1848(5)	0.0270(7)
HW1	4e	-0.147(8)	1.131(5)	0.032	0.032
HW2	4e	-0.159(9)	1.045(5)	0.247(9)	0.032

# Results

Anisotropic thermal displacement parameters  $U_{ij} \times 10^4 / \text{pm}^2$  of  $\text{Cs}_2\text{Co}(\text{HSeO}_3)_4 \cdot 2\text{H}_2\text{O}$

Atom	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
Cs	0.0205(2)	0.0371(2)	0.0304(2)	0.00328(9)	0.0033(1)	-0.00052(1)
Co	0.0149(3)	0.0211(4)	0.0130(3)	0.0006(2)	0.0041(2)	0.0006(2)
Se1	0.0159(2)	0.0251(3)	0.01751(2)	-0.00089(1)	0.00345(1)	0.00097(1)
O11	0.0207(1)	0.043(2)	0.0181(1)	-0.0068(1)	-0.0013(1)	0.0085(1)
O12	0.0264(2)	0.043(2)	0.0198(1)	-0.0009(1)	0.0089(1)	-0.0094(1)
O13	0.0219(1)	0.034(2)	0.048(2)	0.0053(1)	0.0080(1)	-0.009(2)
Se2	0.0179(2)	0.0232(2)	0.0160(2)	0.00109(1)	0.00393(1)	-0.0001(1)
O21	0.0283(1)	0.024(2)	0.0161(1)	0.0008(1)	0.0036(1)	-0.0042(1)
O22	0.0225(1)	0.032(2)	0.044(2)	-0.0058(1)	0.0147(1)	-0.0055(1)
O23	0.0206(1)	0.030(2)	0.0240(1)	0.0018(1)	0.0055(1)	-0.0076(1)
OW	0.0336(2)	0.028(2)	0.0260(2)	0.0009(1)	0.0210(1)	-0.0006(1)

The anisotropic displacement factor is defined as:  $\exp \{-2p^2[U_{11}(ha^*)^2 + \dots + 2U_{12}hka^*b^*]\}$

# Results

Some selected bond lengths (/pm) and angles(/°) of  $\text{Cs}_2\text{Co}(\text{HSeO}_3)_4 \cdot 2\text{H}_2\text{O}$

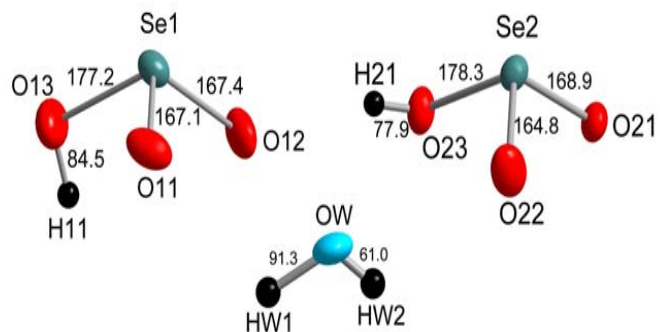
<b>CsO<sub>9</sub> polyhedron</b>			
Cs-O11	316.6(3)	O22-Cs-OW	78.76(8)
Cs-O13	318.7(4)	O22-Cs-O12	103.40(9)
Cs-O22	323.7(3)	O23-Cs-O11	94.80(7)
Cs-O23	325.1(3)	O13-Cs-O11	42.81(8)
Cs-OW	330.2(4)	O11-Cs-O23	127.96(8)
Cs-O21	331.0(3)	O13-Cs-O22	65.50(9)
Cs-O12	334.2(4)	O22-Cs-O22	66.96(5)
Cs-O22	337.1(4)	O11-Cs-OW	54.05(8)
Cs-O13	349.0(4)	O23-Cs-O22	130.85(9)
<b>CoO<sub>6</sub> octahedron</b>			
Co-OW	210.5(3)	OW-Co-OW	180
Co-O11	210.8(3)	OW-Co-O21	90.45(13)
Co-O21	211.0(3)	OW-Co-O11	89.55(13)

<b>SeO<sub>3</sub><sup>2-</sup> anions</b>					
Se1-O11	167.1(3)	O12- Se1-O11	104.49(18)		
Se1-O12	167.4(3)	O12- Se1-O13	101.34(18)		
Se1-O13	177.2(3)	O11- Se1-O13	99.66(17)		
Se2-O21	168.9(3)	O22- Se2-O21	104.46(17)		
Se2-O22	164.8(3)	O22- Se2-O23	102.51(17)		
Se2-O23	178.3(3)	O21- Se2-O23	94.14(15)		
<b>Hydrogen bonds</b>		<b>d(O-H)</b>	<b>d(O...H)</b>	<b>d(O...O)</b>	<b>&lt;OHO</b>
O13-H11...O12	85(7)	180(7)	263.3(5)	166(6)	
O23-H21...O21	78(6)	187(7)	263.7 (4)	168(7)	
OW-HW1...O22	91(7)	177(7)	267.7 (5)	174(6)	
OW-HW2...O12	61(6)	206(6)	264.3 (4)	161(8)	

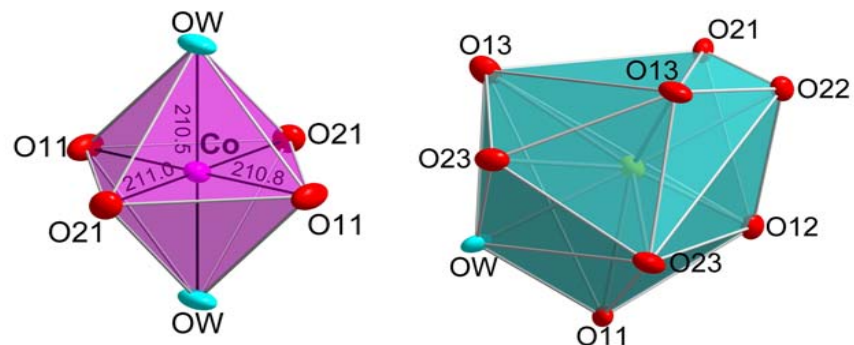
## Symmetry codes:

- |                       |                        |                        |
|-----------------------|------------------------|------------------------|
| 1. -x, -y+2, -z       | 2. -x+1, -y+2, -z      | 3. -x+1, y-1/2, -z+1/2 |
| 4. x-1, -y+3/2, z-1/2 | 5. x, -y+3/2, z-1/2    | 6. x, -y+3/2, z+1/2    |
| 7. -x, y-1/2, -z-1/2  | 8. -x+1, y+1/2, -z+1/2 | 9. x+1, -y+3/2, z+1/2  |
| 10. -x, y+1/2, -z-1/2 | 11. -x+1, -y+1, -z     | 12. x-1, -y+3/2, z+1/2 |

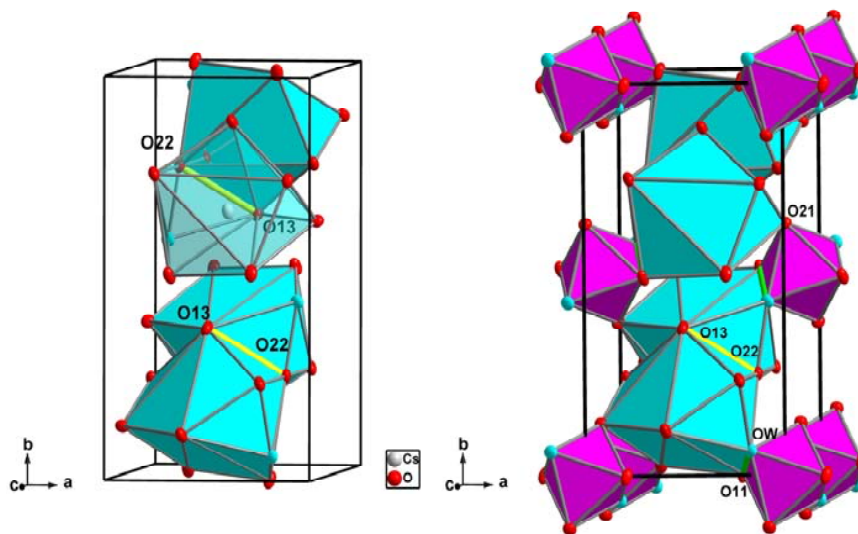
# Results



Molecular units of  $\text{Cs}_2\text{Co}(\text{HSeO}_3)_4 \cdot 2\text{H}_2\text{O}$

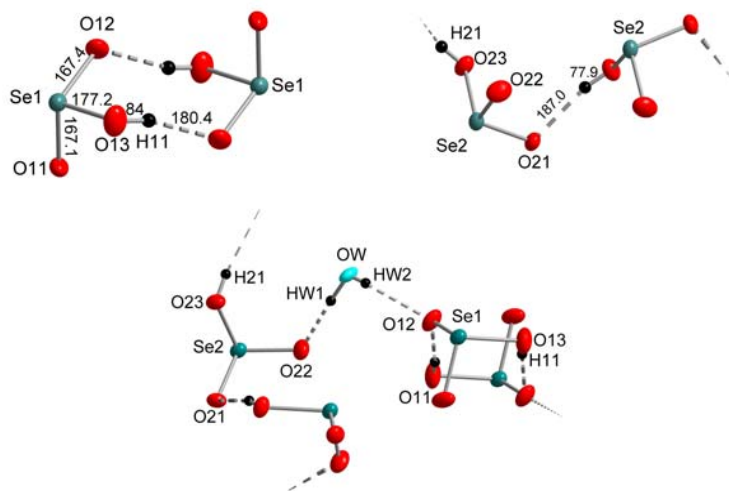


Coordination polyhedra of  $\text{Cs}_2\text{Co}(\text{HSeO}_3)_4 \cdot 2\text{H}_2\text{O}$

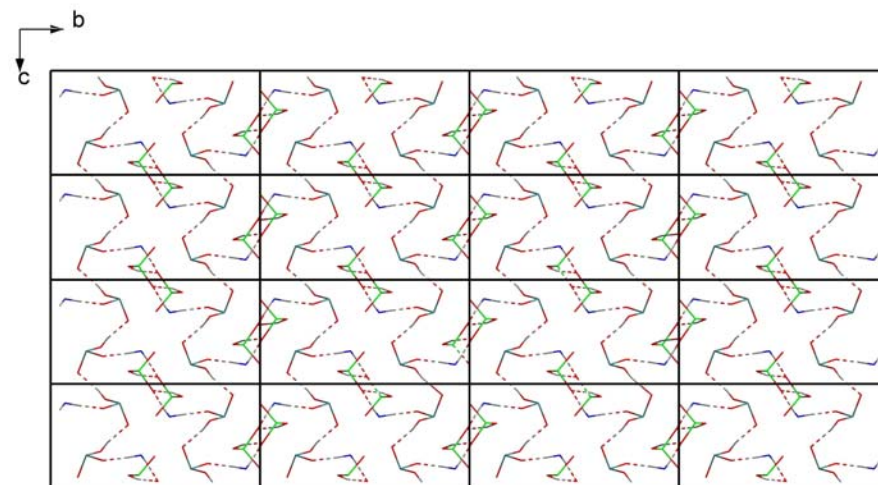


Connectivity of the coordination polyhedra of  $\text{Cs}_2\text{Co}(\text{HSeO}_3)_4 \cdot 2\text{H}_2\text{O}$

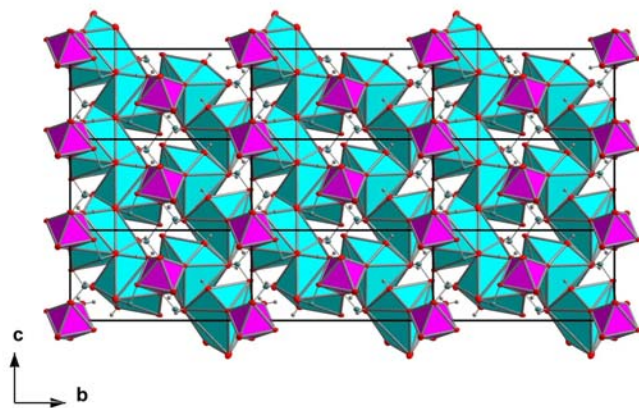
# Results



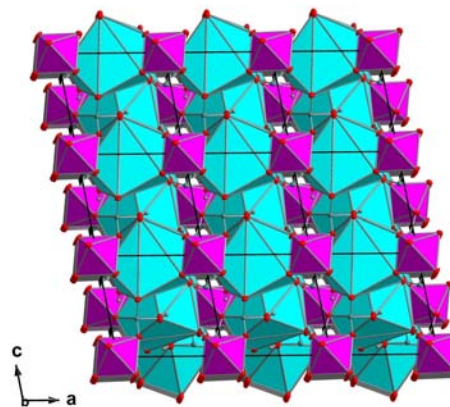
Hydrogen bonds of  $\text{Cs}_2\text{Co}(\text{HSeO}_3)_4 \cdot 2\text{H}_2\text{O}$



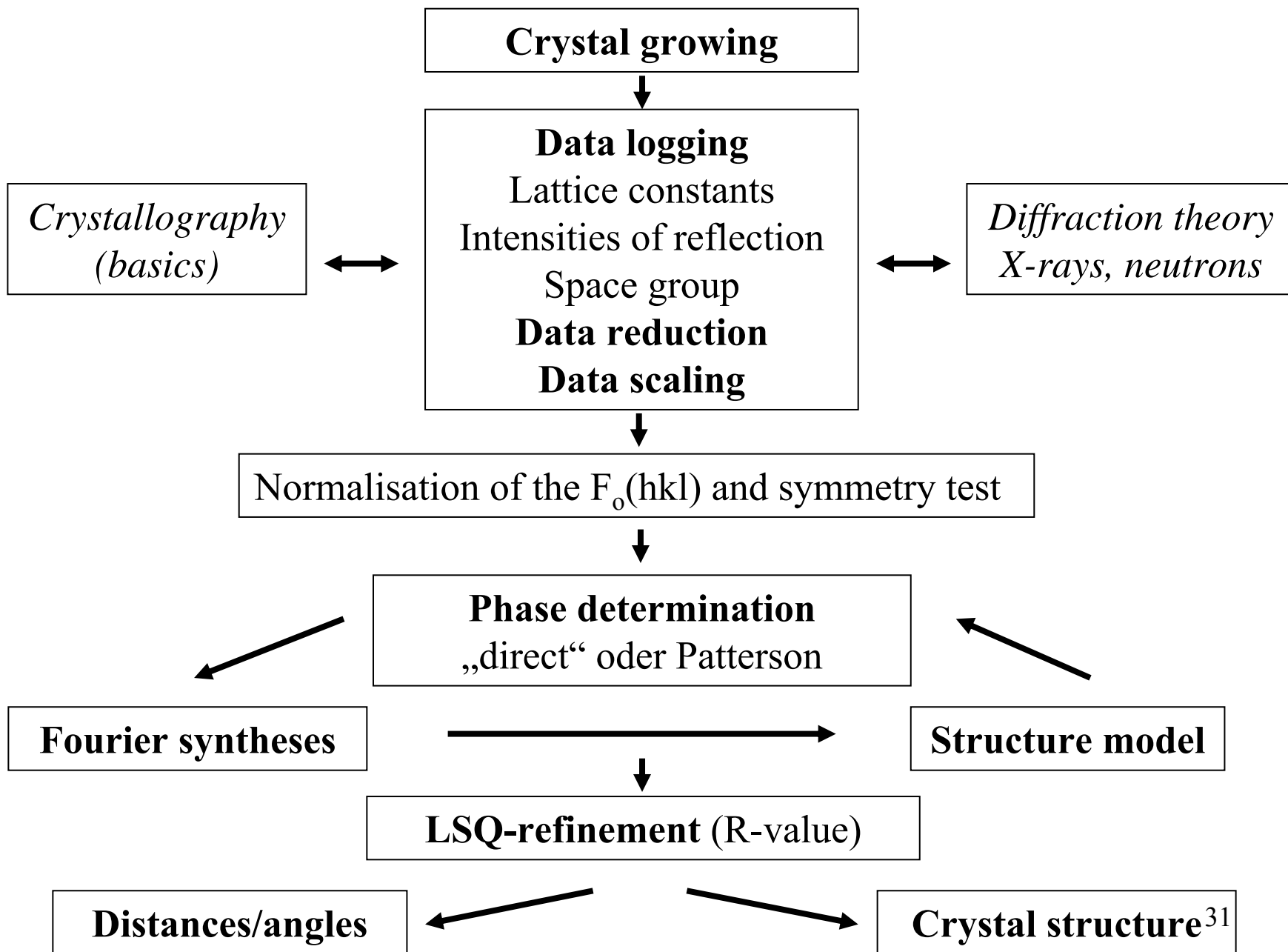
Anions and hydrogen bonds of  $\text{Cs}_2\text{Co}(\text{HSeO}_3)_4 \cdot 2\text{H}_2\text{O}$



Crystal structure of  $\text{Cs}_2\text{Co}(\text{HSeO}_3)_4 \cdot 2\text{H}_2\text{O}$



# Course of a crystal structure analysis



# Literature

- *Röntgenfeinstrukturanalyse* von **H. Krischner**, Vieweg  
(Allgemeine Einführung, Schwerpunkt Pulvermethoden)  
oder alternativ
- *Röntgen-Pulverdiffraktometrie* von **Rudolf Allmann**, Clausthaler  
Tektonische Hefte 29, Sven von Loga, 1994
- *Kristallstrukturbestimmung* von **W. Massa**, Teubner, Stuttgart, 1984
- *Untersuchungsmethoden in der Chemie* von **H. Naumer und W. Heller**,  
Wiley-VCH  
(Einführung in die moderne Analytik und Strukturbestimmungsmethoden)
- *X-Ray Structure Determination* von **G. H. Stout, L.H. Jensen**, MacMillan,  
London  
(Einführung in die Kristallstrukturanalyse für Fortgeschrittene)