X-ray structure determination

For determination of the crystal or molecular structure you need:

- a crystalline sample (powder or single crystal)
- an adequate electromagnetic radiation ($\lambda \sim 10^{-10}$ m)
- some knowledge of properties/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

Electromagnetic Radiation

tranversal waves, velocity $c_0 \approx 3 \cdot 10^8$ m s^{-1}

Characteristics

1. Energy (eV, kJ mol^{-1})

-frequency	ν	($\nu = c_0 / \lambda$; s^{-1}, Hz)
-wavelength	λ	($\lambda = c_0 / \nu$; Å, nm, ..., m, ...)
-wavenumber	$\tilde{\nu}$	($\tilde{\nu} = 1/\lambda = \nu / c_0$; cm^{-1}, Kaiser)

energy ~ frequency	($E = h \cdot \nu$)
~ wavenumber	($E = h \cdot \tilde{\nu} \cdot c_o$)
~ wavelength^{-1}	($E = h \cdot c_0 / \lambda$)

2. Intensity	cross-section	$I \sim \lvert\vec{S}\rvert^2 = \lvert\vec{E} \times \vec{H}\rvert$
3. Direction	wavevector	$\vec{s}_0$
4. Phase	phase	φ

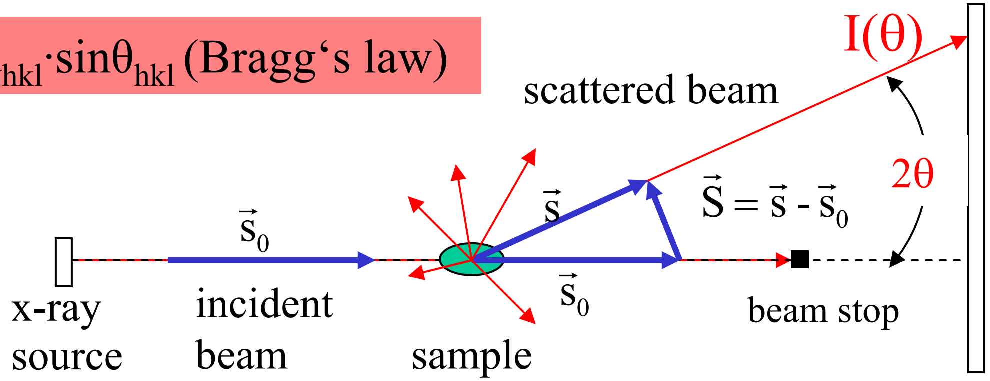
Range of frequencies for structural analysis: 10^6-10^{20} Hz i.e. 10^{-12} – 10^2 m

γ-ray, x-ray, ultraviolet (UV), visible (VIS), infrared (IR), micro-, radiowaves

(X-ray) Diffraction of a Sample

(gas, liquid, glass, (single-) crystal (-powder))

$\lambda = 2d_{hkl} \cdot \sin\theta_{hkl}$ (Bragg's law)



detector
(film, imaging plate)

$\vec{s}_0$: WVIB

$\vec{s}$: WVSB; $|\vec{s}| = |s_0| = 1/\lambda$ (or 1)

$\vec{S}$: Scattering Vector

$\vec{S} = \vec{H}$ (Bragg's law)

Fouriertransform of the Electron-Density Distribution

sample

$\rho(\vec{r})$

$$R(S) = \int_V \rho(\vec{r}) \exp(2\pi i \vec{r} \cdot \vec{S}) dV$$

$$\rho(\vec{r}) = 1/V \int_{V^*} R(\vec{S}) \exp(-2\pi i \vec{r} \cdot \vec{S}) dV^*$$

diffr. pattern

$R(\vec{S})$

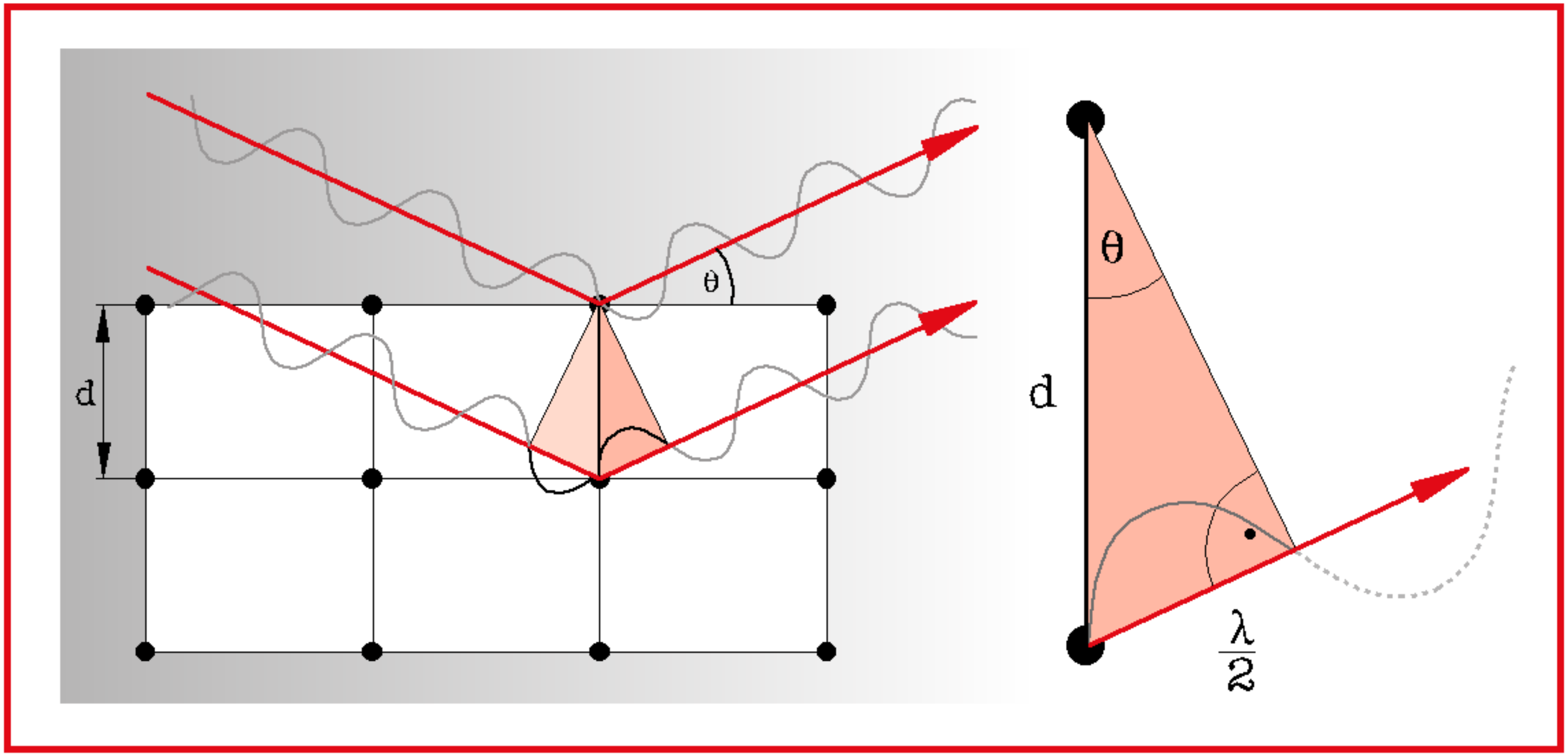
V : volume of sample

$\vec{r}$: vector in space

R : scattering amplitude

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

Superposition (diffraction) of scattered X-rays - Bragg´s law

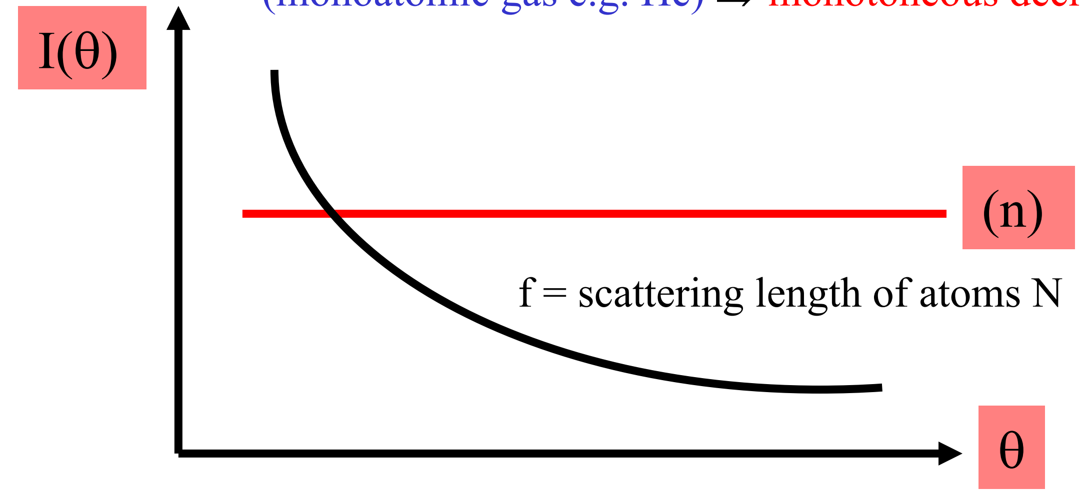


Only if $\mathbf{n\lambda = 2d\cdot\sin\theta}$ **or** $\mathbf{\lambda = 2d_{hkl}\cdot\sin\theta_{hkl}}$ (Bragg‘s law, hkl: Miller indices), scattered X-rays are „in phase“ and intensity can be non-zero.

Depending on the degree of order of the scattering sample this leads to:

A. X-ray scattering diagram of an amorphous sample

no long-range order, no short range order
(monoatomic gas e.g. He) ⇒ monotoneous decrease

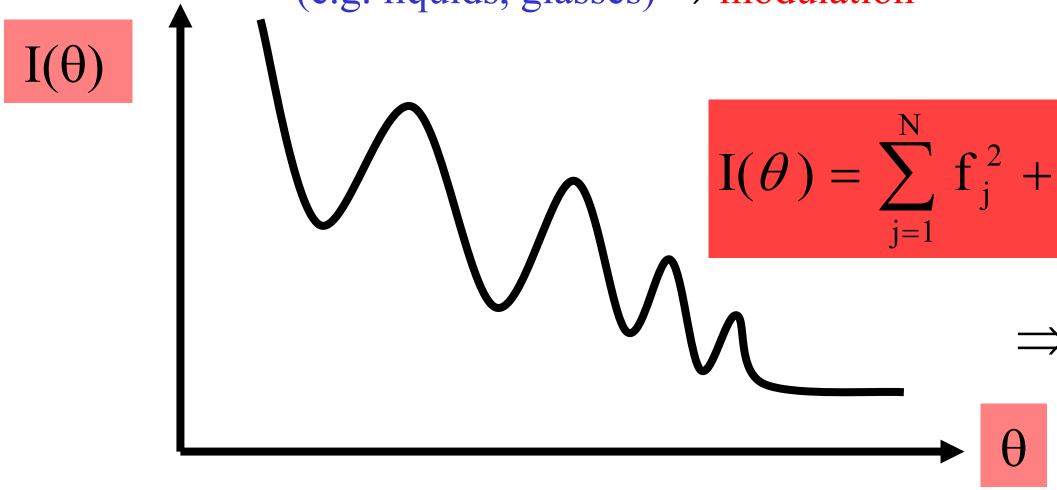


f = scattering length of atoms N

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

⇒ no information

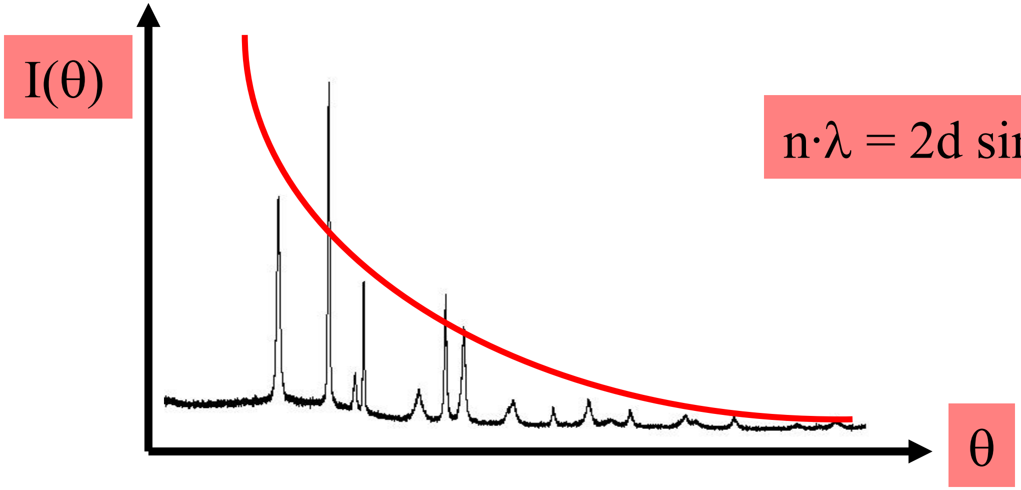
no long-range, but short range order
(e.g. liquids, glasses) ⇒ modulation



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

⇒ radial distribution function
atomic distances

B. X-ray scattering diagram of a crystalline sample



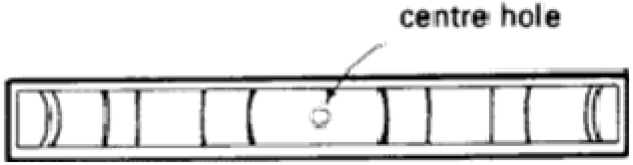
$n \cdot \lambda = 2d \sin\theta$ (Bragg‘s law)

$I(\theta) = f(f_j, \vec{r}_j)$

crystal powder

orientation statistical, λ fixed

⇒ cones of interference

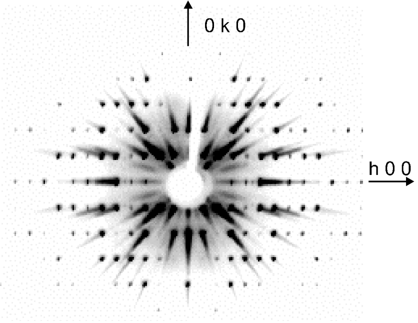


Debye-Scherrer diagram

single crystal

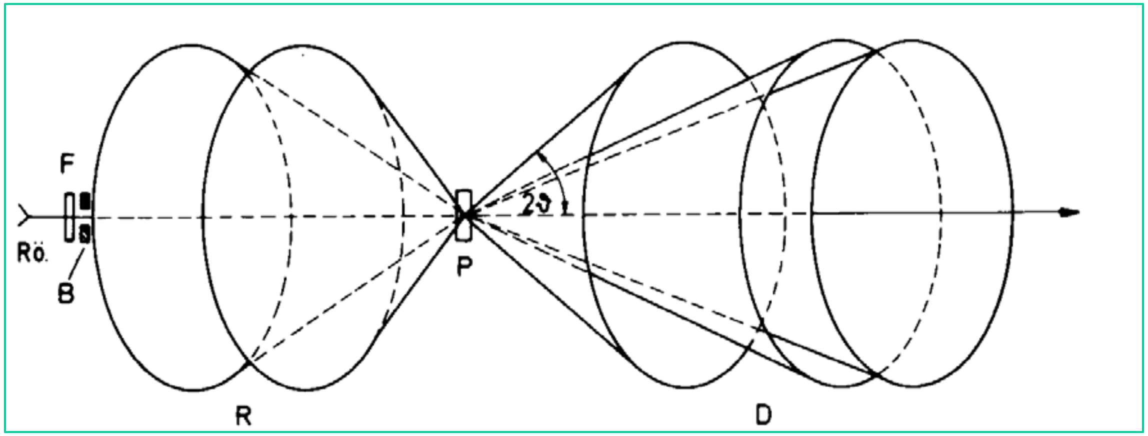
orientation or λ variable

⇒ dots of interference (reflections)



precession diagram

Principle of Powder Diffraction



A powder sample results in cones with high intensity of scattered beams.

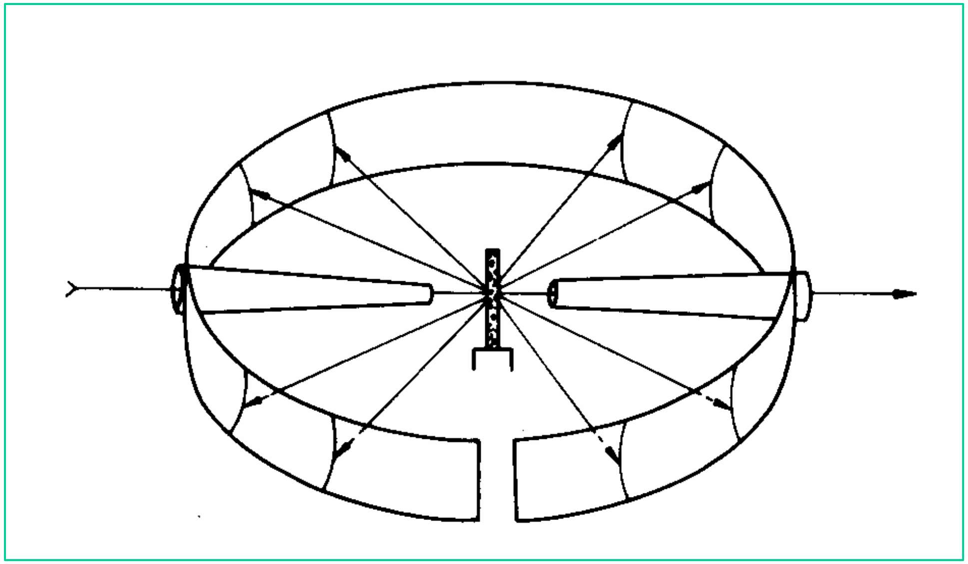
Above conditions result in **Bragg's** law/equation.

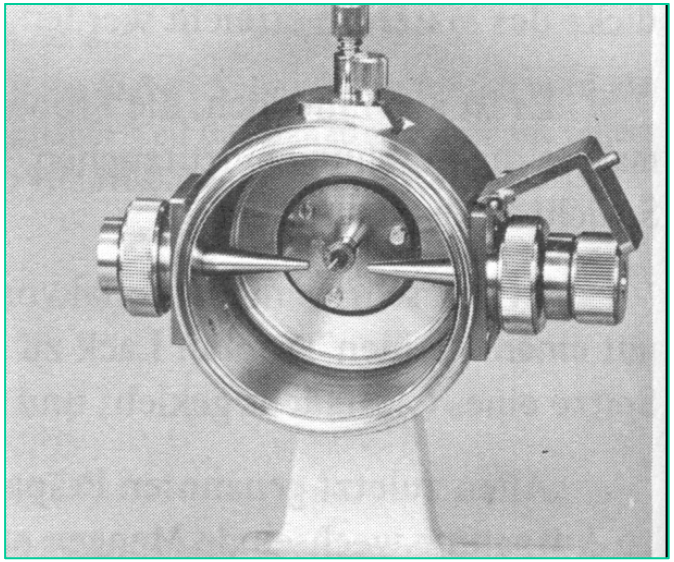
$$\boxed{n \cdot \lambda = 2 \cdot d \cdot \sin\theta}$$

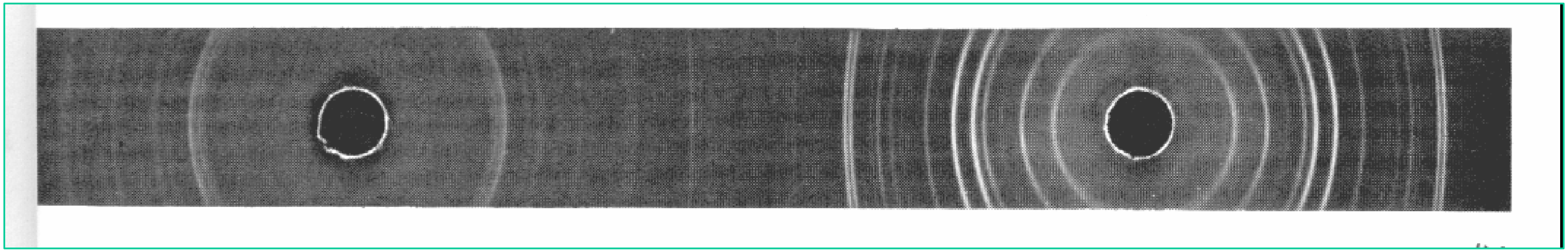
or

$$\boxed{d = \frac{n \cdot \lambda}{2 \cdot \sin\theta}}$$

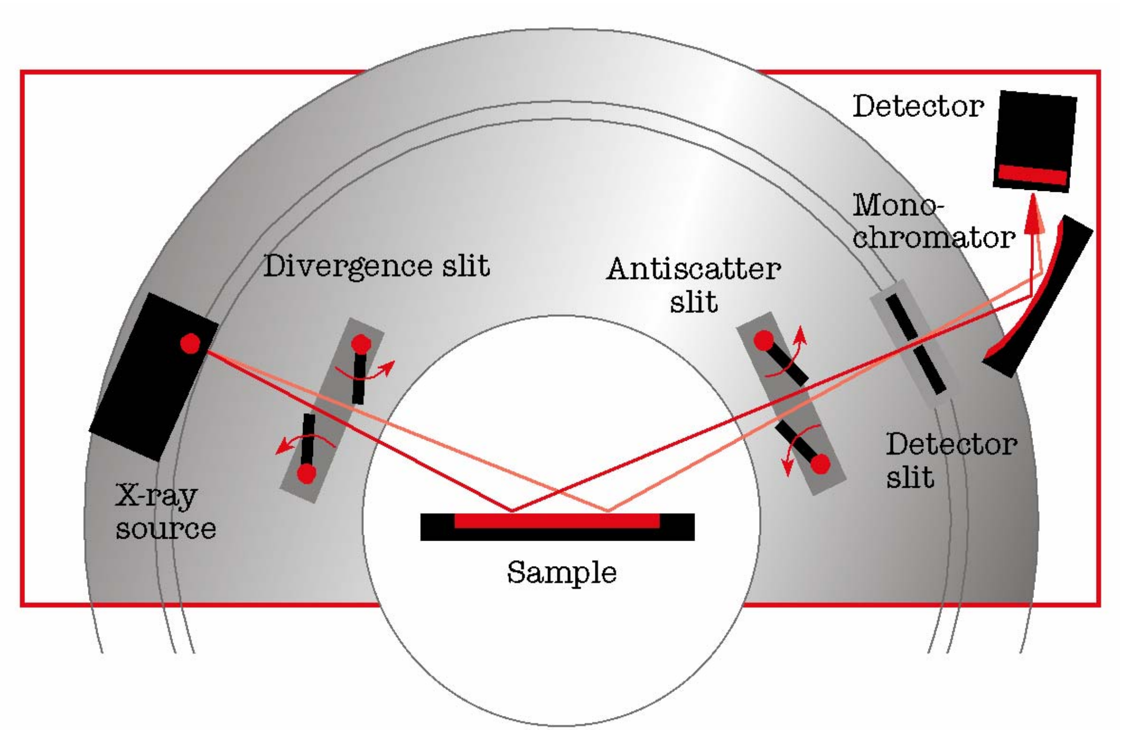
Debye-Scherrer Geometry





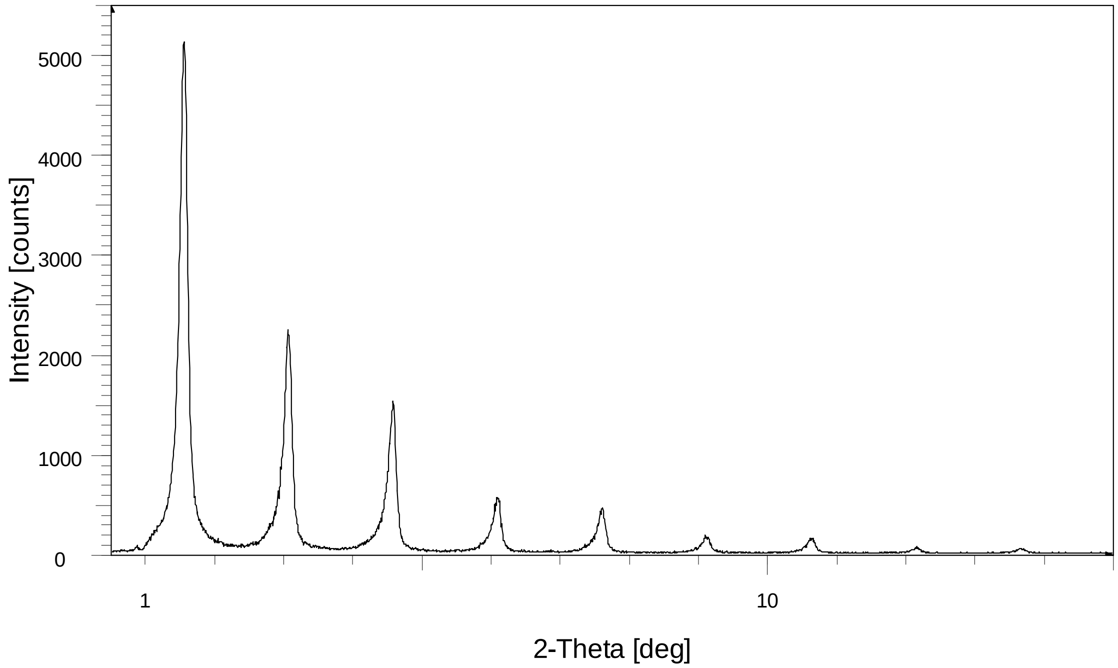


Powder Diffractometer (Bragg-Brentano Geometry)



Powder Diffraction (Bragg-Brentano Geometry)

Silver-Behenate

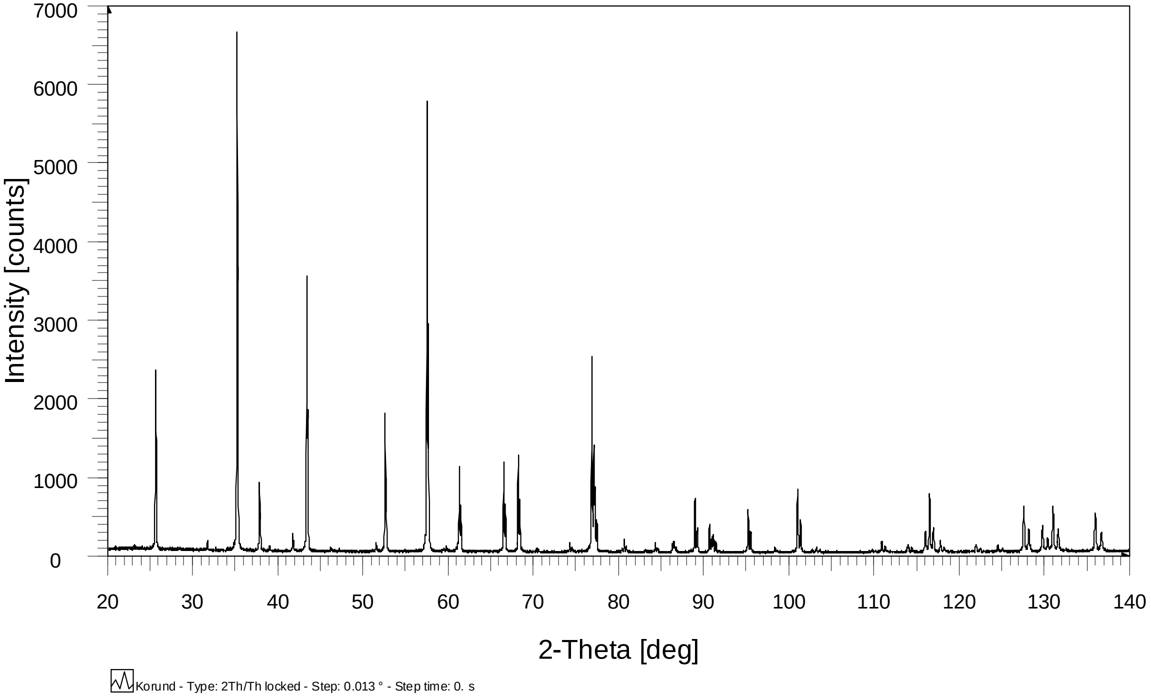


agbehenate 0.1dg divergence 2.3 soller 1-3mm slits ni filt - Type: 2Th/Th locked - Start: 0.500 ° - End: 19.998 ° - Step: 0.007 ° -

- **D8 ADVANCE,**
- **Cu radiation, 40kV / 40mA**
- **Divergence slit: 0,1°**
- **Step range: 0.007°**
- **Counting time / step: 0.1 sec**
- **Velocity: 4.2°/minute**
- **Total measure. time: 3:35 min.**

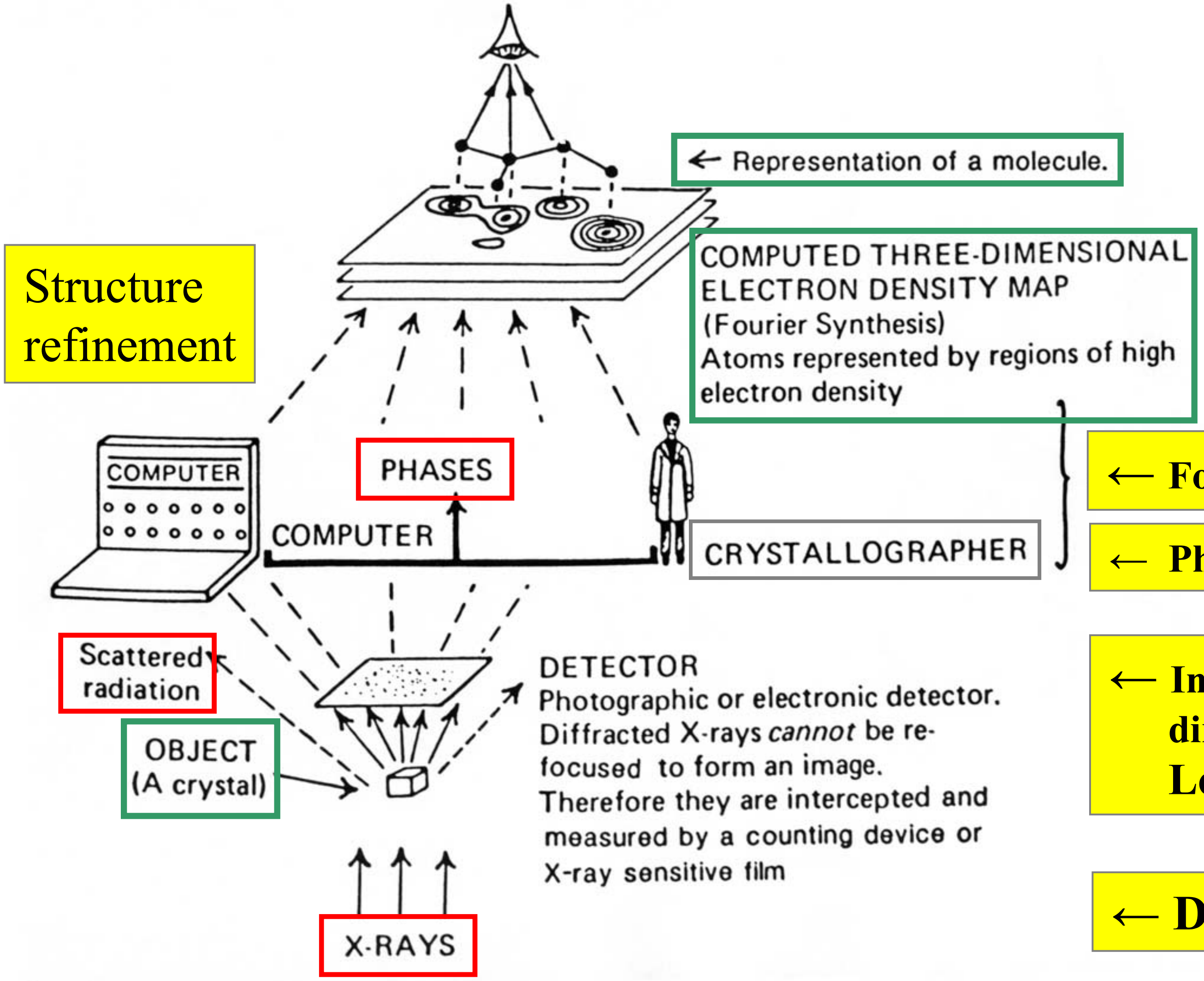
Powder Diffraction (Bragg-Brentano Geometry)

Sample: NIST 1976, corundum plate



- **D8 ADVANCE,**
- **Cu radiation, 40 kV, 40 mA**
- **Step range: 0,013°**
- **Counting time / step: 0,02 sec**
- **Velocity: 39°/ min.**
- **Total measur. time: 3:05 min.**

X-ray structure analysis with a single crystal



Atoms represented by regions of high electron density

Photographic or electronic detector. Diffracted X-rays *cannot* be re-focused to form an image. Therefore they are intercepted and measured by a counting device or X-ray sensitive film

Structure refinement

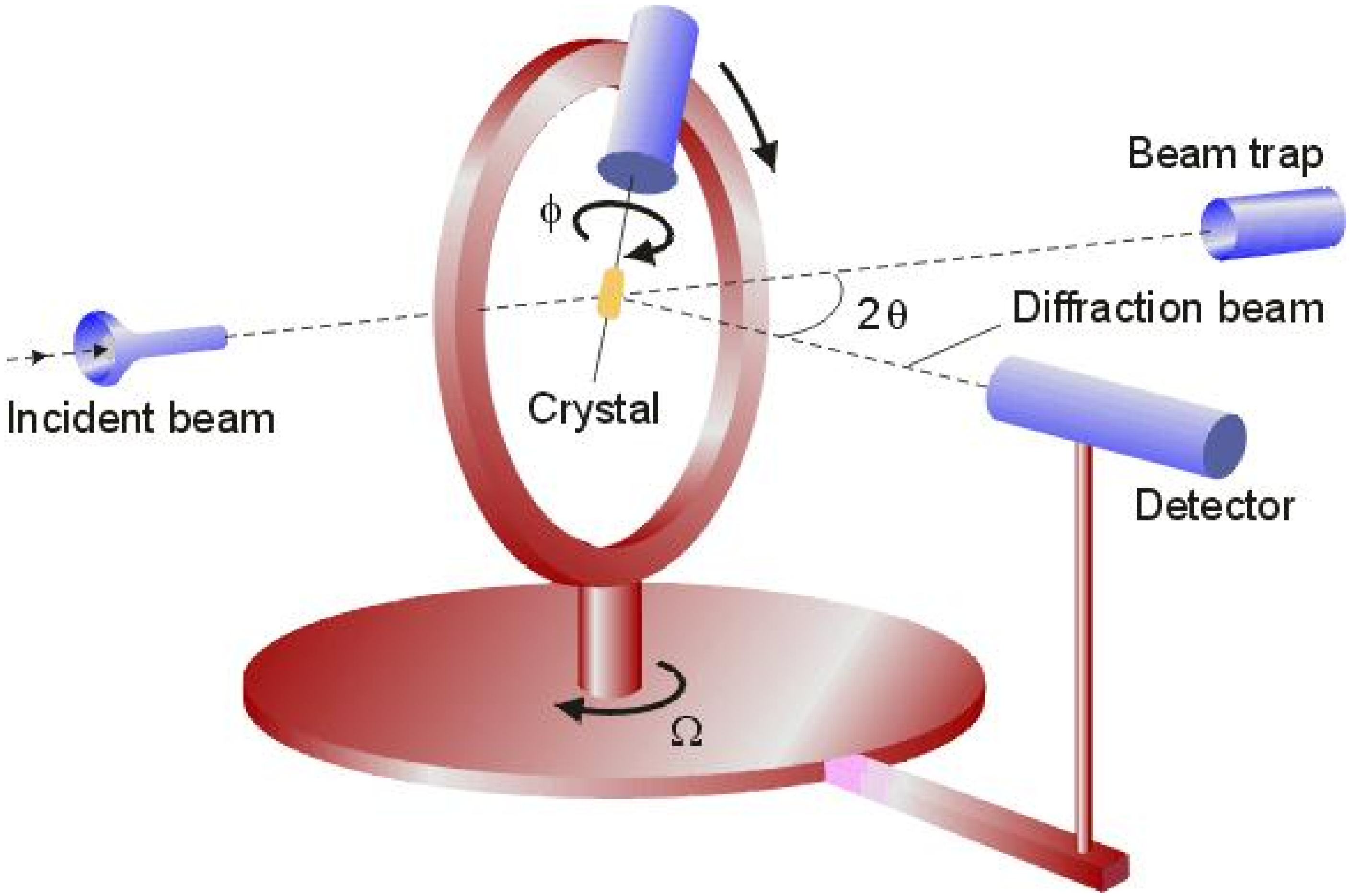
← **Fourier syntheses**

← **Phase redetermin.**

← **Intensities** and **directions** only. **Loss of phases**

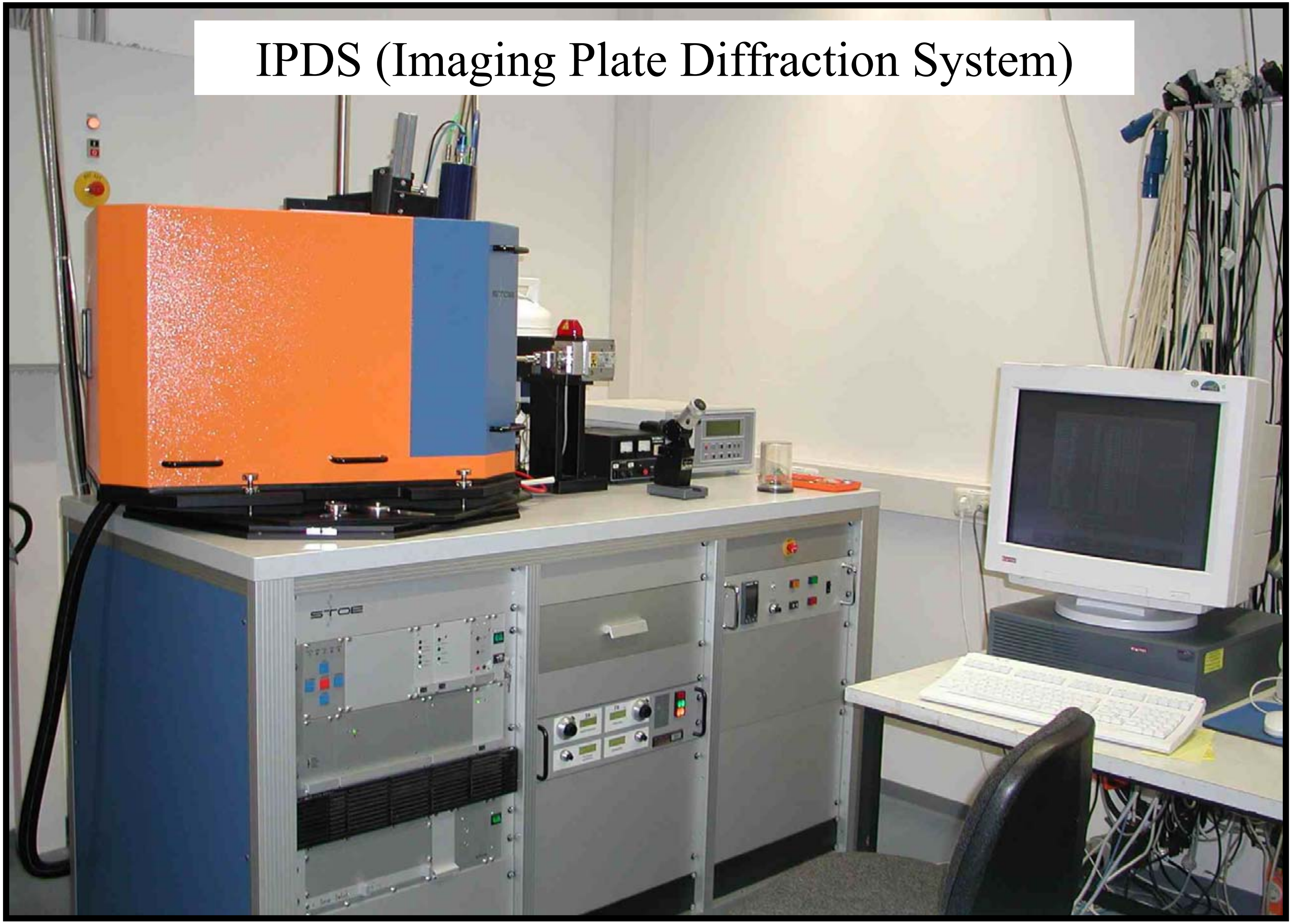
← **Direction ≡ 2θ**

Principle of a four circle X-ray diffractometer for single crystal structure analysis

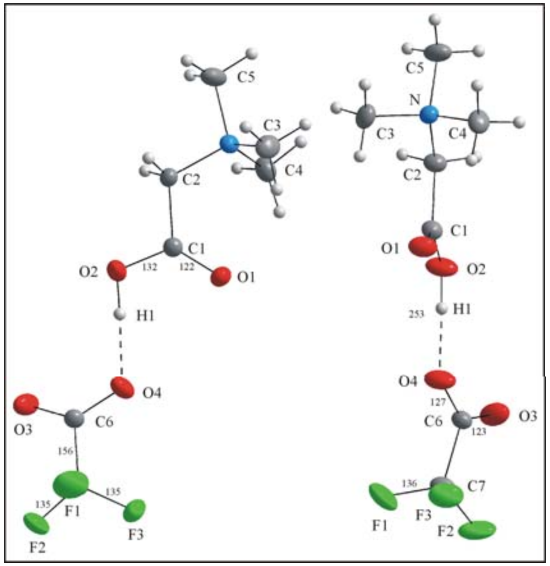


CAD4 (Kappa Axis Diffractometer)

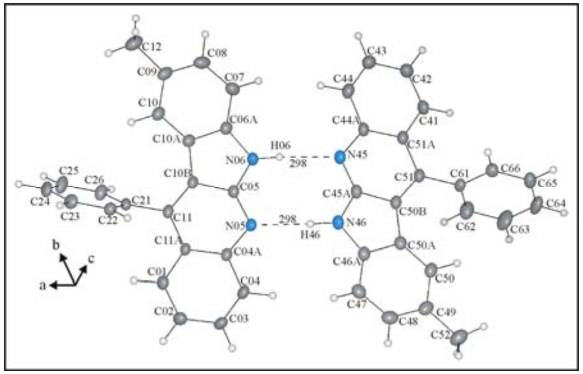
IPDS (Imaging Plate Diffraction System)



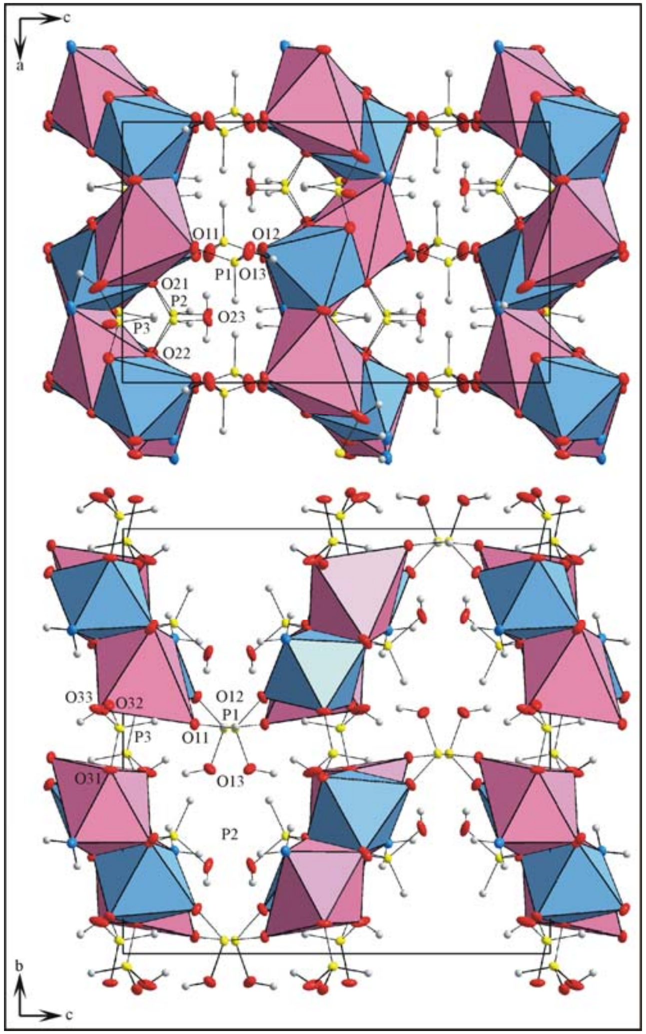
Results (Some crystal structures prepared by using DIAMOND)



Betainiumtrichloracetate



Methylphenylindolo-quinoline



$NaMg(HPO_2OH)_3 \cdot H_2O$

Results

Crystallographic and structure refinement data of $Cs_2Co(HSeO_3)_4 \cdot 2H_2O$

Name	Figure		Name	Figure
Formula	$Cs_2Co(HSeO_3)_4 \cdot 2H_2O$		Diffractometer	IPDS (Stoe)
Temperature	293(2) K		Range for data collection	$3.1° \leq \Theta \leq 30.4°$
Formula weight	872.60 g/mol		*hkl* 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^{-1}
	$b =$ 1438.80(30) pm		No. of measured reflections	9177
	$c =$ 729.40(10) pm		No. of unique reflections	2190
	$\beta =$ 100.660(30) °		No. of reflections ($I_0 \geq 2\sigma(I)$)	1925
Volume	781.45(45) × 10^6 pm^3		Extinction coefficient	$\varepsilon = 0.0064$
Formula units per unit cell	Z = 2		$\Delta\rho_{min} / \Delta\rho_{max}$ / e/pm^3 × 10^{-6}	-2.128 / 1.424
Density (calculated)	3.71 g/cm^3		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 $Cs_2Co(HSeO_3)_4\cdot 2H2O$

Atom	**WS**	**x**	**y**	**z**	**U_{eq}/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 *Uij* × 104 / pm2 of $Cs_2Co(HSeO_3)_4 \cdot 2H_2O$

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 {-2p2[*U*11(*ha**)2 +…+ 2*U*12*hka***b**]}

Results

Some selected bond lengths (/pm) and angles(/°) of $Cs_2Co(HSeO_3)_4 \cdot 2H_2O$

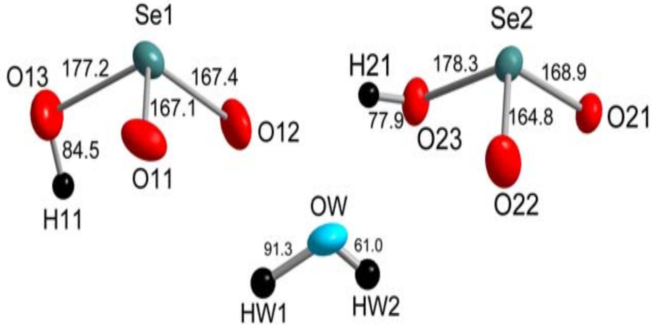
CsO_9 polyhedron				
Cs-O11	316.6(3)		O22-Cs-OW	78.76(8)
Cs-O13	318.7(4)		O22-Cs-O12	103.40(9)
Cs-O22	323.7(3)		O23-Cs-O11	94.80(7)
Cs-O23	325.1(3)		O13-Cs-O11	42.81(8)
Cs-OW	330.2(4)		O11-Cs-O23	127.96(8)
Cs-O21	331.0(3)		O13-Cs-O22	65.50(9)
Cs-O12	334.2(4)		O22-Cs-O22	66.96(5)
Cs-O22	337.1(4)		O11-Cs-OW	54.05(8)
Cs-O13	349.0(4)		O23-Cs-O22	130.85(9)
CoO_6 octahedron				
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)

SeO_3^{2-} anions					
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)	
Hydrogen bonds		**d(O-H)**	**d(O···H)**	**d(O···O)**	**<OHO**
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)

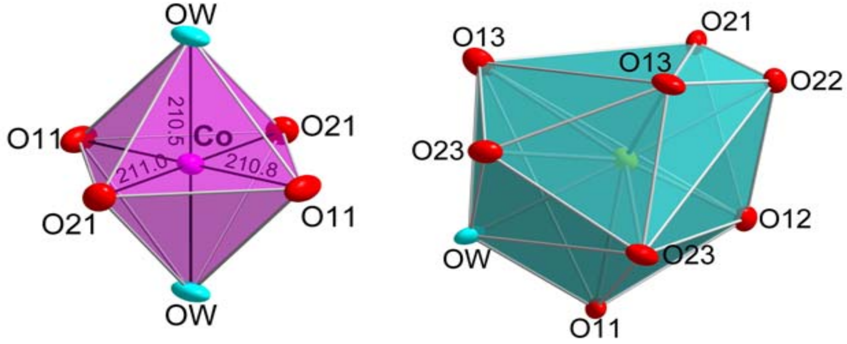
Symmetry codes:

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

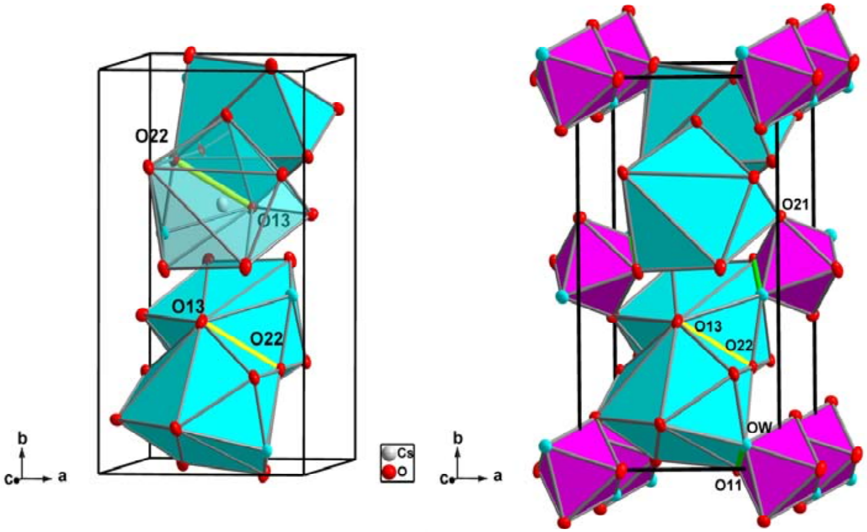
Results



Molecular units of $Cs_2Co(HSeO_3)_4 \cdot 2H_2O$

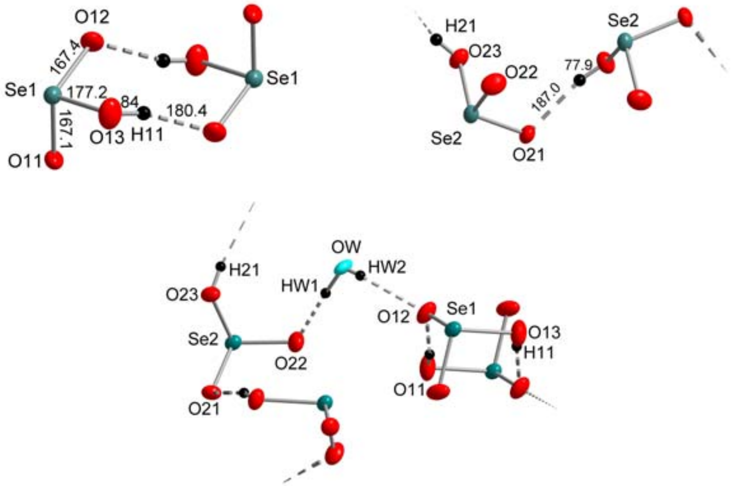


Coordination polyhedra of $Cs_2Co(HSeO_3)_4 \cdot 2H_2O$

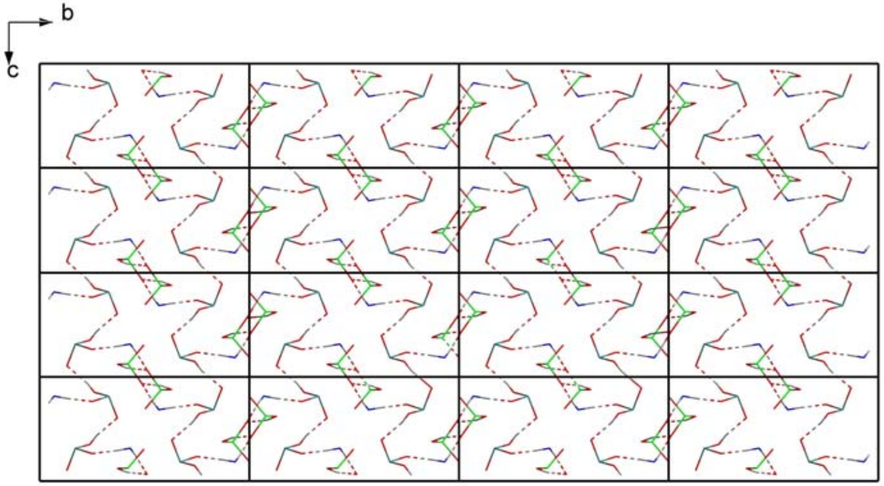


Connectivity of the coordination polyhedra of $Cs_2Co(HSeO_3)_4 \cdot 2H_2O$

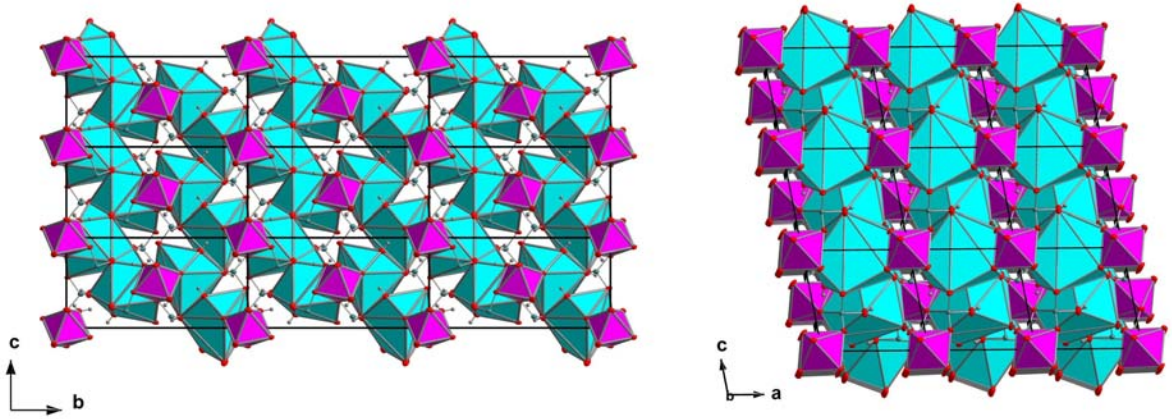
Results



Hydrogen bonds of $Cs_2Co(HSeO_3)_4{\cdot}2H_2O$



Anions and hydrogen bonds of $Cs_2Co(HSeO_3)_4{\cdot}2H_2O$



Crystal structure of $Cs_2Co(HSeO_3)_4{\cdot}2H_2O$