Chapter 4: Physical methods in Solid State Chemistry

4.1 Electromagnetic radiation

4.2 Microscopic techniques: OM, SEM, CTEM, HREM

4.3 X-ray diffraction: XRD, XRPD

4.4 Photoelectron spectroscopy: ESCA

4.5 X-ray absorption spectroscopy: EXAFS, XANES

4.6 Moessbauer spectroscopy

4.7 Impedance spectroscopy (ionic conductivity)

4.8 Magnetic measurements

4.9 Thermal analysis: TA, DTA, DSC, TG

4.10 Comparison of some techniques for structural studies

4. Physical methods in Solid State Chemistry

Physical methods in Solid State Chemistry must/ should/can be sensitiv with respect to the:

- Composition of a compound/molecule
- States/energies of spins, electrons, rotations, vibrations, atoms/molecules etc.
- States/energies of compounds/reactions
- Sites/positions of the atoms/ions/molecules etc.
- Extension etc.

Resulting in microscopic, spectroscopic, thermal, … methods/techniques.

Most of the methods use electromagnetic radiation.

4.1 Electromagnetic Radiation: Characteristics

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

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 $I \sim |\vec{S}|^2 = |\vec{E} \times \vec{H}|$

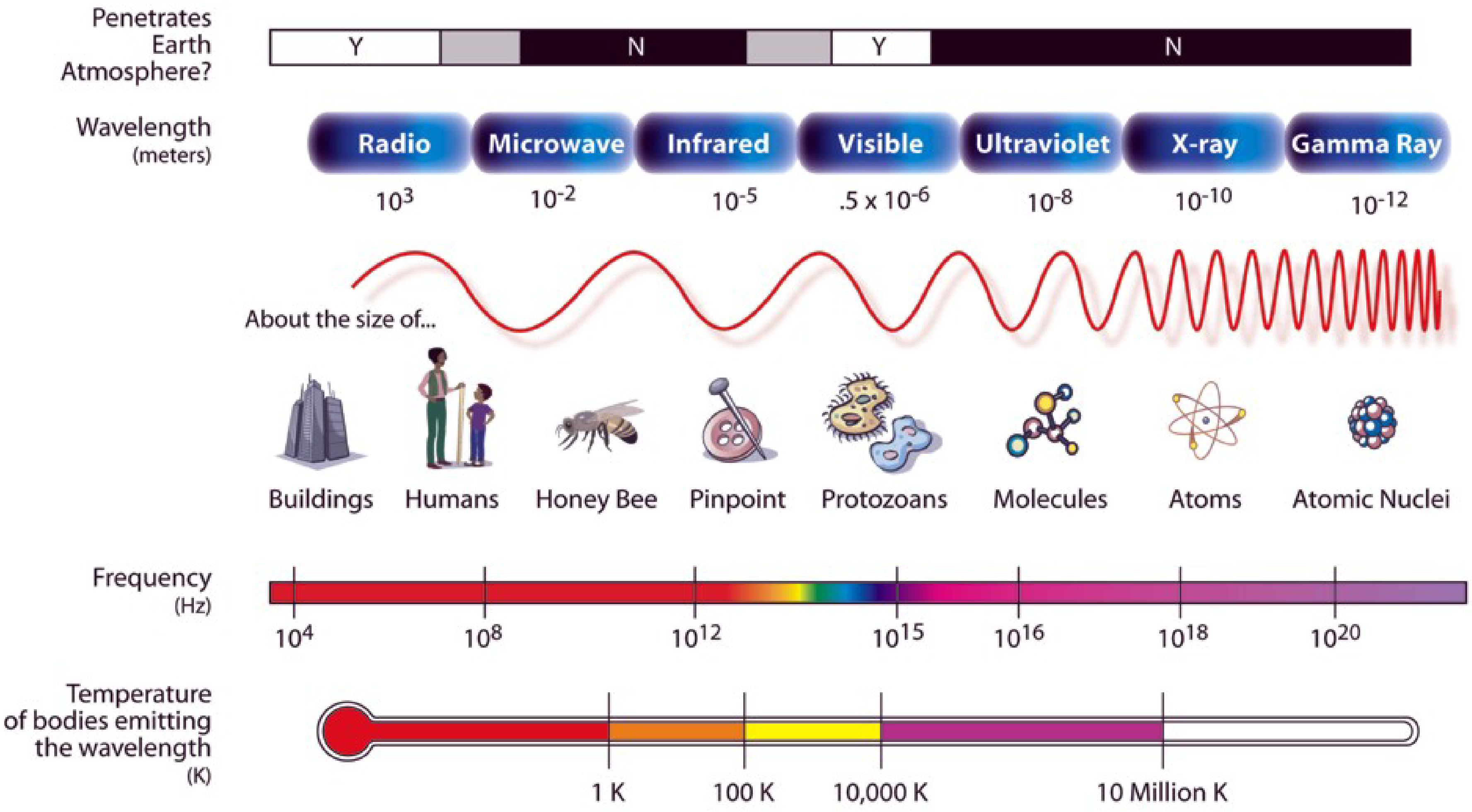
3. Direction wavevector $\vec{s}_0$

4. Phase phase φ

Range of frequencies for structural analysis: 10^6-10^{20} Hz, 10^2 -10^{-12}m, 10^{-8}-10^6 eV

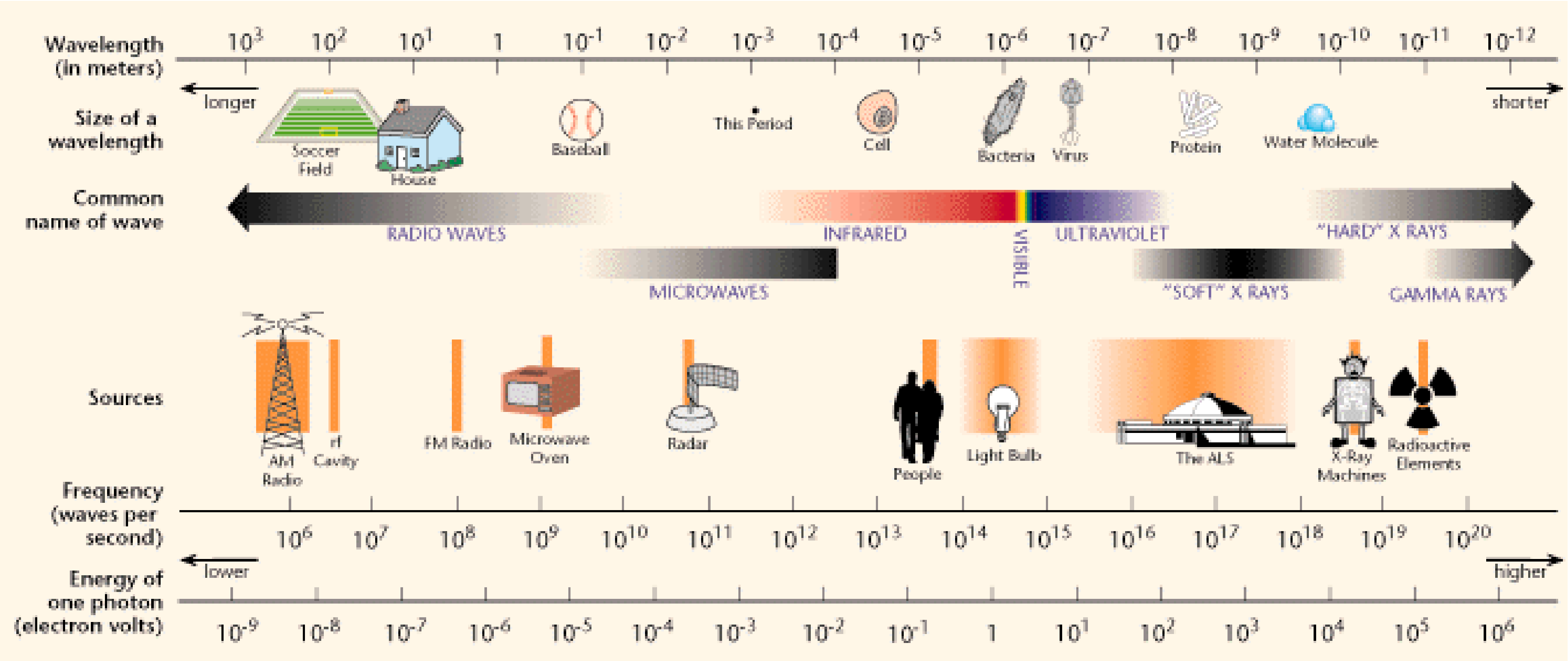
radio-, microwaves, infrared (IR), visible (VIS), ultraviolet (UV), X-ray, γ-ray^3

4.1 Electromagnetic radiation: Sprectral ranges



Orders of magnitude in wavelength, frequency, energy, temperature

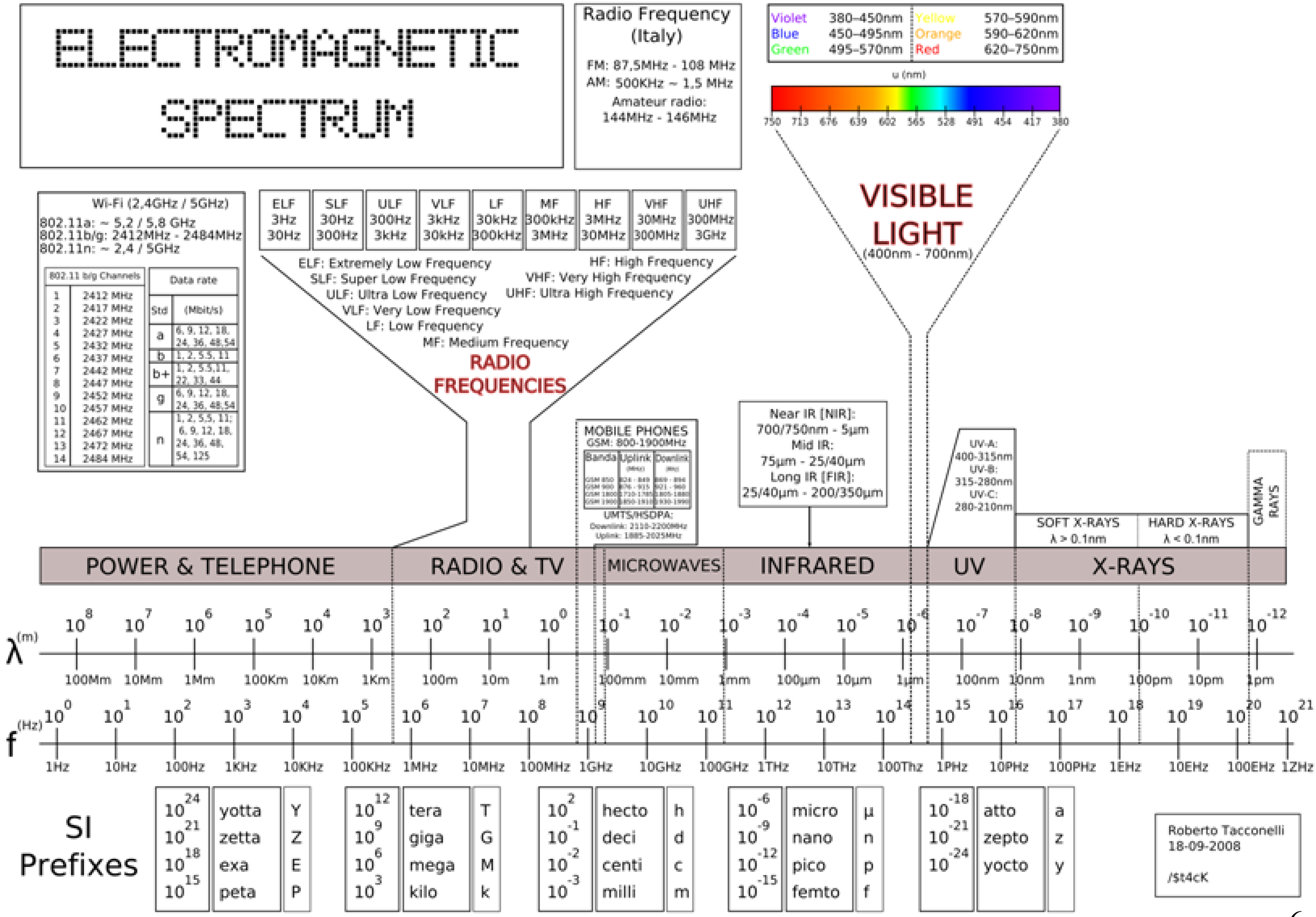
4.1 Electromagnetic radiation: Sprectral ranges



$$1\ \mathrm{eV} = 1{,}602 \cdot 10^{-19}\ \mathrm{J} = 96{,}485\ \mathrm{kJ\ mol^{-1}} = 8065{,}5\ \mathrm{cm^{-1}}$$

Orders of magnitude in wavelength, frequency, energy, temperature

4.1 Electromagnetic radiation: Sprectral ranges



Violet	380–450nm	Yellow	570–590nm
Blue	450–495nm	Orange	590–620nm
Green	495–570nm	Red	620–750nm

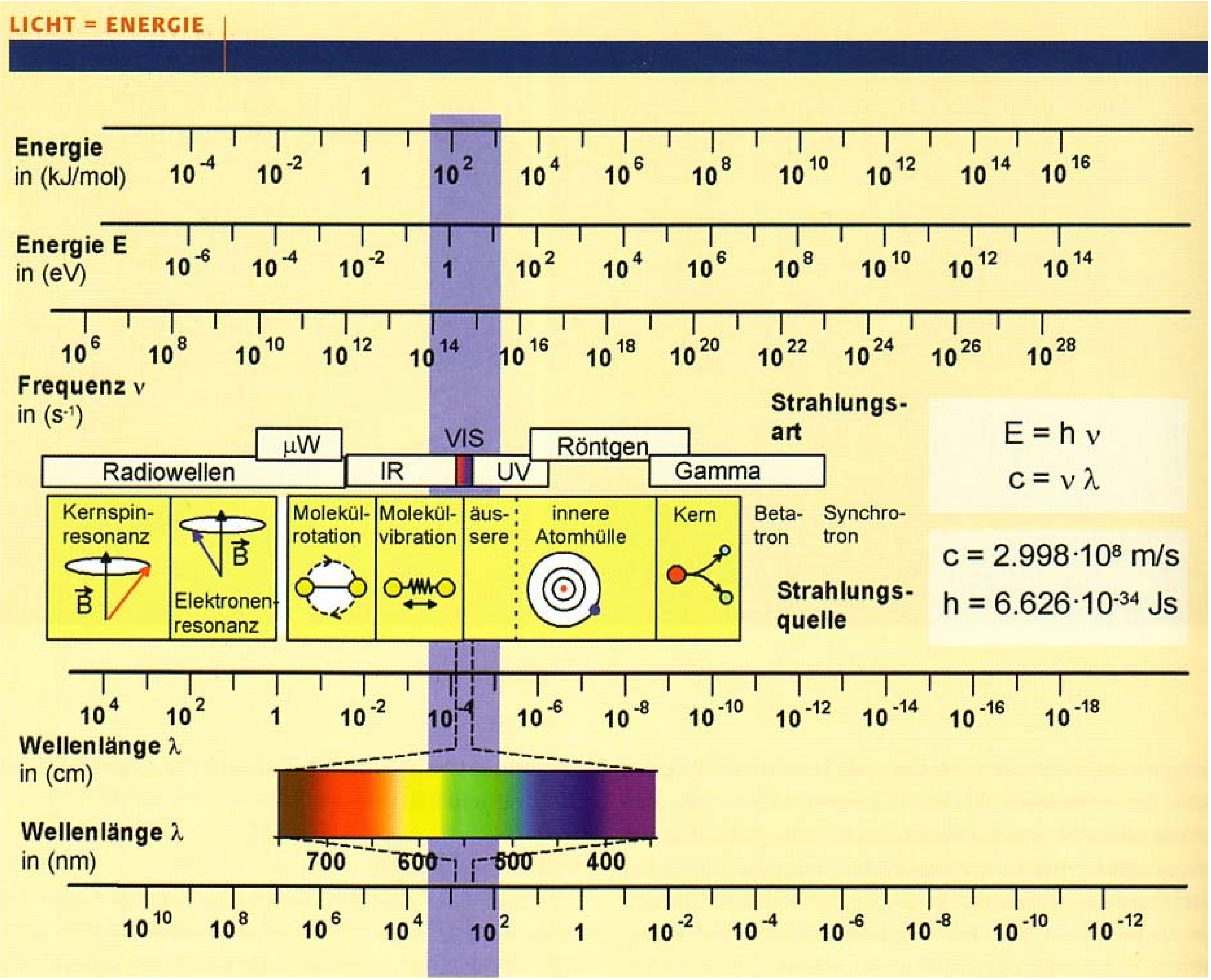
802.11 b/g Channels	
1	2412 MHz
2	2417 MHz
3	2422 MHz
4	2427 MHz
5	2432 MHz
6	2437 MHz
7	2442 MHz
8	2447 MHz
9	2452 MHz
10	2457 MHz
11	2462 MHz
12	2467 MHz
13	2472 MHz
14	2484 MHz

Data rate	
Std	(Mbit/s)
a	6, 9, 12, 18, 24, 36, 48,54
b	1, 2, 5.5, 11
b+	1, 2, 5.5,11, 22, 33, 44
g	6, 9, 12, 18, 24, 36, 48,54
n	1, 2, 5.5, 11; 6, 9, 12, 18, 24, 36, 48, 54, 125

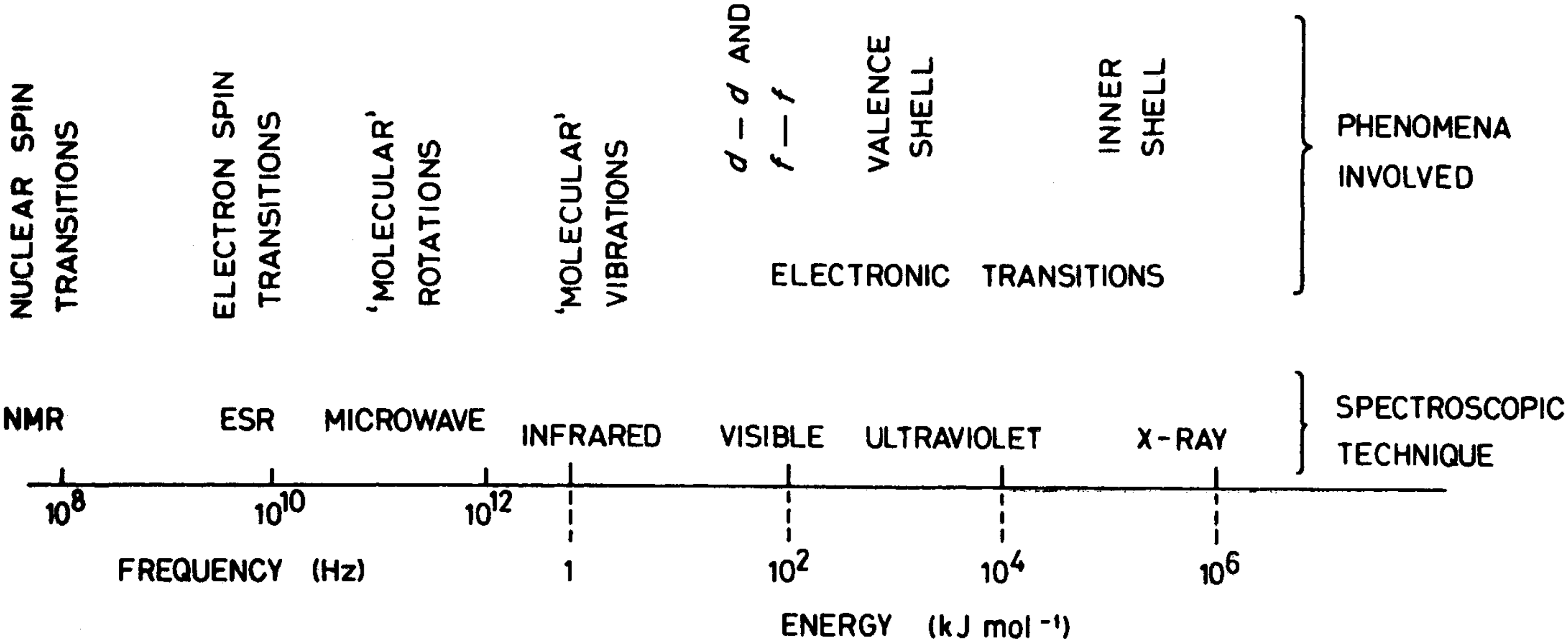
Banda	Uplink (MHz)	Downlink (MHz)
GSM 850	824 - 849	869 - 894
GSM 900	876 - 915	921 - 960
GSM 1800	1710-1785	1805-1880
GSM 1900	1850-1910	1930-1990

10^{24}	yotta	Y
10^{21}	zetta	Z
10^{18}	exa	E
10^{15}	peta	P
10^{12}	tera	T
10^{9}	giga	G
10^{6}	mega	M
10^{3}	kilo	k
10^{2}	hecto	h
10^{-1}	deci	d
10^{-2}	centi	c
10^{-3}	milli	m
10^{-6}	micro	µ
10^{-9}	nano	n
10^{-12}	pico	p
10^{-15}	femto	f
10^{-18}	atto	a
10^{-21}	zepto	z
10^{-24}	yocto	y

4.1 Electromagnetic radiation: Sprectral ranges



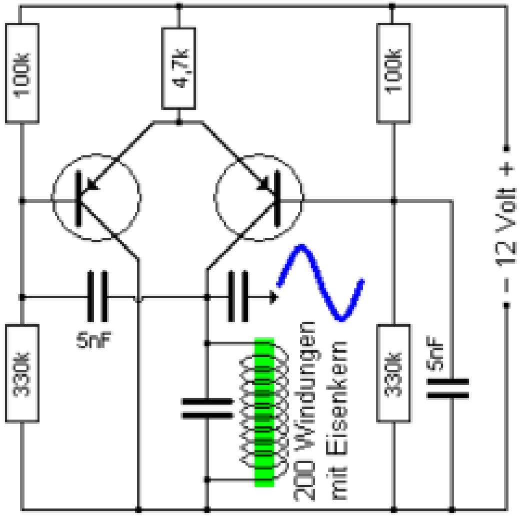
4.1 Electromagnetic radiation: Origins and techniques



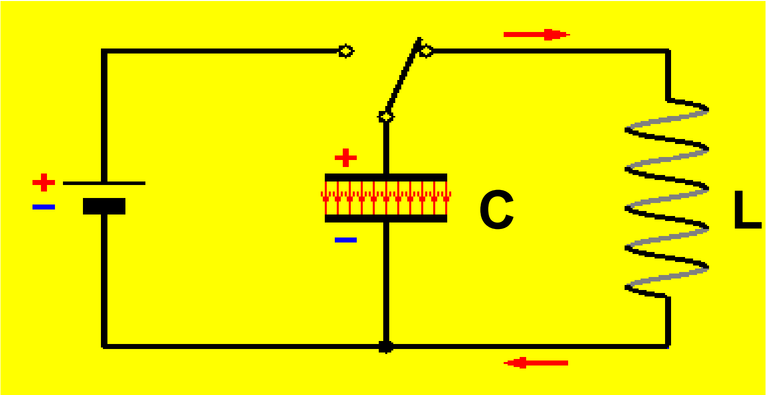
4.1 Electromagnetic radiation: Sources
Radio waves/NMR

Radio valve, 500 W graphite anode

Anode



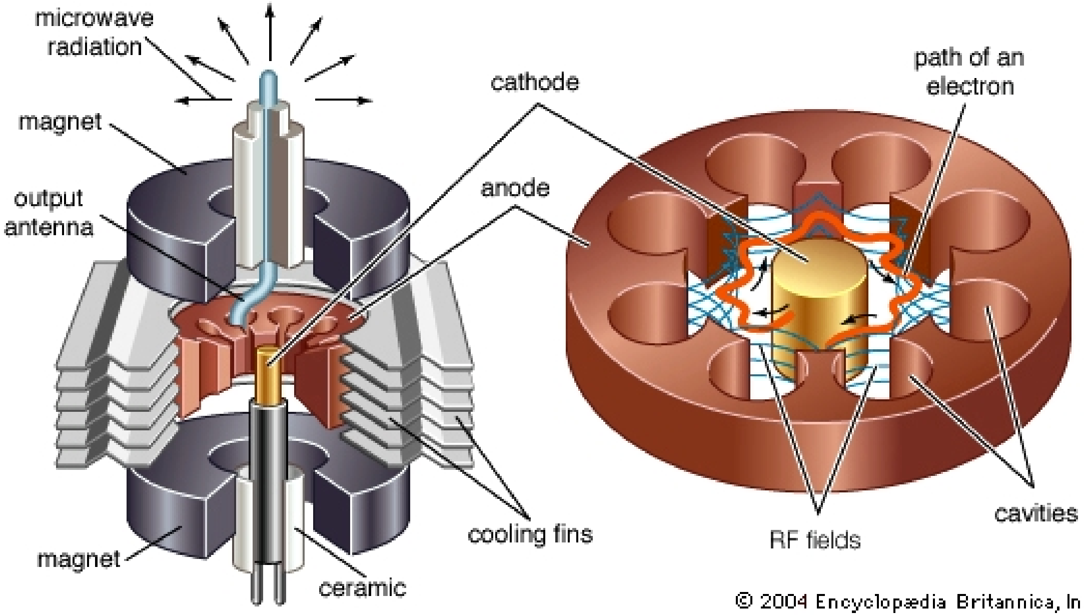
Sinus-Oszillator für etwa 1 kHz mit PNP-Transistoren.



$$f = \frac{1}{2\pi}\sqrt{\frac{1}{LC}}$$

Electromagnetic waves are produced (a.o.), when charges or charged or dipolar species are oscillating with frequencies in the respective range. For **microwaves**, the charges oscillate in a **resonance or tank circuit**, consisting of a capacitor with **capacitance C** and a coil with **self-inductance L**.

4.1 Electromagnetic radiation: Sources
Microwave radiation



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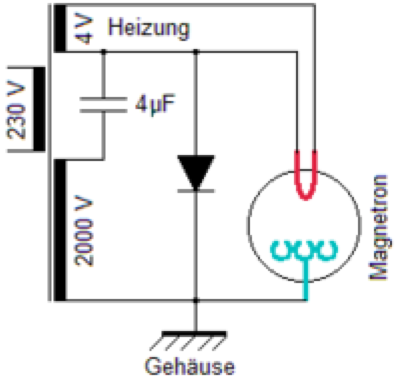
Schematic view of a magnetron for the production of microwaves (left) and the anode with an even number of anode vanes (right)



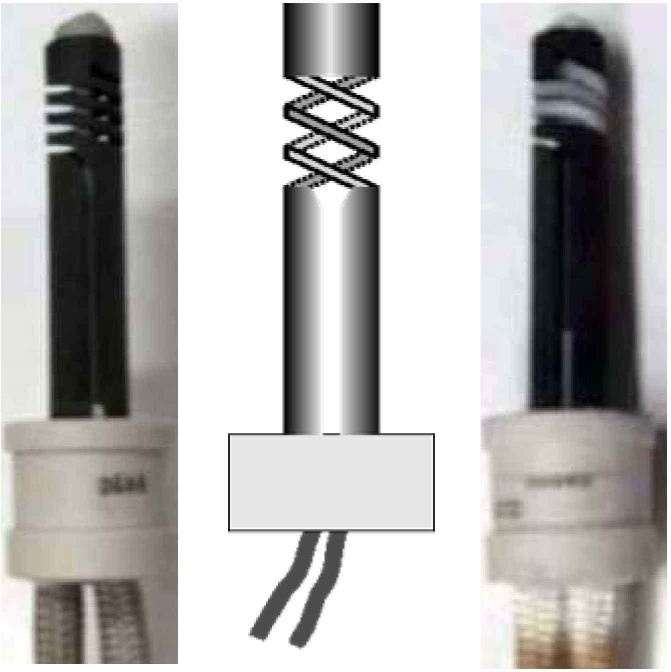
Principal circuit of a magnetron

Impulsmagnetron MI-189W (ca. 9 GHz)
Bordradar, Russia

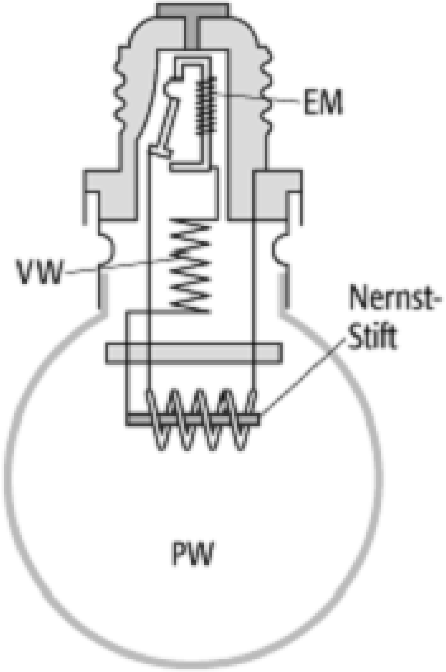
Magnetrons and Gyrotrons are diode-type electron tubes (~ 1-10 kV) with a trapezoid anode (*resonant cavities*) surrounded by permanent magnets producing an axial magnetic field. Under the combined influence of the electric and the magnetic field, the electrons are forced in a circular motion of travel to the anode resulting in electromagnetic radiation of 0.3 - 300 GHz .

ikon.net/d/nernst-brenner/nernst-

4.1 Electromagnetic radiation: Sources
IR-Sources, Globar, Nernst lamp


new sketch used

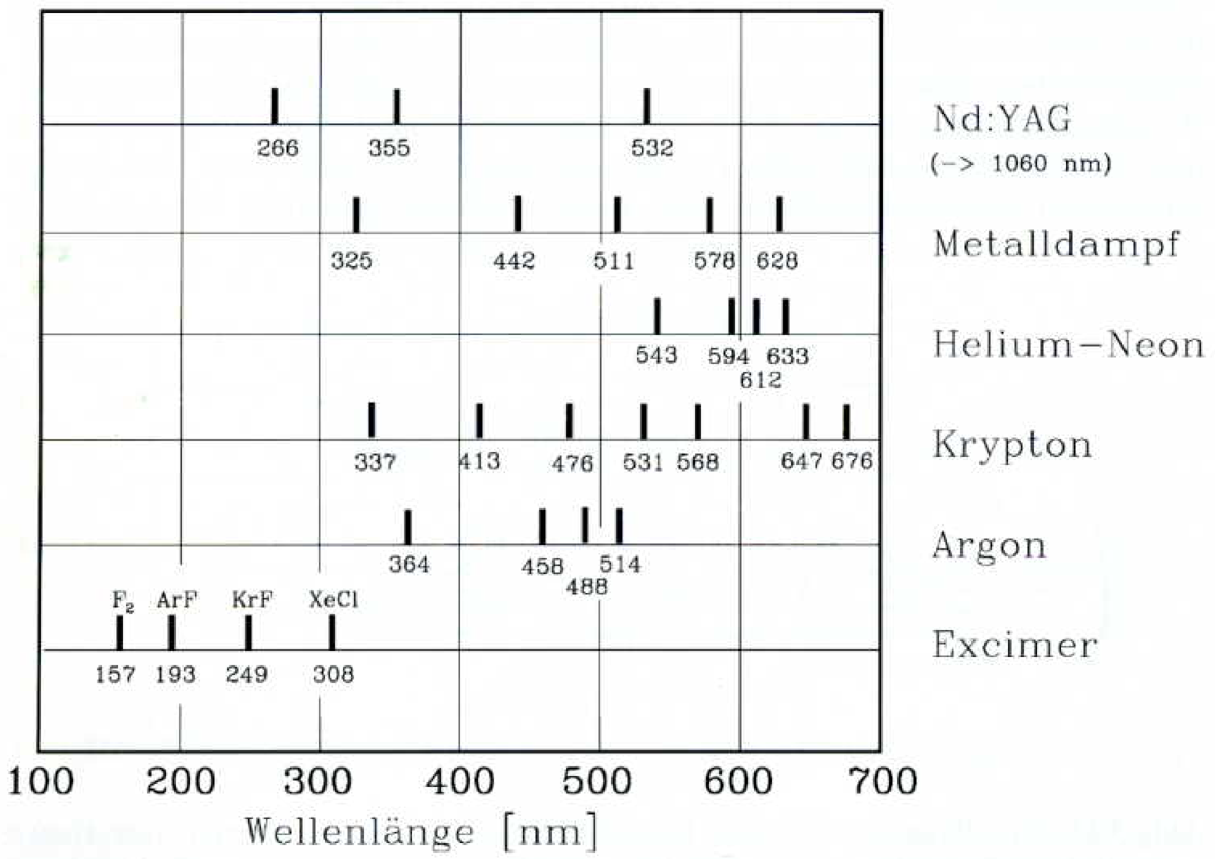
Globar (SiC, ~1.500 K)



Nernst lamp with Nernst rod, a ZrO_2/Y_2O_3 ion conductor 1.900 K

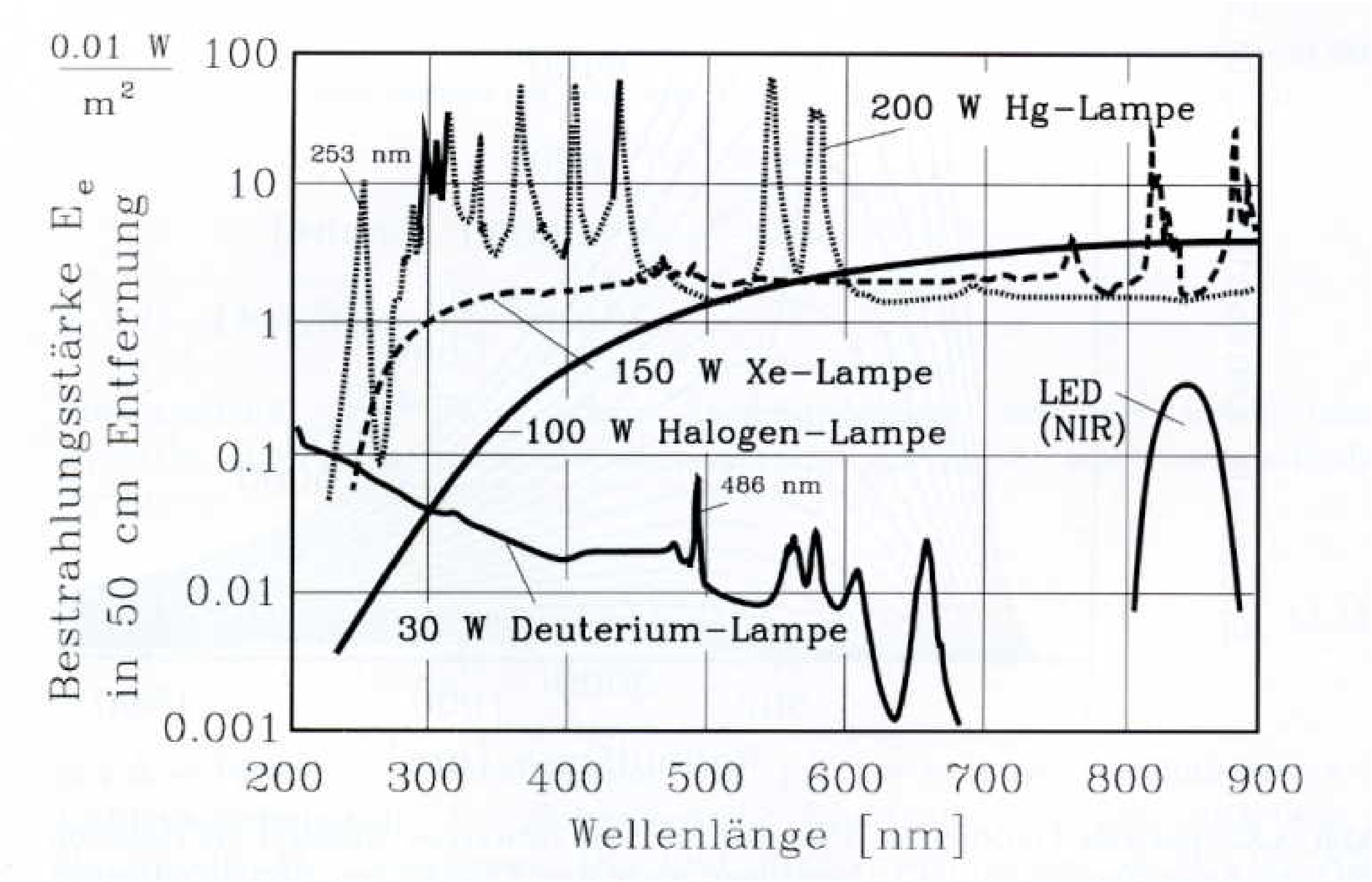
Any heated material will produce infrared radiations

4.1 Electromagnetic radiation: Sources UV and NIR radiation

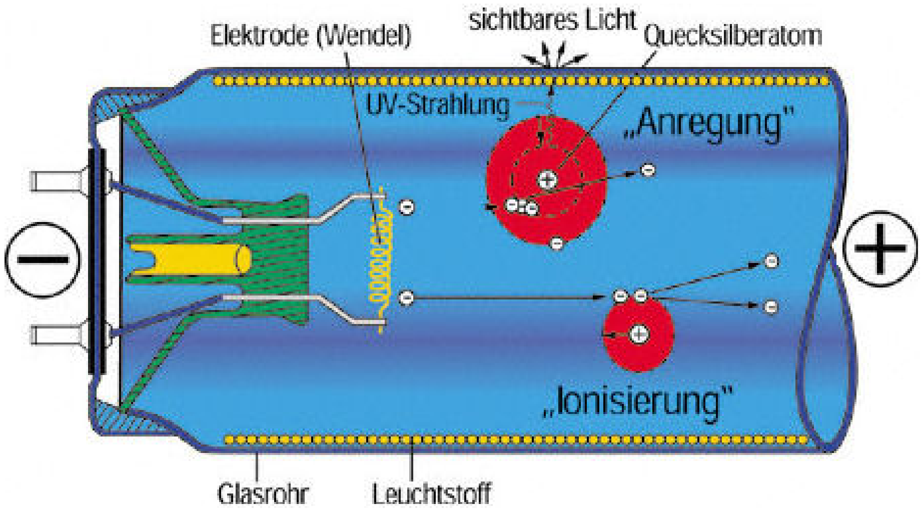


Wave lengths of some lasers for UV, visible and Raman specroscopy

4.1 Electromagnetic radiation: Sources
UV and NIR radiation



4.1 Electromagnetic radiation: Sources
UV radiation

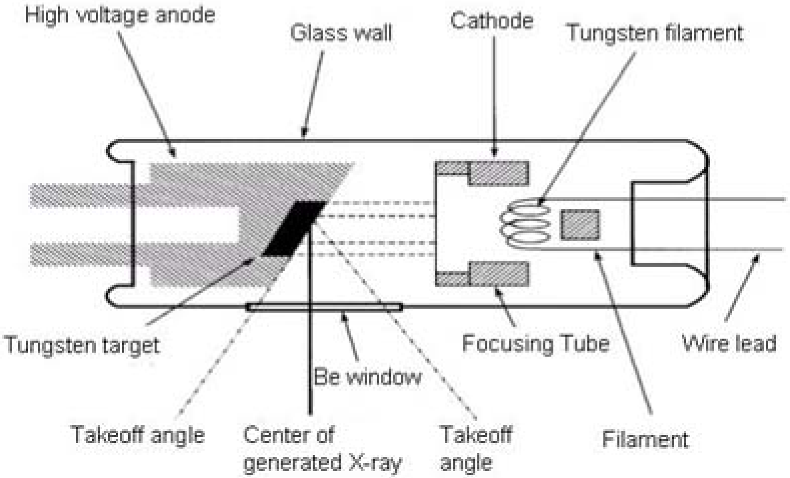


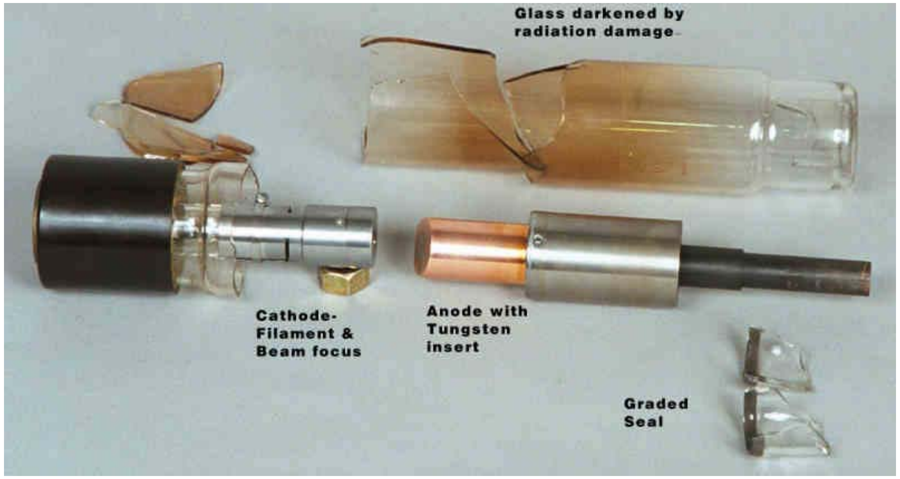
Sketch of a mercury (low pressure) lamp
Excitation/ionisation of Hg by fast electrons
(Importent Hg lines are 313 nm, 365 nm (i line), 405 nm (h line), 434 nm (g line), 546 nm (e line) and 577/579 nm und nm (orange dubble line)).

UV or black light lamp

4.1 Electromagnetic radiation: Sources
X-rays

X-rax tube

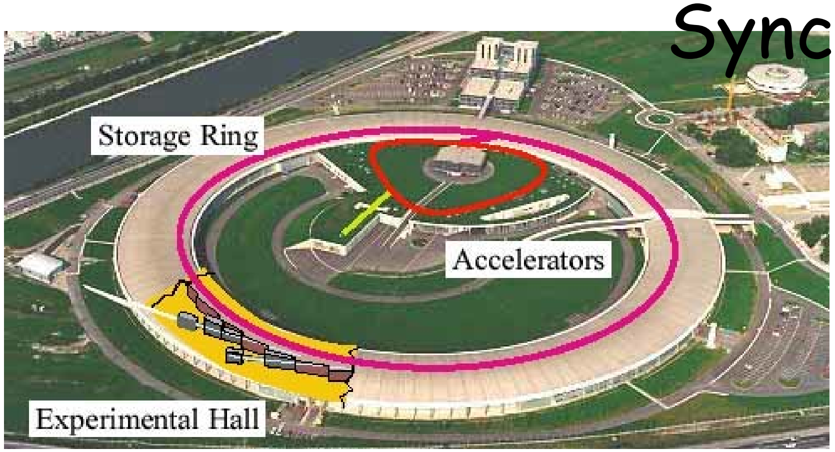


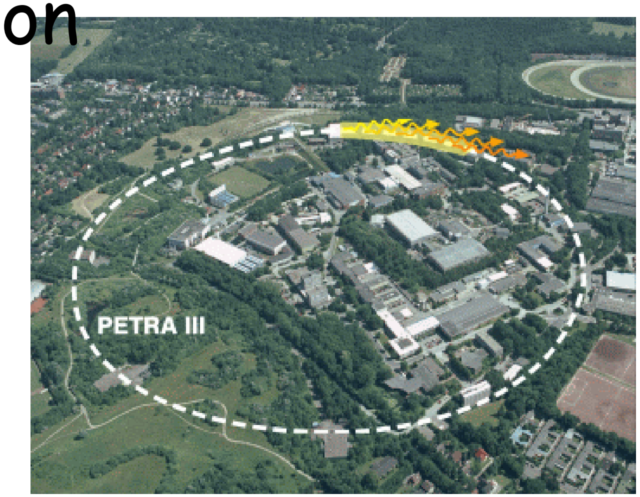


X-rax tube: sketched and dashed

4.1 Electromagnetic radiation: Sources

Synchroton





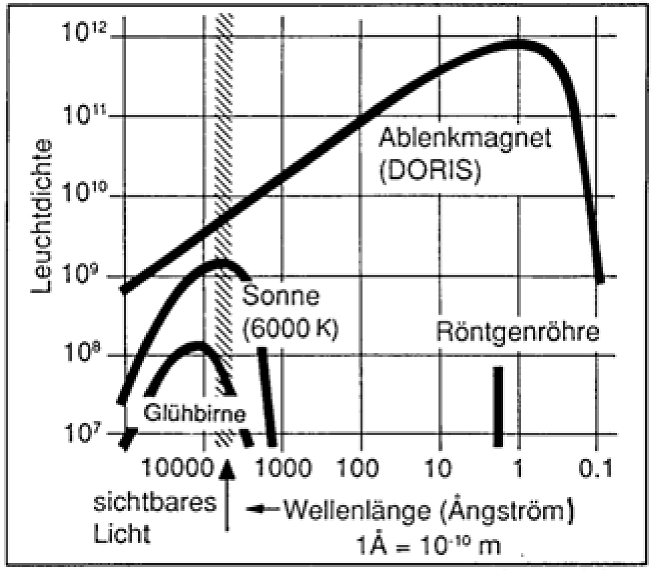
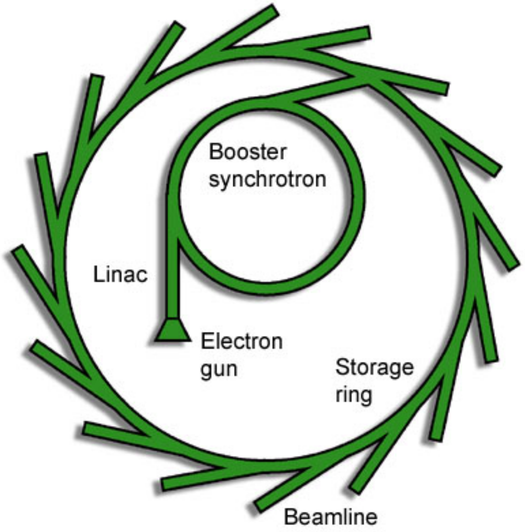
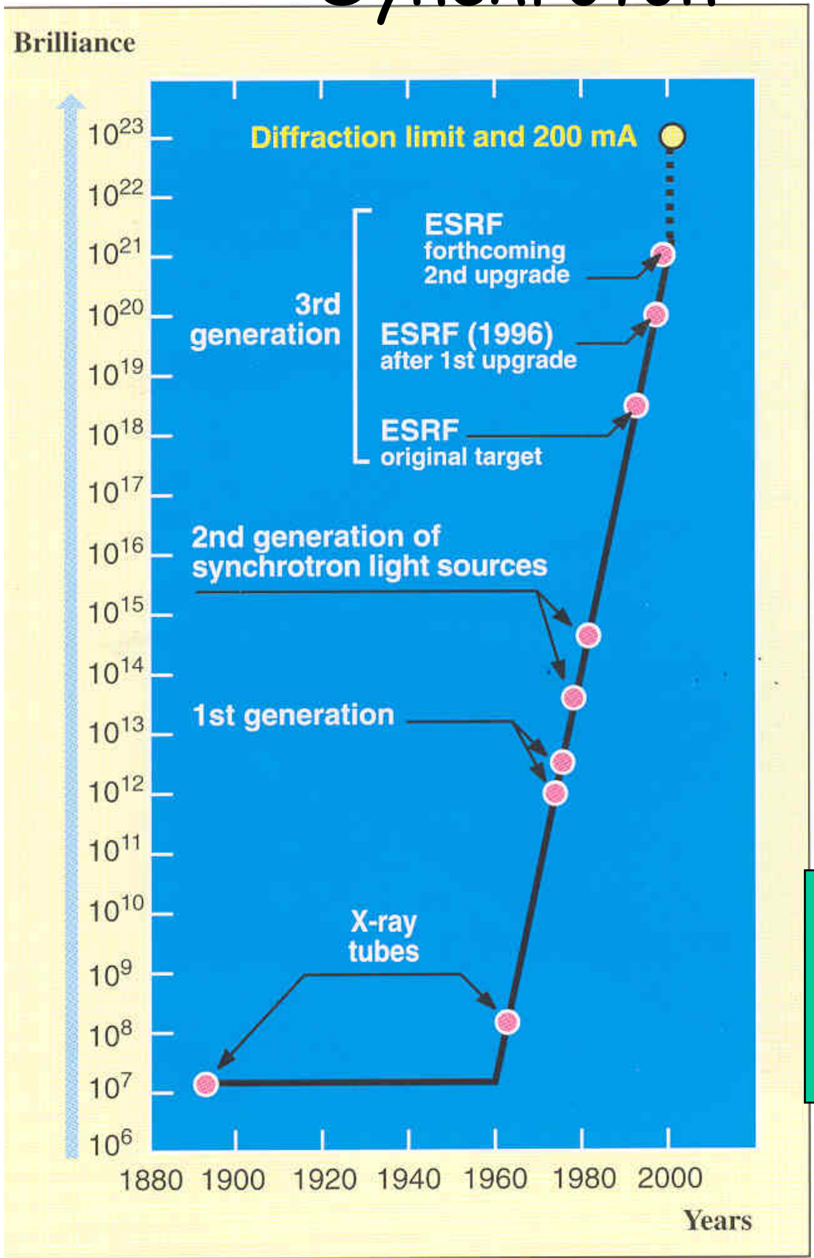


Abb. 5: Die Leuchtdichte von DORIS im Vergleich zu einigen bekannten Strahlungsquellen. (Die Leuchtdichte ist die Zahl der Photonen, die pro Sekunde und Wellenlängenintervall in eine bestimmte Richtung abgestrahlt wird.)



tunable electromagnetic radiation

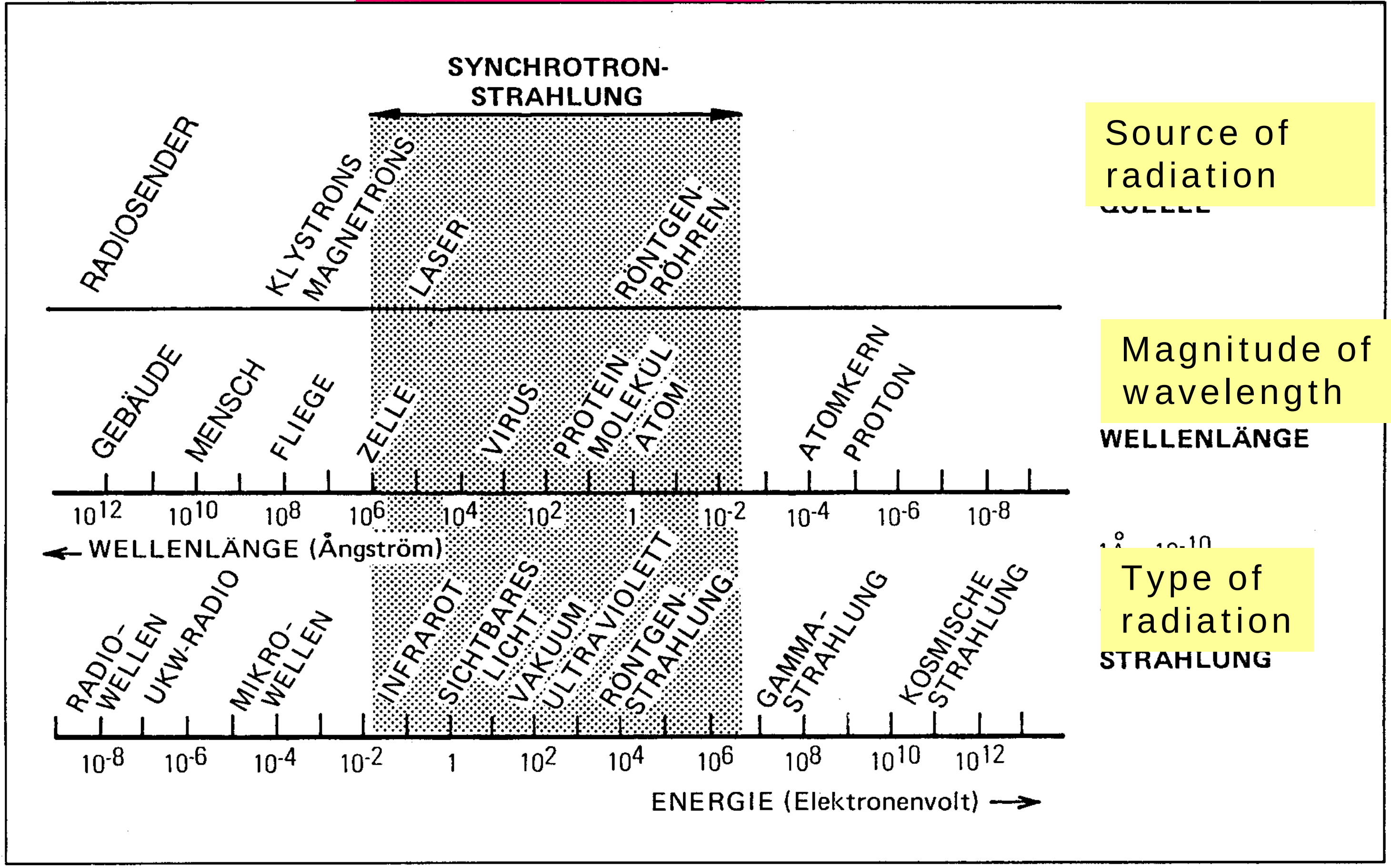
4.1 Electromagnetic radiation: Sources Synchroton



increase of brilliance over the years

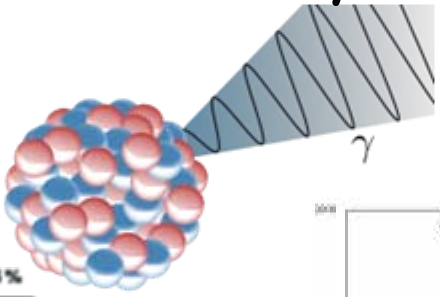
4.1 Electromagnetic radiation: Sources
Synchroton

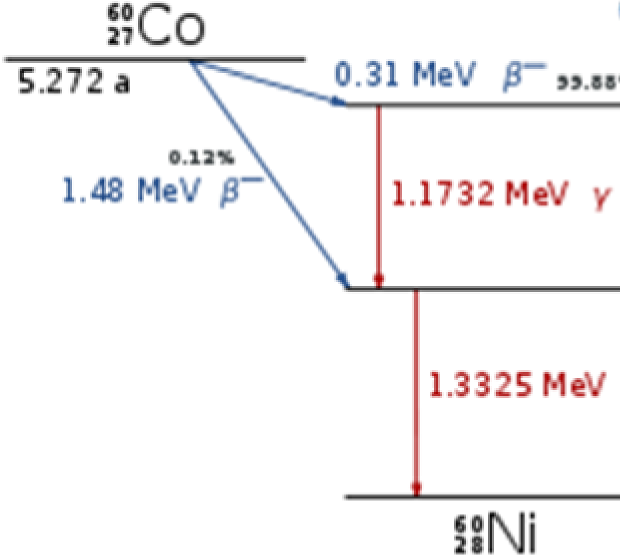
(range of tunability)



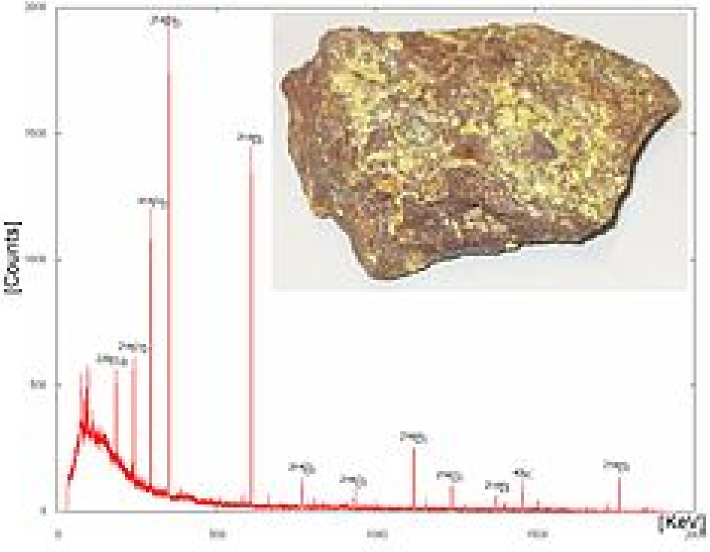
Use of Synchroton Radiation in materials science

4.1 Electromagnetic radiation: Sources
Gamma-rays





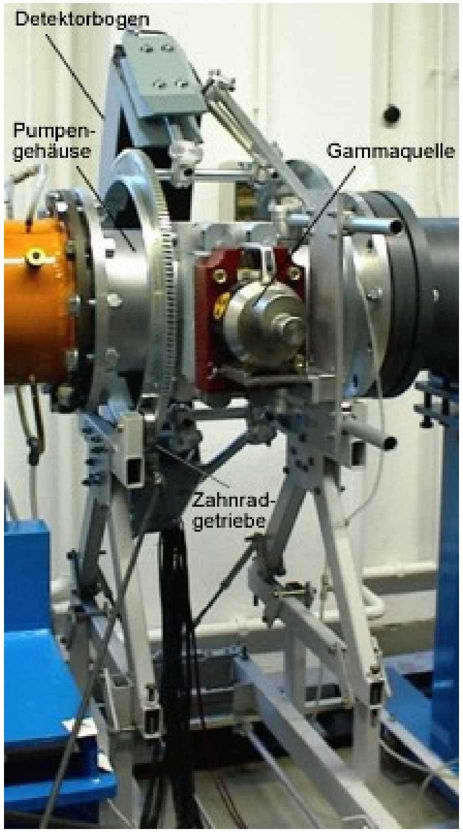
Decay scheme of ^{60}Co



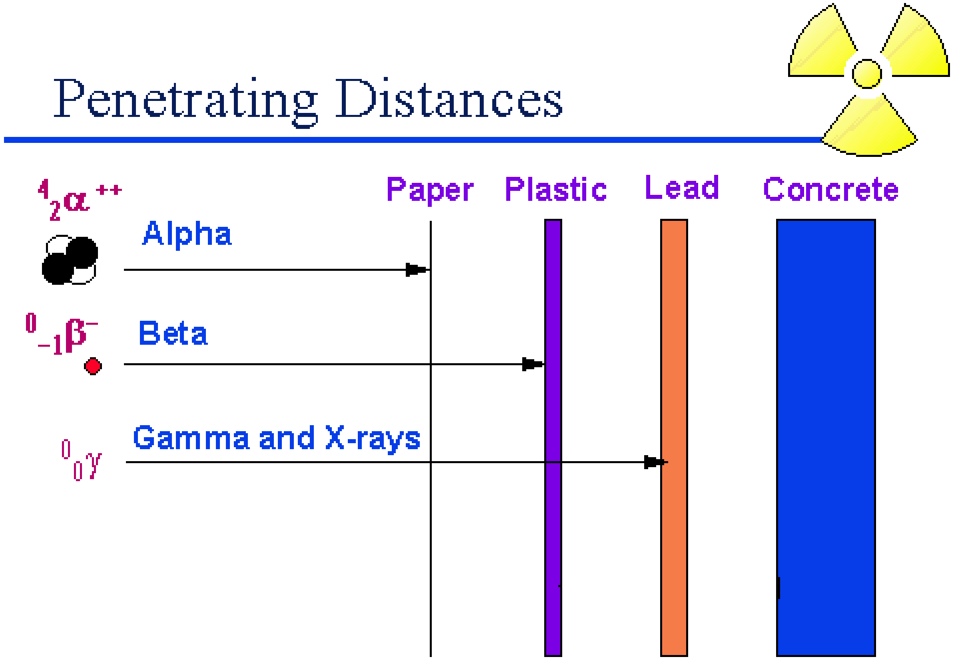
Gamma-ray spectrum of ^{238}U

Gamma rays can occur whenever charged particles pass through magnetric fields or pass within certain distances of each other or by nuclear reactions (e.g. fusion or decay processes)

4.1 Electromagnetic radiation: Sources
Gamma-rays

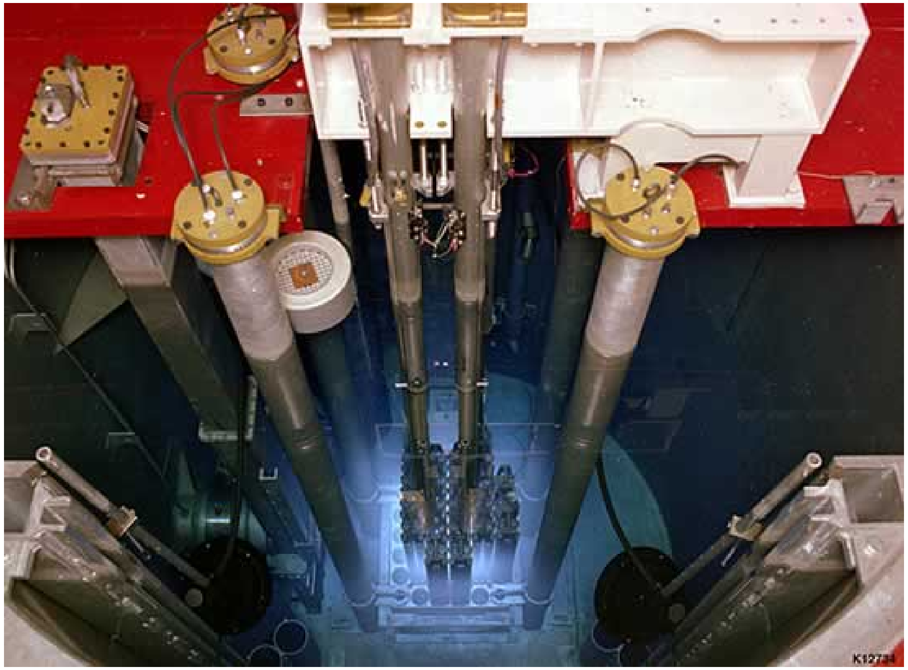


Gamma-radiation source

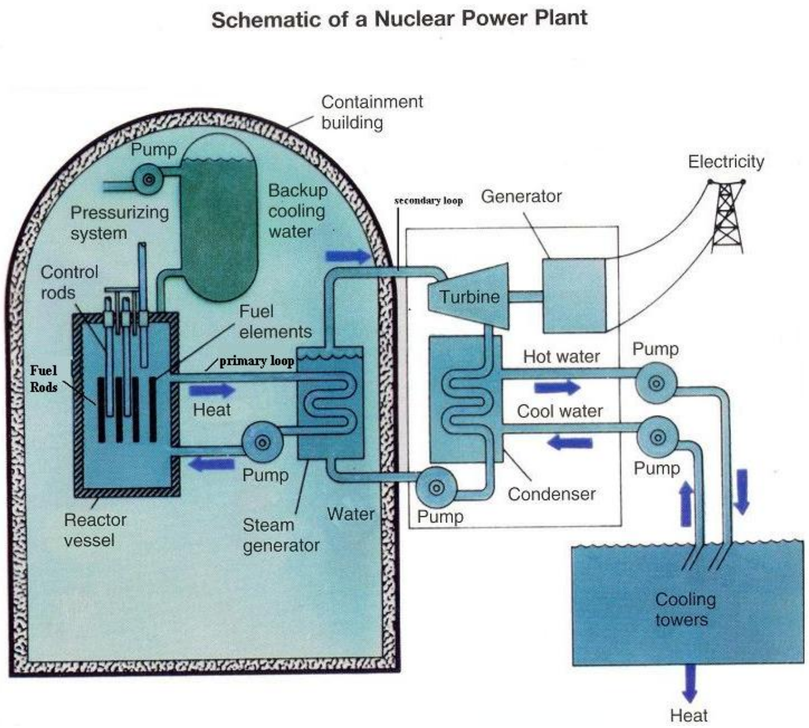


Nuclear decay products

4.1 Electromagnetic radiation: Sources
Neutrons



View into a nuclar reactor
with Cherenkov radiation



Scetch of a nuclear power plant

De Broglie wave length: $\lambda = h/(m \cdot v)$
e.g. n with $v = 3.300$ m/s → 0,05 eV → 1,2 Å (0,12 nm)

4.2 Microscopic techniques: OM, SEM, CTEM, HREM

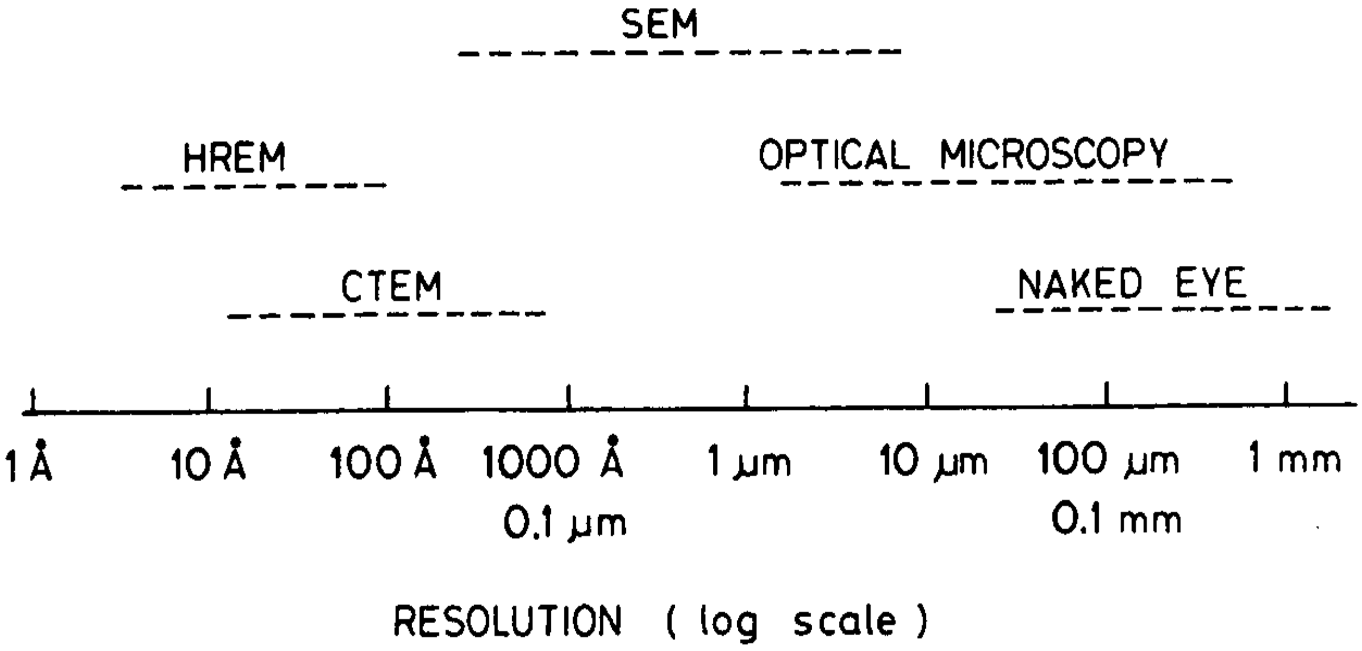


Fig. 4.2 Working ranges of various techniques used for viewing solids. CTEM = conventional transmission electron microscopy; HREM = high-resolution electron microscopy; SEM = scanning electron microscopy

4.3 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, α, β, γ)
- 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.

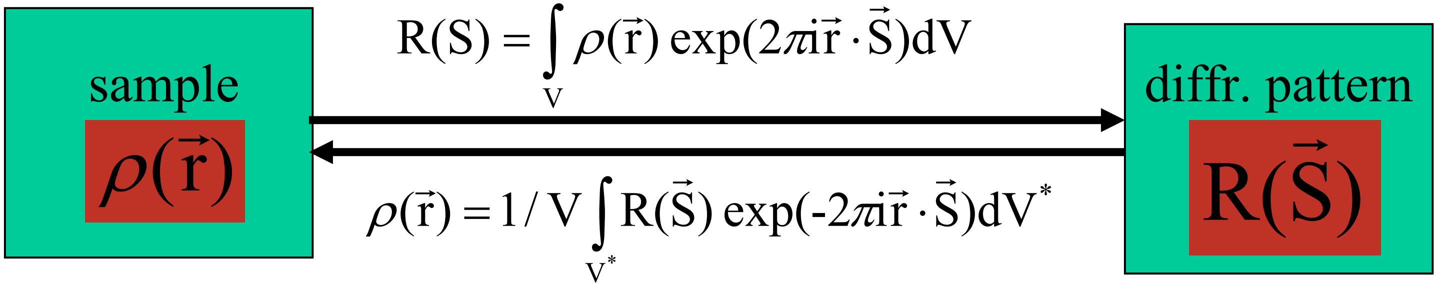
4.3 Crystal structure analysis/determination

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~0.01mm^3)
- an adequate electromagnetic radiation ($\lambda \sim 10^{-10}$ 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

4.3 Crystal structure analysis/determination

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



sample

$\rho(\vec{r})$

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

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

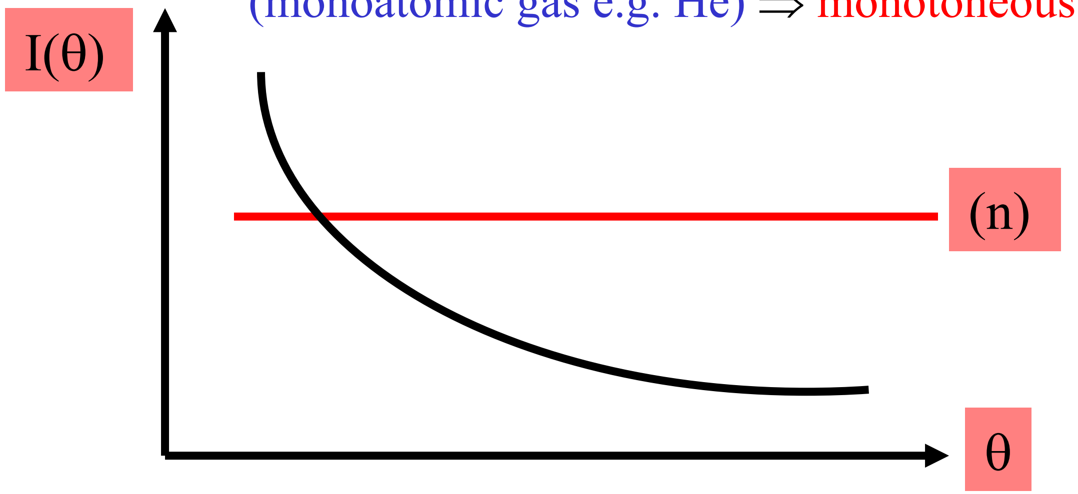
diffr. pattern

$R(\vec{S})$

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) ⇒ monotoneous decrease

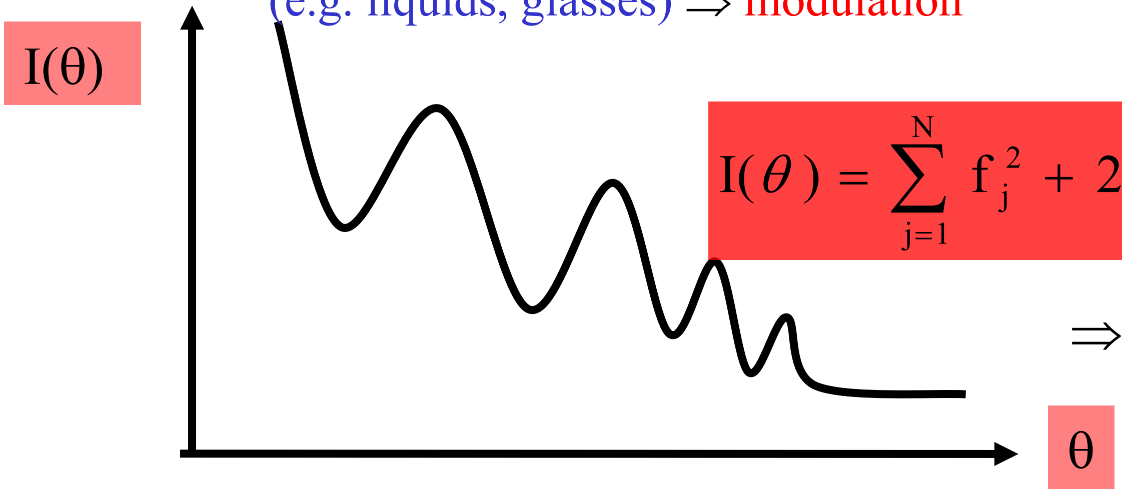


$I(\theta) = N \cdot f^2$

f = scattering length of atoms N

⇒ no information

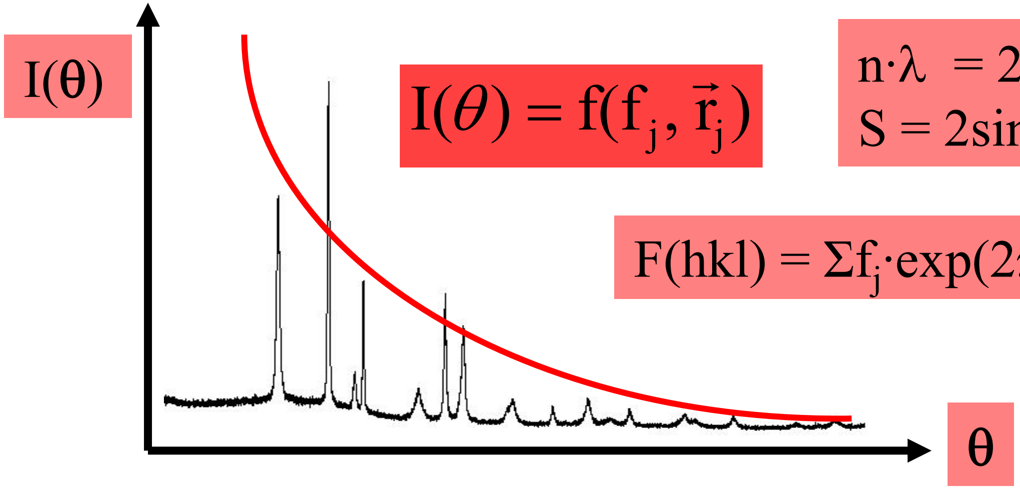
no long-range, but short range order
(e.g. liquids, glasses) ⇒ modulation



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

⇒ radial distribution function
atomic distances

B. X-ray scattering diagram of a crystalline sample



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

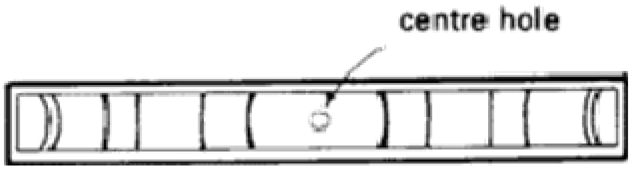
$n\cdot\lambda = 2d\sin\theta$

$S = 2\sin\theta_{hkl}/\lambda = 1/d_{hkl} = H$

$F(hkl) = \Sigma f_j\cdot\exp(2\pi i(hx_j+ky_j+lz_j)$

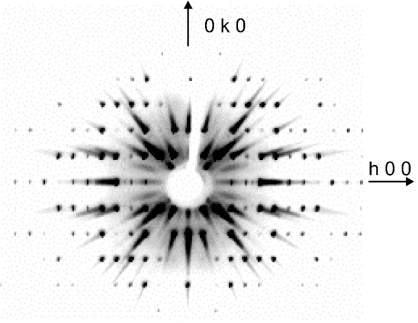
$I(hkl) = |F(hkl)|^2$

crystal powder
orientation statistical, λ fixed
⇒ cones of interference



Debye-Scherrer diagram

single crystal
orientation or λ variable
⇒ dots of interference (reflections)

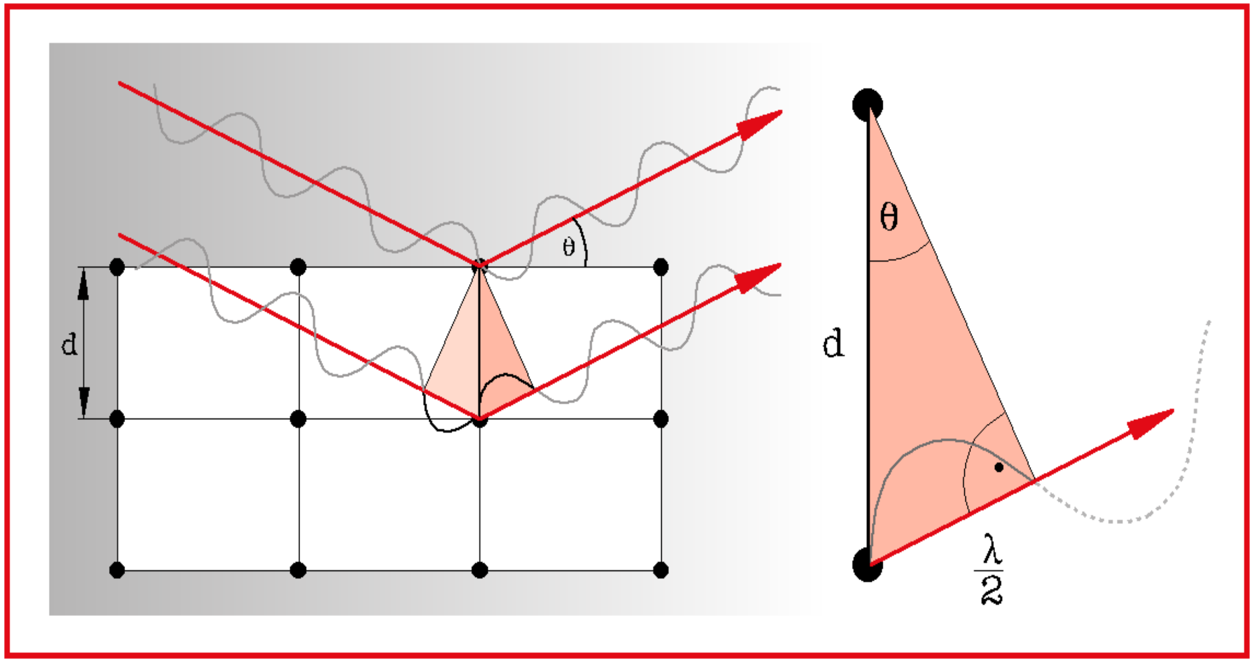


precession diagram

Why that?

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

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



Spacing $d_{(hkl)}$

Lattice planes
(hkl)

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

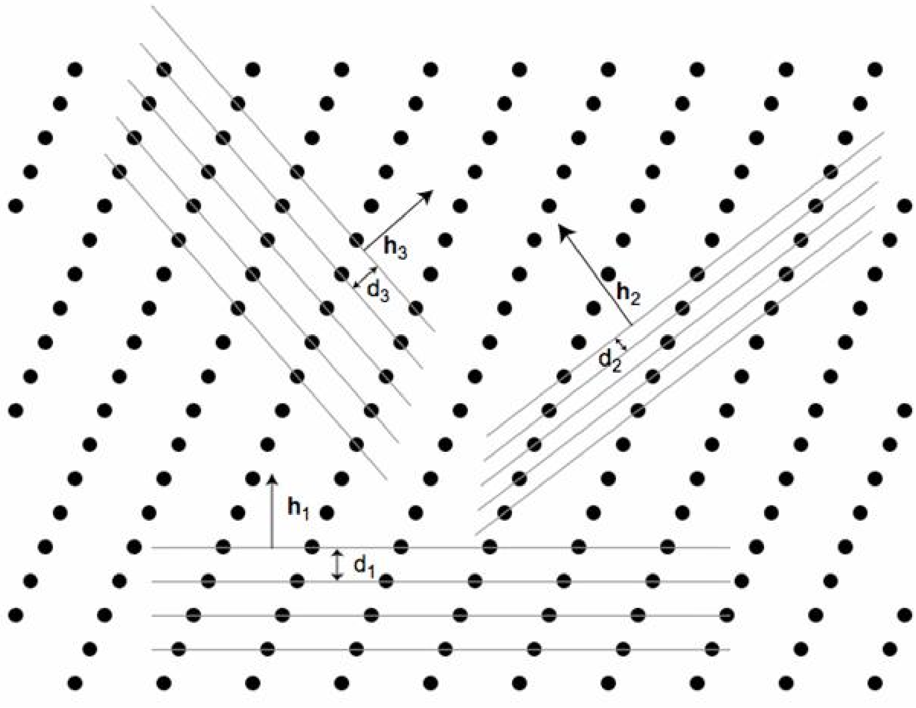
4.3 Basic equation of X-ray analysis: Bragg equation

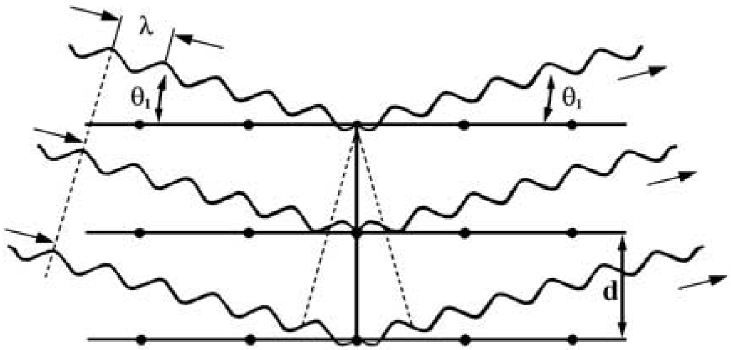
Lattice planes: Why are they important ?

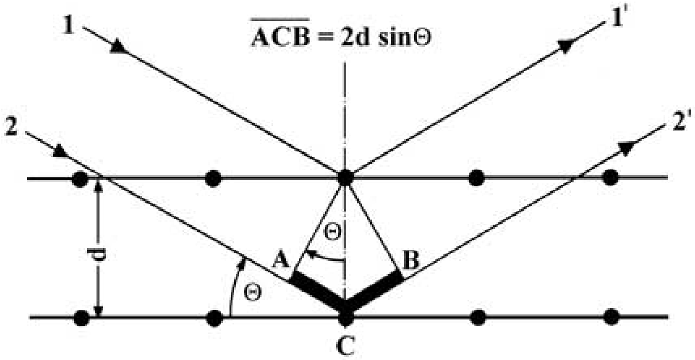
Bragg equation:

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

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

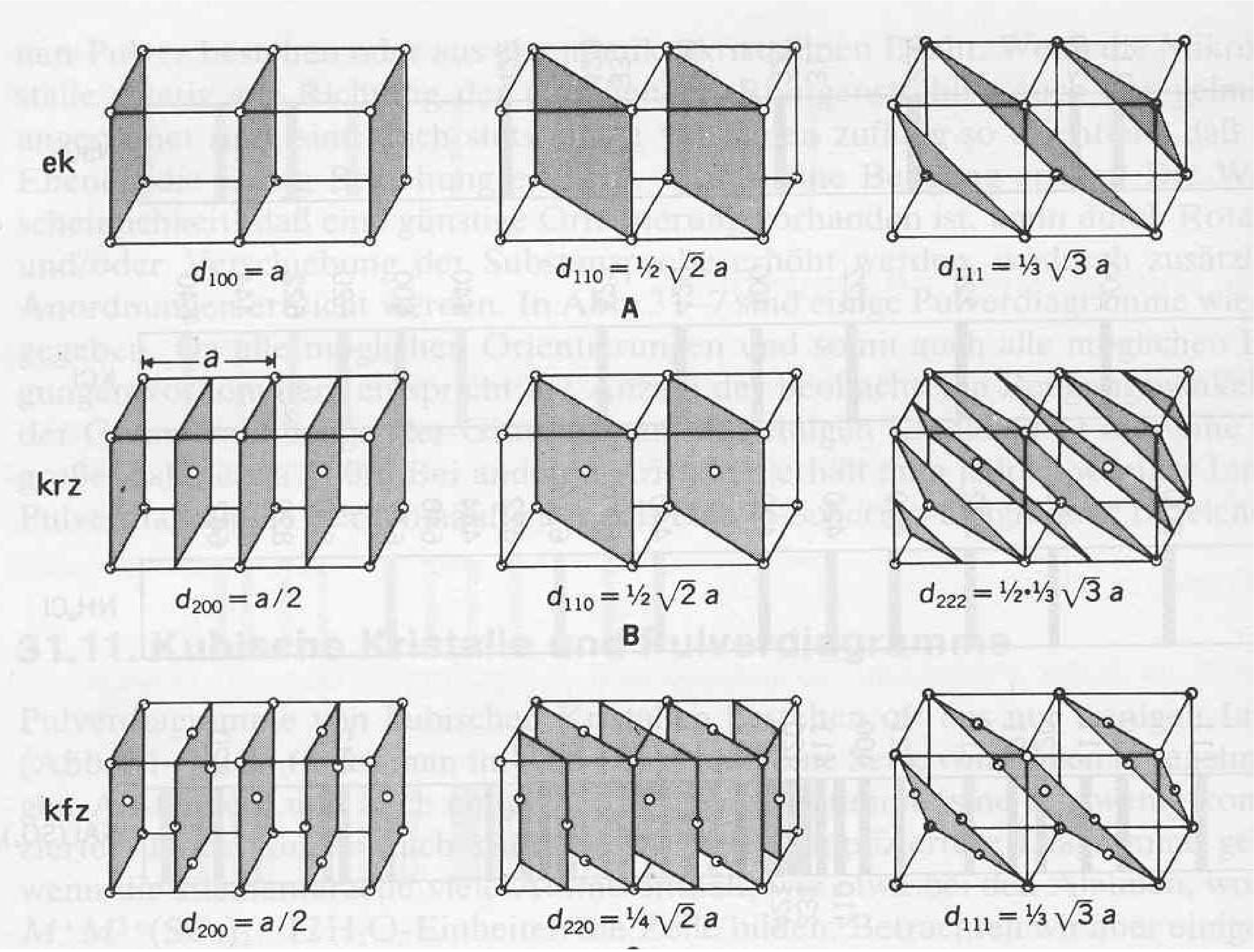






Question: How are directions and planes in a regular lattice defined ?

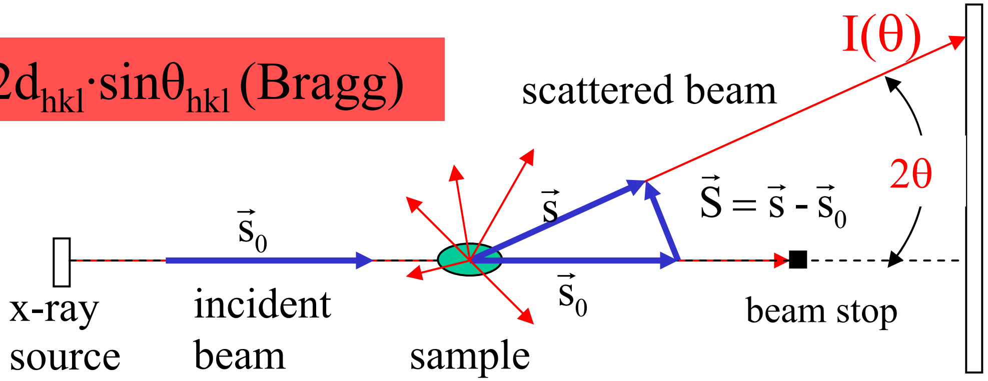
Lattice plane series: Miller indices hkl, d values



(X-ray) diffraction of a crystalline sample

(single crystal or crystal powder)

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



detector
(film, imaging plate)

$\vec{s}_0$: WVIB

$\vec{s}$: WVSB; $|\vec{s}| = |\vec{s}_0| = 1/\lambda$ (or 1)

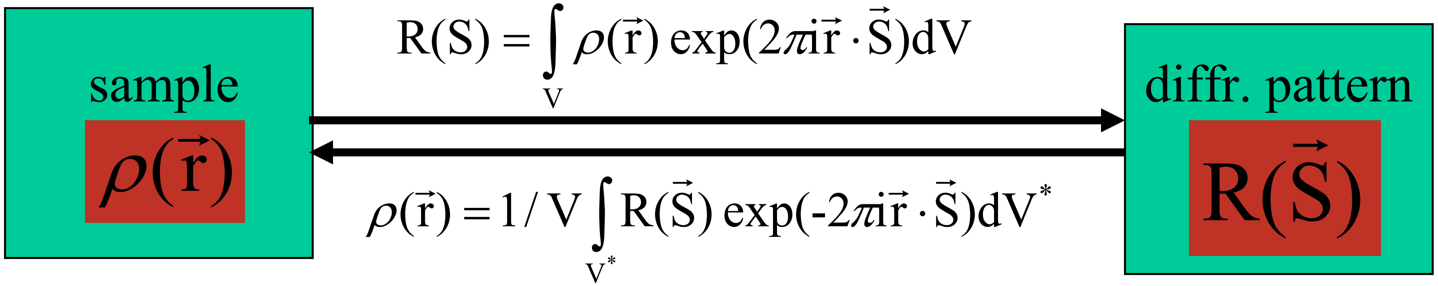
$\vec{S}$: Scattering Vector

$\vec{S} = \vec{H}$ (Bragg)

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

$S = 2\sin\theta_{hkl}/\lambda = 1/d_{hkl} = H$

Fourier transform of the electron density distribution



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

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

$R \neq 0$
only if
$\vec{S} = \vec{H}$

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

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

4.3 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, α, β, γ)
- 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(θ) or I(hkl)**

How does that work?

4.3 Crystal structure analysis/determination

- The geometry (lattice constants a, b, c, α, β, γ) of the unit cell/ compond one can get from the geometry of the diffraction pattern, i.e. from the site of the reflections (diffraction angles θ for a powder; „Euler angles" θ, ω, φ, χ 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 α(hkl).

$$|Fo(hkl)| \approx (I(hkl))^{1/2} \qquad Fc(hkl) = \Sigma f_j \cdot \exp(2\pi i(hx_j+ky_j+lz_j))$$

$$\delta(xyz) = (1/V)\cdot\Sigma\ |Fo(hkl)|\cdot\exp(i\alpha(hkl)\cdot\exp(-2\pi i(hx+ky+lz))$$

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

4.3 Crystal structure analysis/determination

→ The intensitis 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 the square of a quantity called structure factor F(hkl) or F_{hkl} (Fo for observed, Fc for calculated).

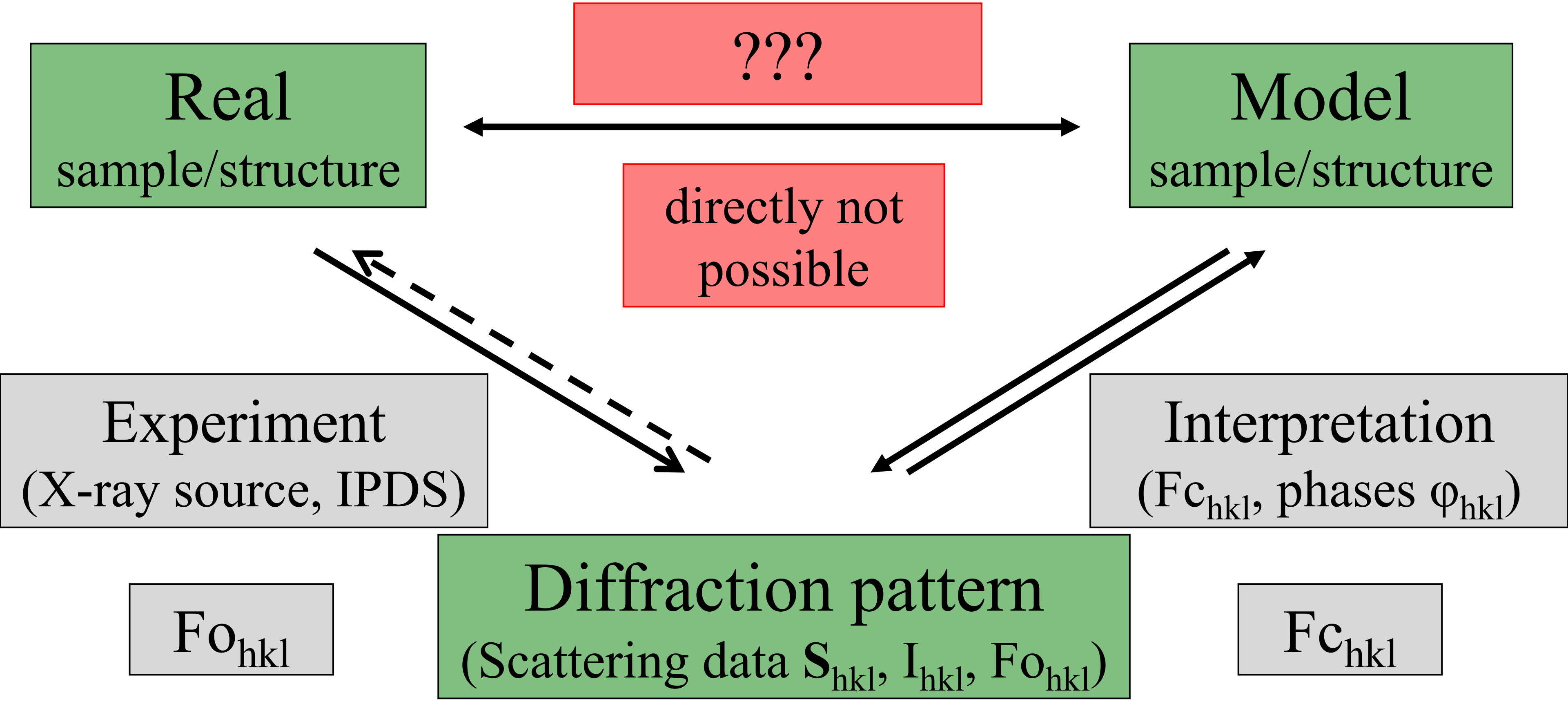
→ The structure factor F(hkl) is a complex number in general but becomes real in case of crystal structures with a centre of symmetry:

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

→ In case of centrosymmetric crystal structures, the phases are 0 or π, 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)

4.3 Crystal structure analysis/determination



???

Real
sample/structure

directly not possible

Model
sample/structure

Experiment
(X-ray source, IPDS)

Interpretation
(Fc_{hkl}, phases φ_{hkl})

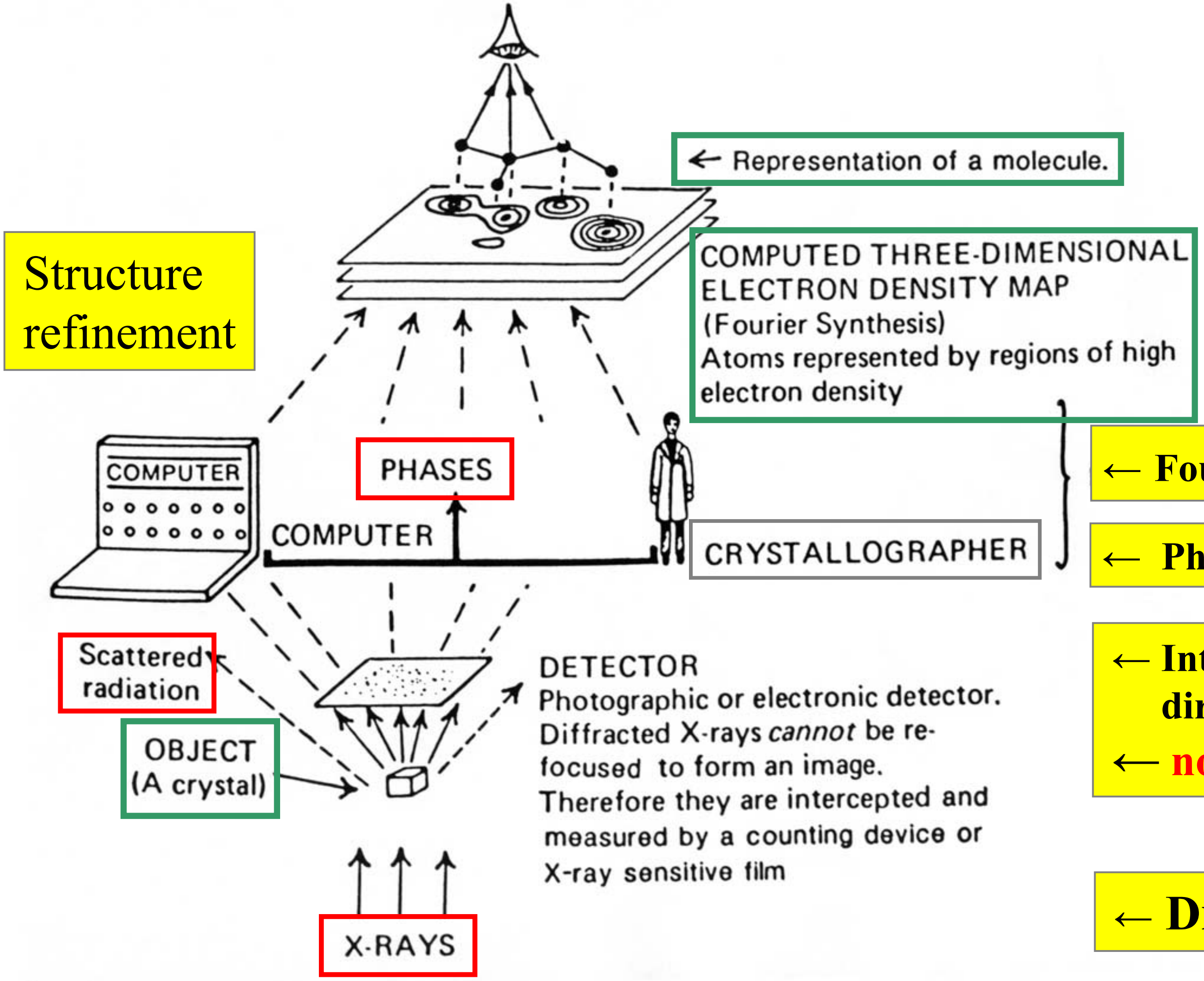
Fo_{hkl}

Diffraction pattern
(Scattering data $\mathbf{S}_{hkl}$, I_{hkl}, Fo_{hkl})

Fc_{hkl}

Structure determination only indirectly possible!

4.3 Crystal structure analysis/determination



COMPUTED THREE-DIMENSIONAL ELECTRON DENSITY MAP (Fourier Synthesis) Atoms represented by regions of high electron density

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

Structure refinement

← **Fourier-Syntheses**

← **Phase determination**

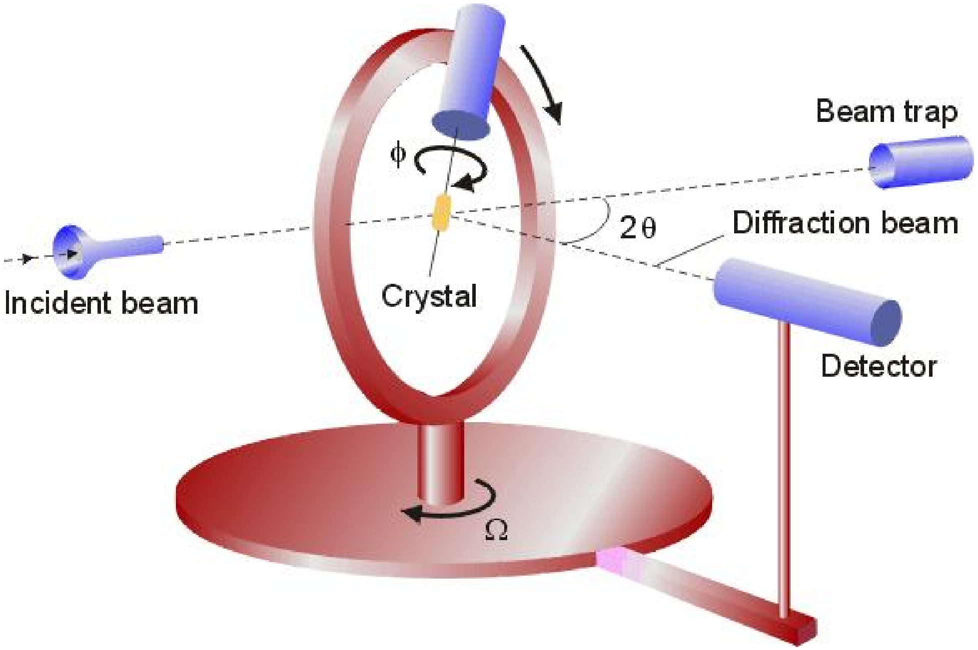
← **Intensities** and **directions** only

← **no phases** available

← **Direction ≡ 2θ**

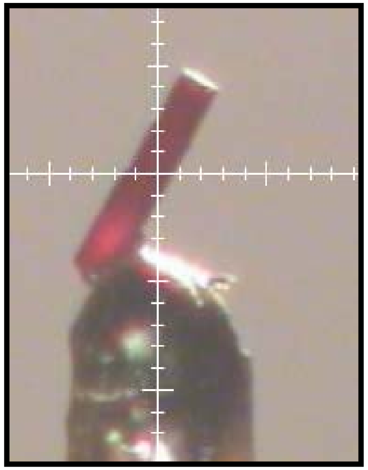
Realisation of a crystal structur determination

1. Fixing und centering of a crystal on a diffractometer and determination of the orientaion matrix M and the lattice constants a, b, c, α, β, γ of the crystal from the Eulerian angles of the reflections (θ, ω, φ, χ) and of the cell content number Z (aus cell volume, density and formula),

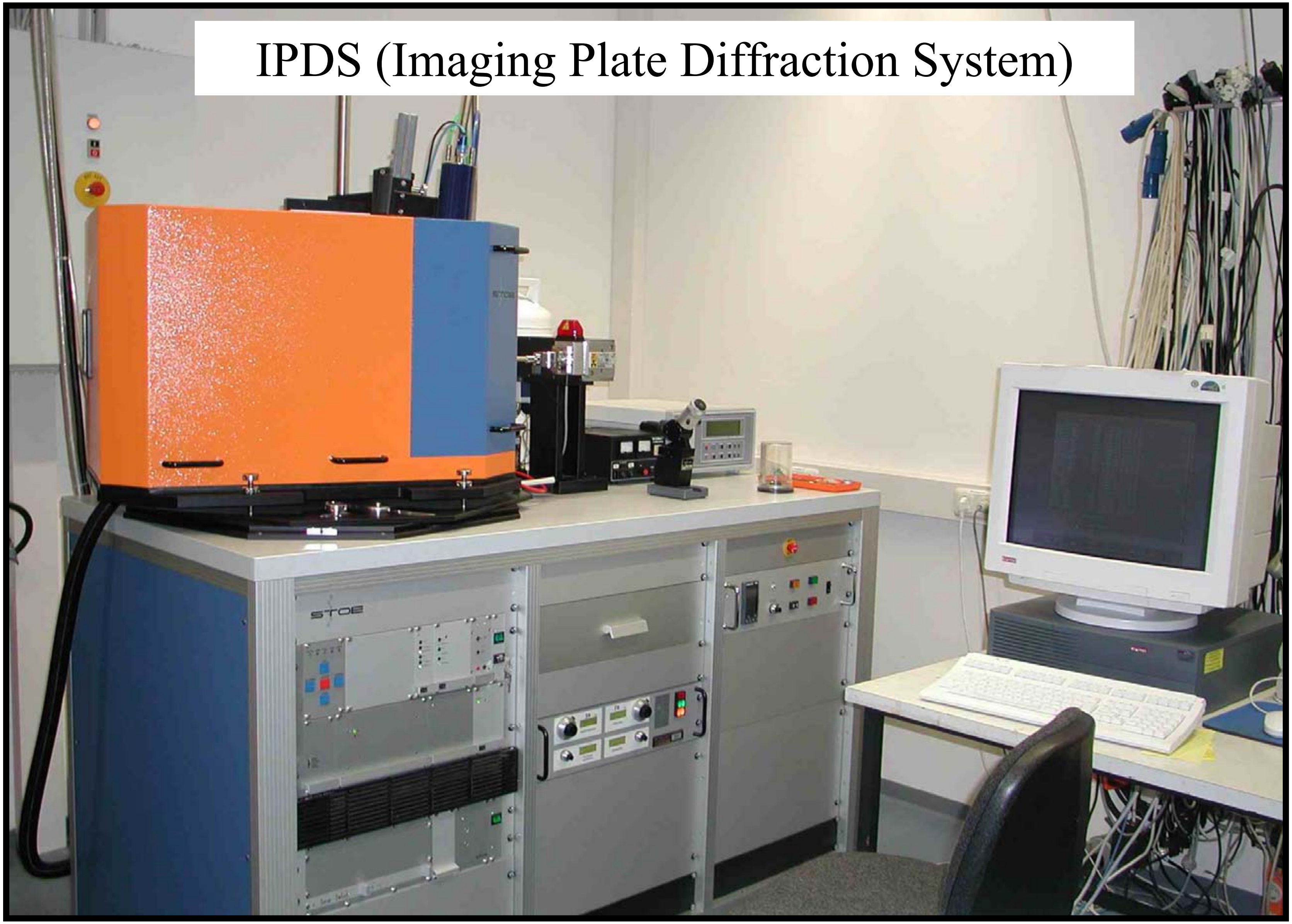


Principle of a four-circle diffraktometer for single crystal stucture determination by use of X-ray or neutron diffraction

CAD4 (Kappa-Axis-Diffraktometer)

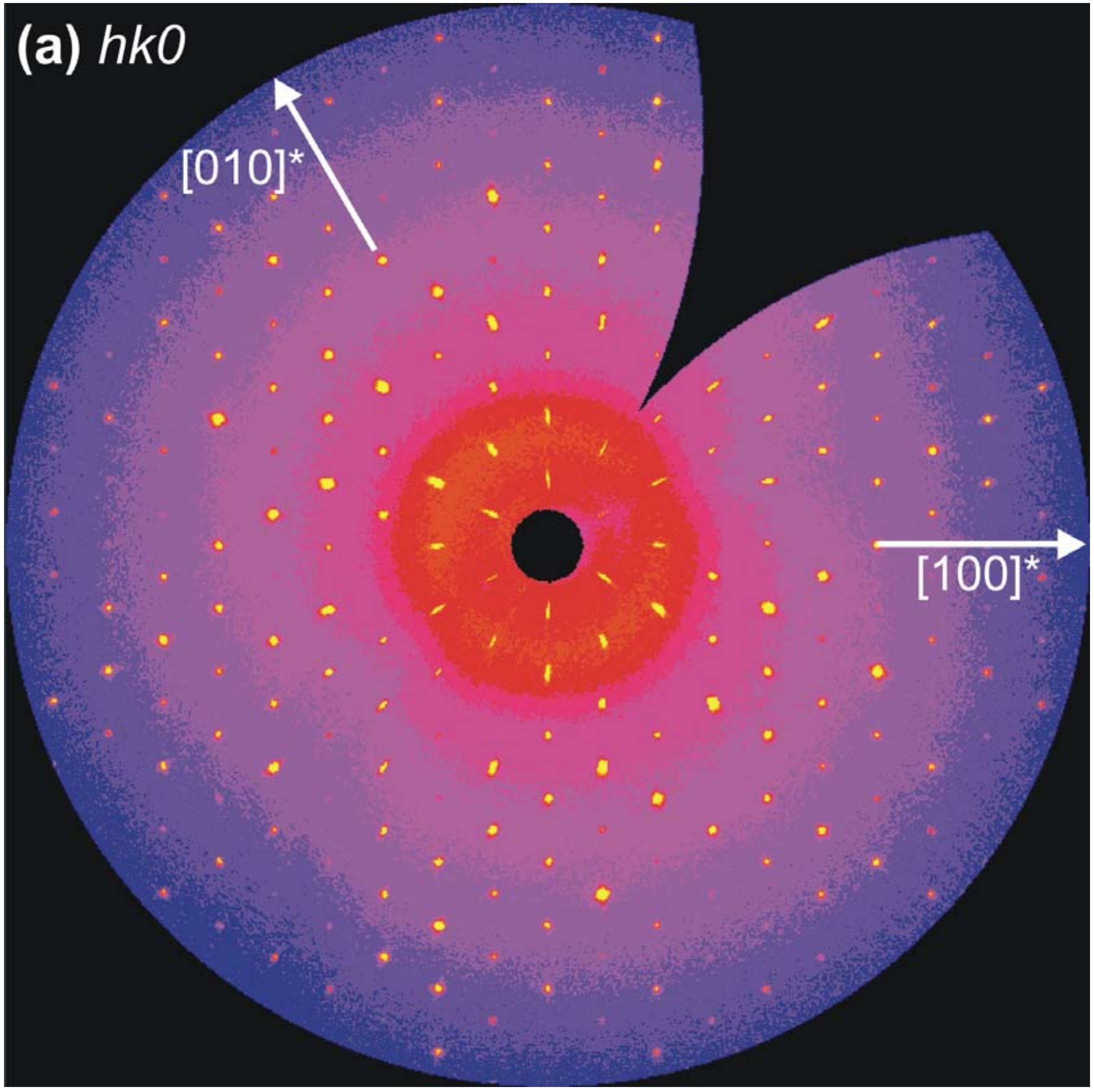


IPDS (Imaging Plate Diffraction System)



4.3 X-ray analysis with single crystals: Reciprocal lattice

(calculated from an IPDS measurement)



Realisation of a crystal structur 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 $|Fo_{hkl}|$ from the I_{hkl} incl. absorption, extinktion, 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 $|Fo_{hkl}|$ values for different small θ ranges θ_m according to $\ln(|Fo|^2/\Sigma f_j^2) = \ln(1/K) - 2B(\sin^2\theta_m)/\lambda^2$ → data skaling

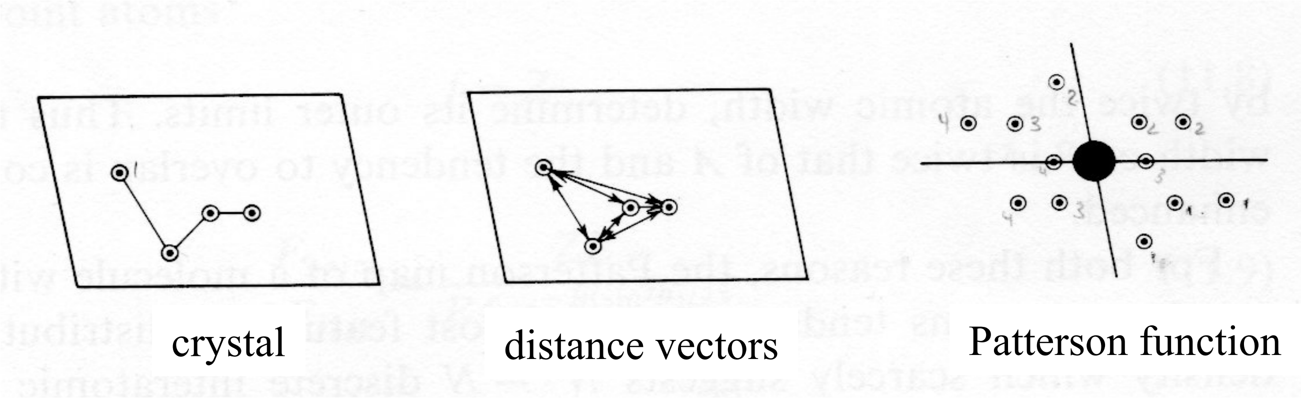
Realisation of a crystal structur determination

6a. Determin. of the phases α_{hkl} of the structure amplitudes $|Fo_{hkl}|$
→ phase determination (phase problem of structure analysis)

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

$$P_{(uvw)} = (1/V)\cdot\Sigma|F_{hkl}|^2\cos2\pi(hu+kv+lw)$$

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 structur determination

6b. Determin. of the phases α_{hkl} of the structure amplitudes $|Fo_{hkl}|$

- direct methodes for phase determination

  phases α_{hkl} and intensity distribution are not indipendant from each other → allowes determination of the phases α_{hk}l

  e.g. $F(hkl) \sim \Sigma\Sigma\Sigma F(h'k'l')\cdot F(h-h',k-k',l-l')$ (Sayre, 1952)

  oder $S(F_{hkl}) \sim S(F_{h'k'l'})\cdot S(F_{h-h',k-k',l-l'})$ (S = sign of F)

  direct methodes today are the most important methodes for the solving the phase problem of structur analysis/determination

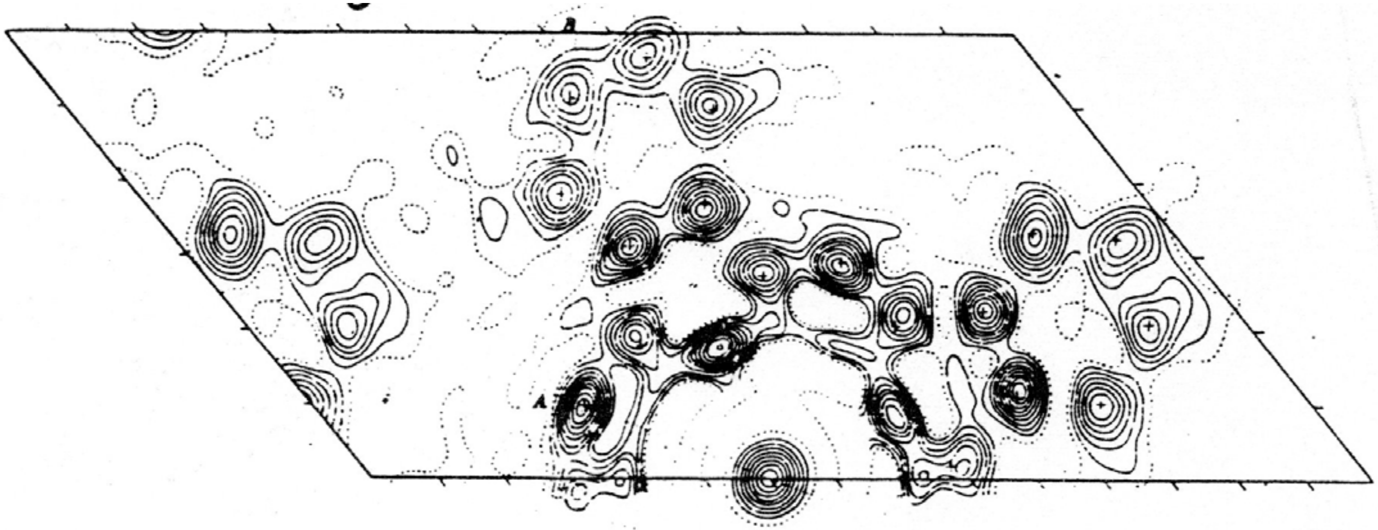
- anomalous dispersion methodes use the phase and intensity differences in the scattering near and far from absorption edges (measuring with X-rays of different wave lengths necessary)

Realisation of a crystal structur determination

7. Calculation of the electron density distribution function

$\delta(xyz) = (1/V)\cdot\Sigma\ |Fo_{hkl}|\cdot\exp(i\alpha_{hkl}\cdot\exp(-2\pi i(hx+ky+lz))$ of the

unit cell from the structure amplitudes $|Fo_{hkl}|$ and the phases α_{hkl} of the reflections hkl (using B and K) → Fourier synthesis



Platin-Phthalocyanin, $PtC_{32}H_{16}N_8$: Elektronendichteprojektion $\rho(xz)$.

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

Realisation of a crystal structur determination

8. Calculation of the structure factors Fc_{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

$$Fc_{hkl} = \Sigma f_j \cdot \exp(2\pi i(hx_j+ky_j+lz_j))$$

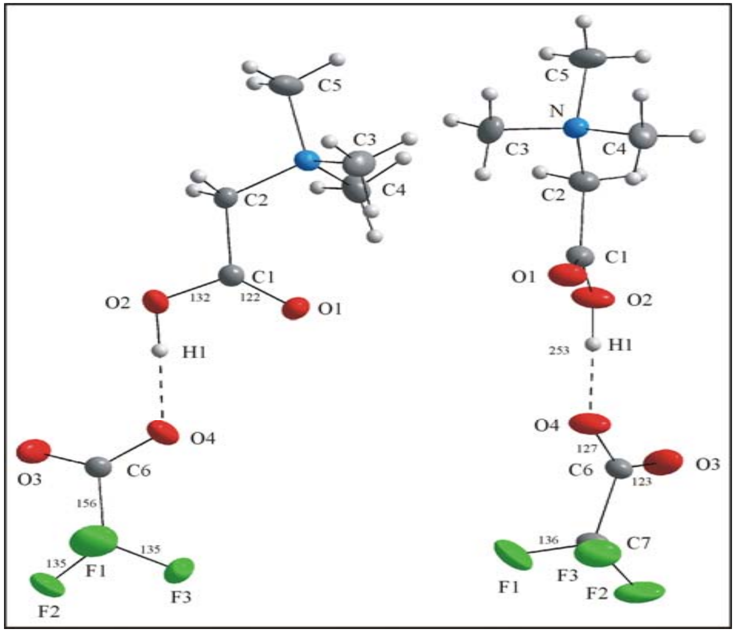
9. Refinement of the scale factor K, the temperature parameter B (or of the individuel B_j of the atoms j of the unit cell) and of the atomic coordinates x_j,y_j,z_j by use of the least squares method, LSQ via minimising the function

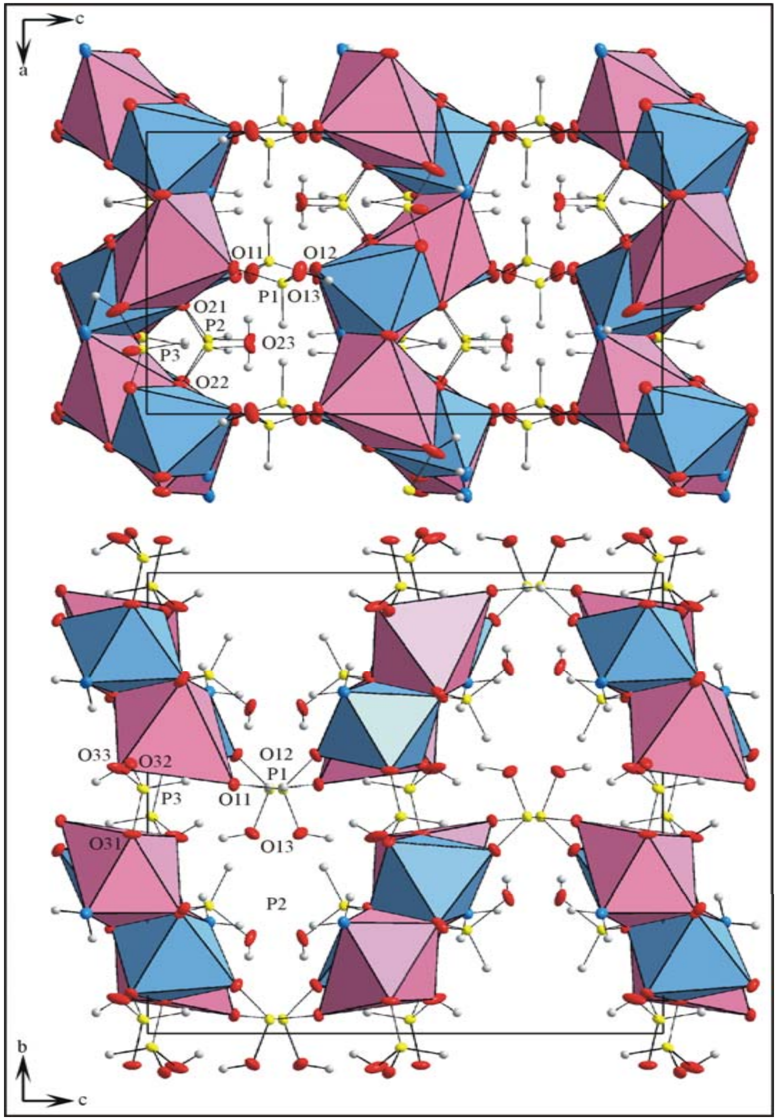
$$(\Delta F)^2 = (|F_o| - |F_c|)^2 \text{ for all measured reflections hkl}$$

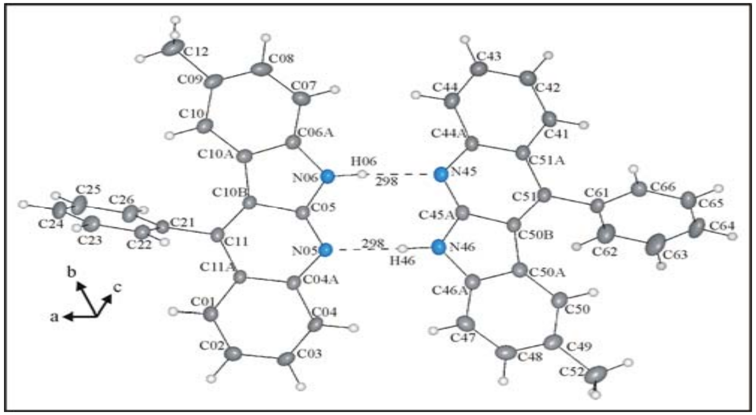
agreement factor: $R = \Sigma|(|F_o| - |F_c|)|/\Sigma|F_o|$

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

Results


C5
C3
C4
C2
C1
O2
132
122
O1
H1
O4
O3
C6
156
135
135
F1
F2
F3
C5
N
C3
C4
C2
C1
O1
O2
253
H1
O4
127
C6
O3
123
136
C7
F1
F3
F2


c
a
O11
O12
P1
O13
O21
P2
P3
O23
O22
O33
O32
O12
P1
P3
O11
O31
O13
P2
b
c


C12
C08
C09
C07
C10
C06A
C10A
H06
N06
298
N45
C44A
C43
C44
C42
C41
C51A
C10B
C05
C25
C26
C24
C21
C23
C22
C11
N05
298
H46
N46
C45A
C51
C61
C66
C65
C64
C50B
C62
C63
C50A
C11A
C04A
C01
C04
C02
C03
C46A
C47
C48
C49
C50
C52
b
c
a

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	$3.1^\circ \leq \Theta \leq 30.4^\circ$
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) º		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[U11(ha*)2 +…+ 2U12hka*b*]}

Results

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

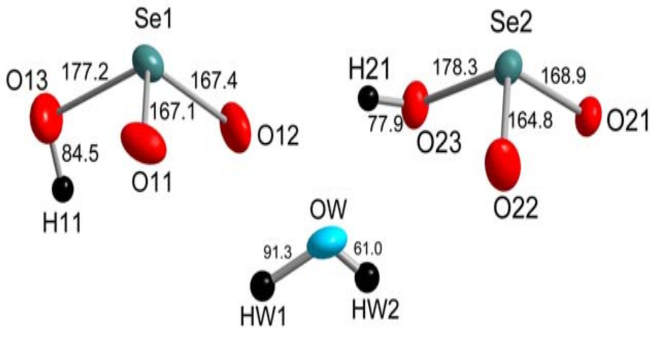
CsO$_9$ polyhedron				
Cs-O11	316.6(3)		O22-Cs-OW	78.76(8)
Cs-O13	318.7(4)		O22-Cs-O12	103.40(9)
Cs-O22	323.7(3)		O23-Cs-O11	94.80(7)
Cs-O23	325.1(3)		O13-Cs-O11	42.81(8)
Cs-OW	330.2(4)		O11-Cs-O23	127.96(8)
Cs-O21	331.0(3)		O13-Cs-O22	65.50(9)
Cs-O12	334.2(4)		O22-Cs-O22	66.96(5)
Cs-O22	337.1(4)		O11-Cs-OW	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)

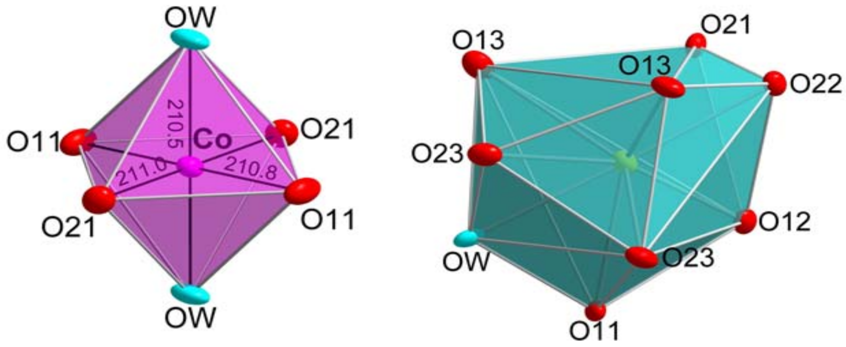
Symmetry codes:

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

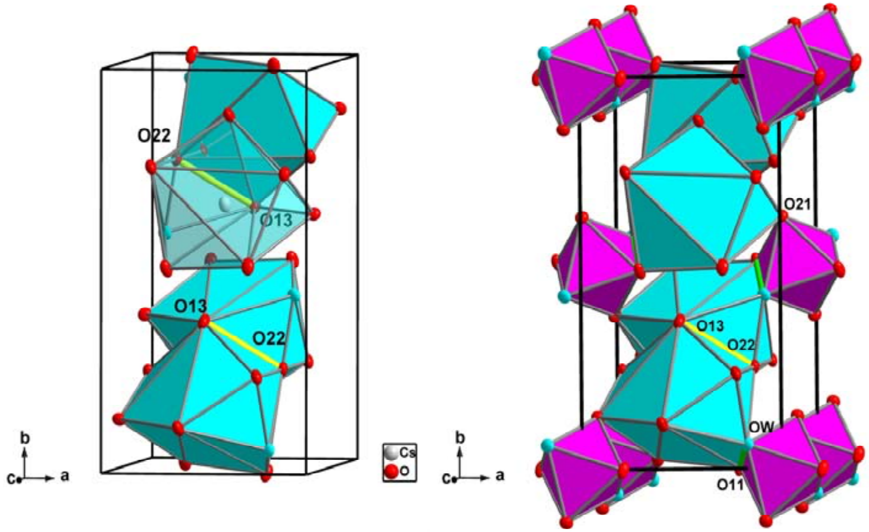
Results



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

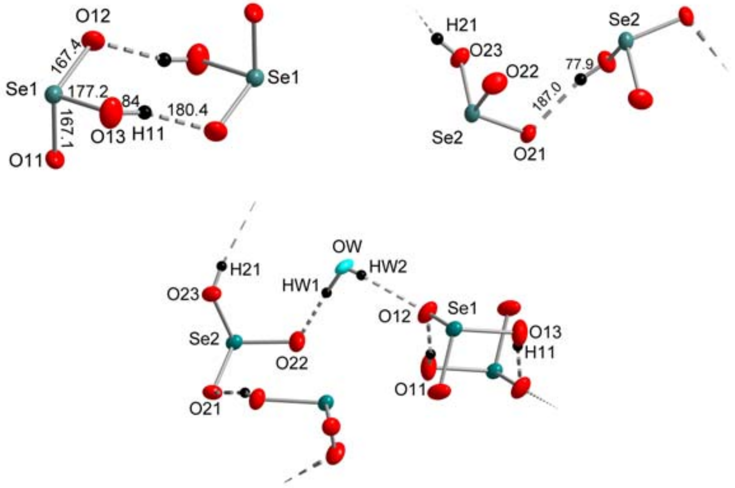


Coordination polyhedra of $Cs_2Co(HSeO_3)_4 \cdot 2H_2O$

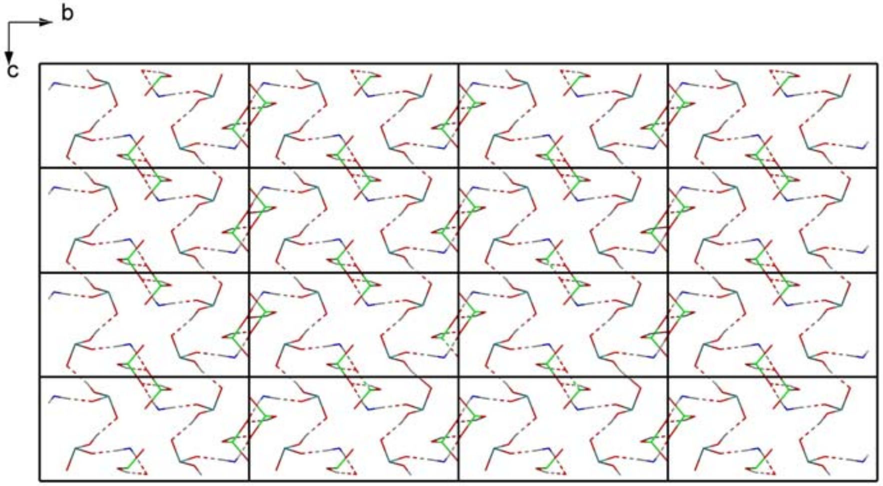


Connectivity of the coordination polyhedra of $Cs_2Co(HSeO_3)_4 \cdot 2H_2O$

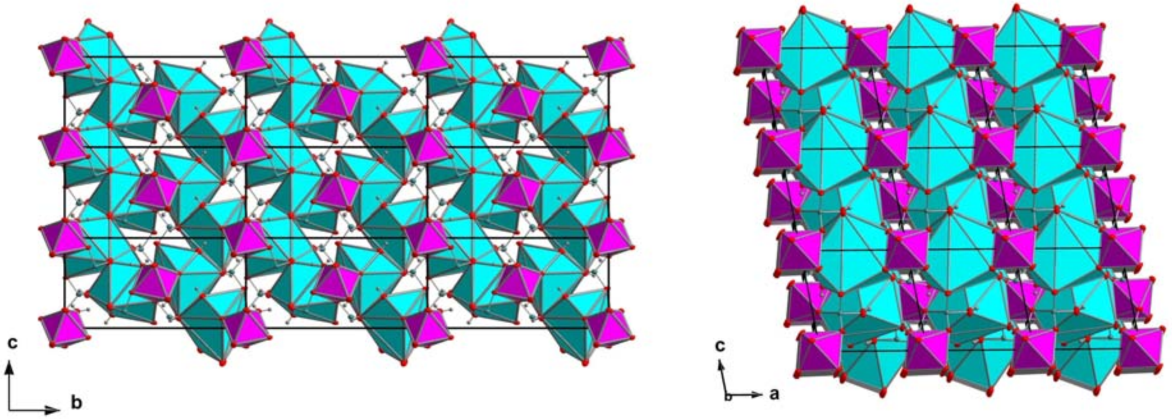
Results



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

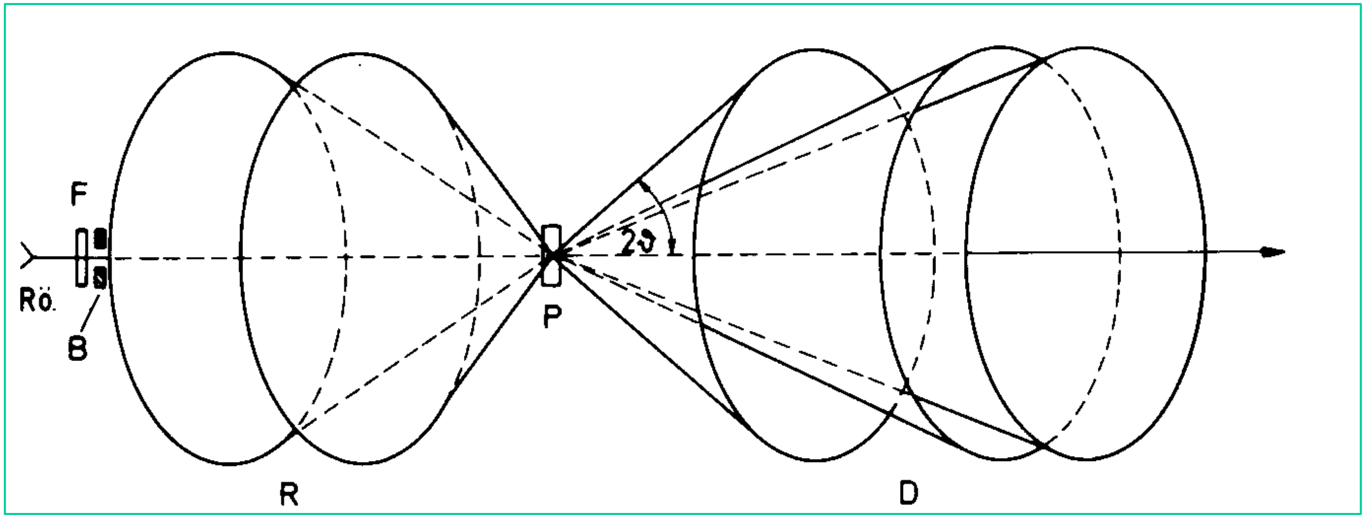


Anions and hydrogen bonds of $Cs_2Co(HSeO_3)_4{\cdot}2H_2O$



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

4.3 X-ray powder diffraction (principle)

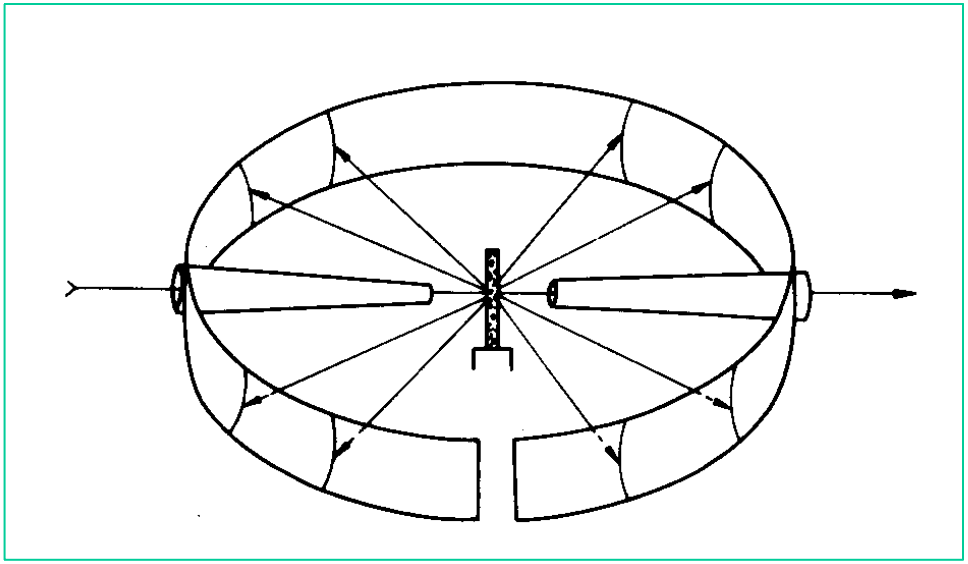


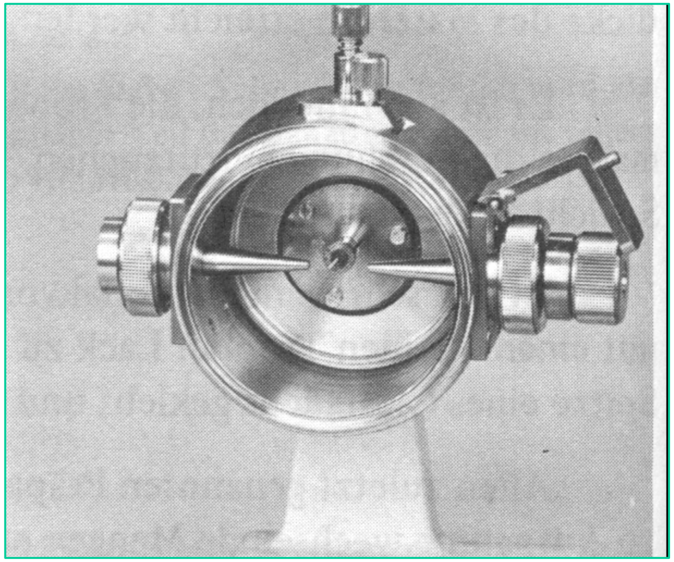
Because of the random orientation of the crystallites in a powder sample, X-ray diffraction results in cones of central angle θ_{hkl} with high intensity of scattered beams each representing a set of lattice planes hkl with the corresponding Bragg angle θ_{hkl} and spacing d_{hkl}.

Above conditions are due to **Bragg's** law/equation.

$$\boxed{\frac{1}{d_{hkl}} = \frac{2 \cdot \sin \theta_{hkl}}{\lambda}} \quad \text{or} \quad \boxed{\lambda = 2 \cdot d_{hkl} \cdot \sin \theta_{hkl}} \quad \text{or} \quad \boxed{d_{hkl} = \frac{\lambda}{2 \cdot \sin \theta_{hkl}}}$$

4.3 X-ray powder diffraction (Debye-Scherrer Geometry)



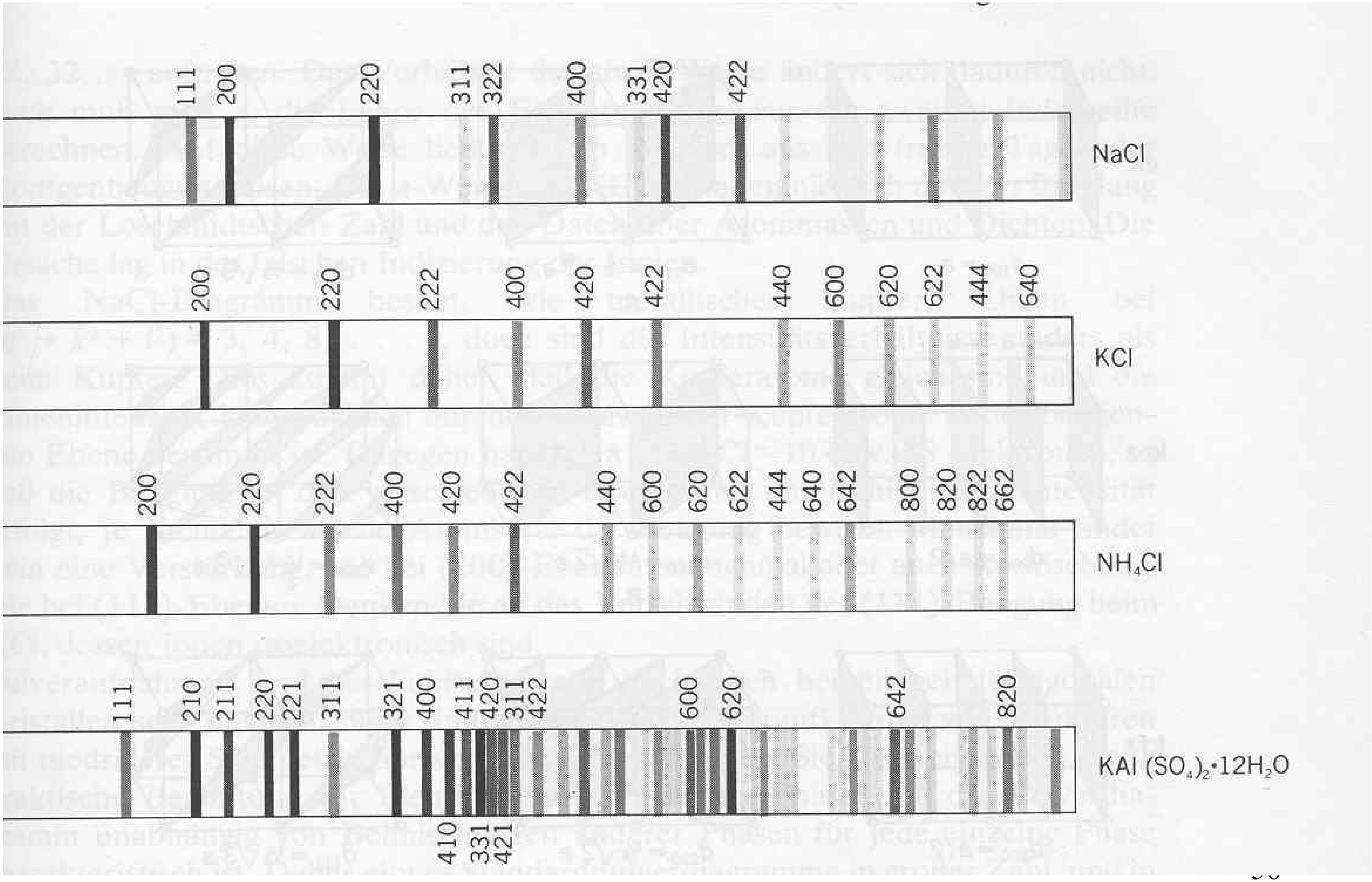


←----------- $180^{o} \geq 2\theta_{hkl} \geq 0^{o}$--------→

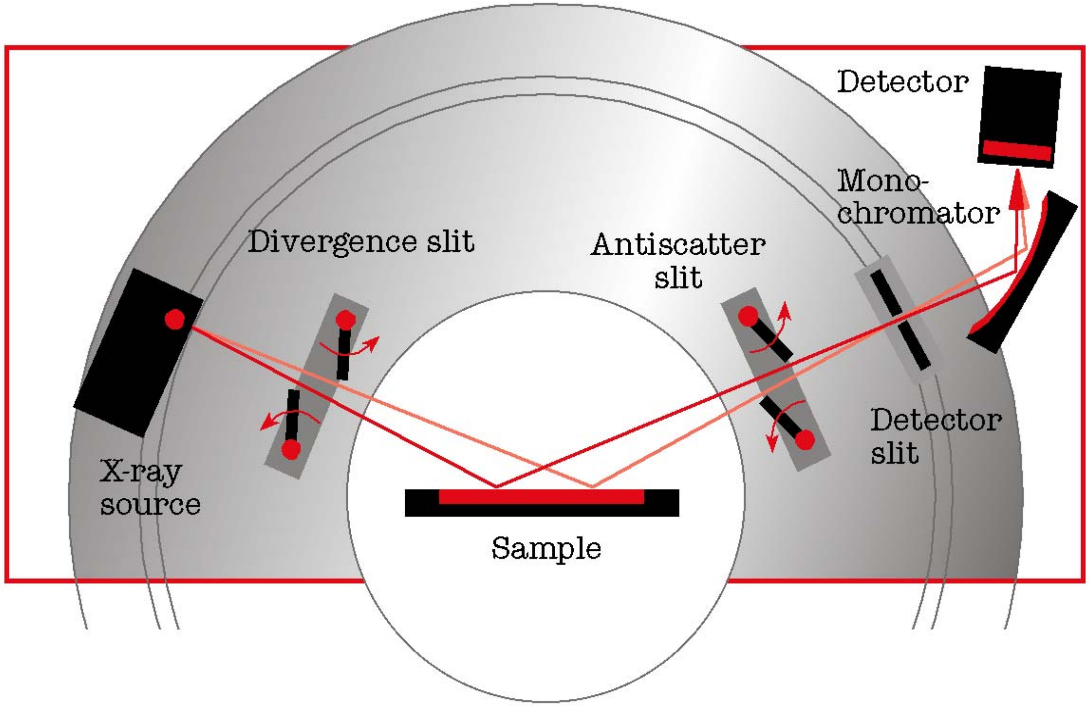
← $360\text{-}4\theta_{hkl}$ →

← $4\theta_{hkl}$ →

4.3 X-ray powder diagrams: Miller indices of Bragg reflections



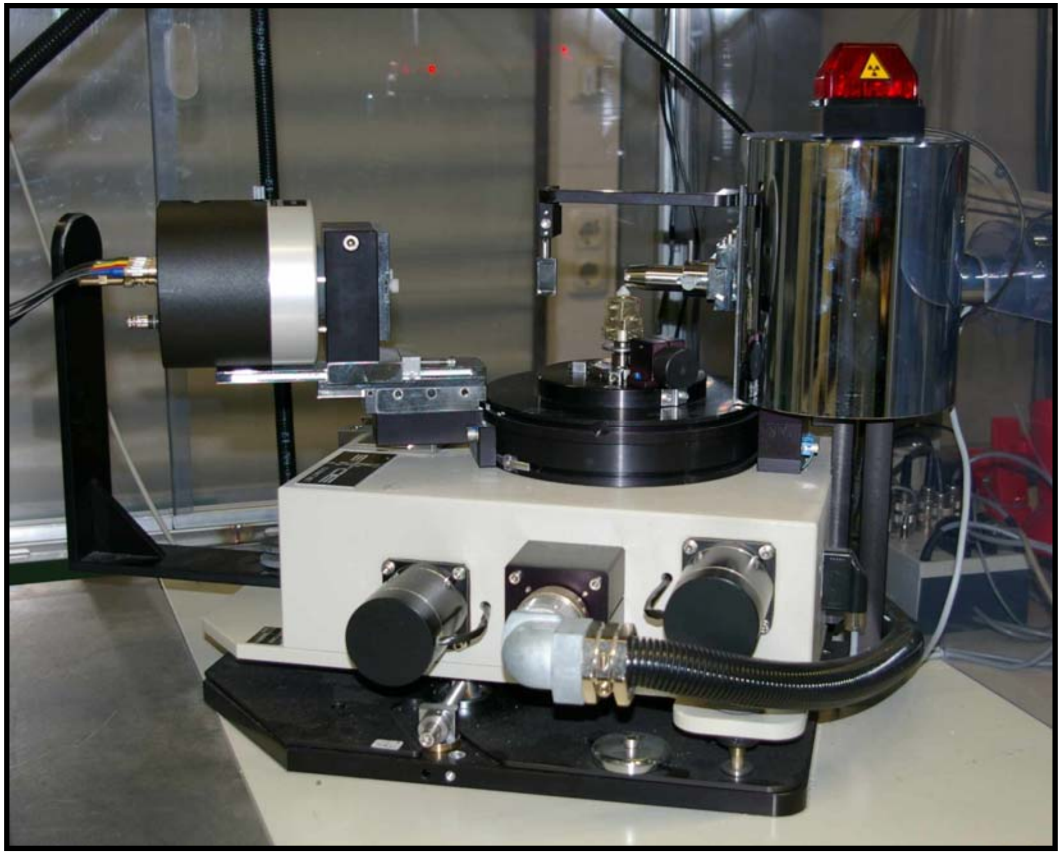
4.3 X-ray powder diffraction (Bragg-Brentano diffractometer)



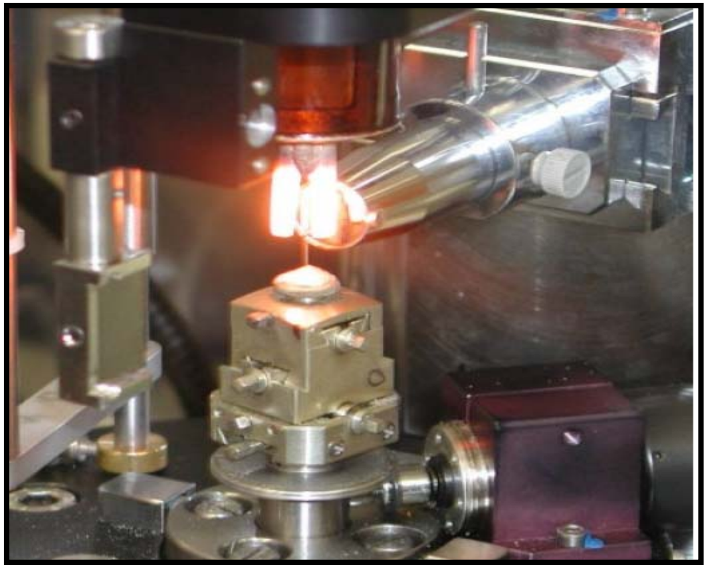
Bragg-Brentano diffractometer

4.3 X-ray powder diffraction (polycrystalline samples)

Powder sample holder



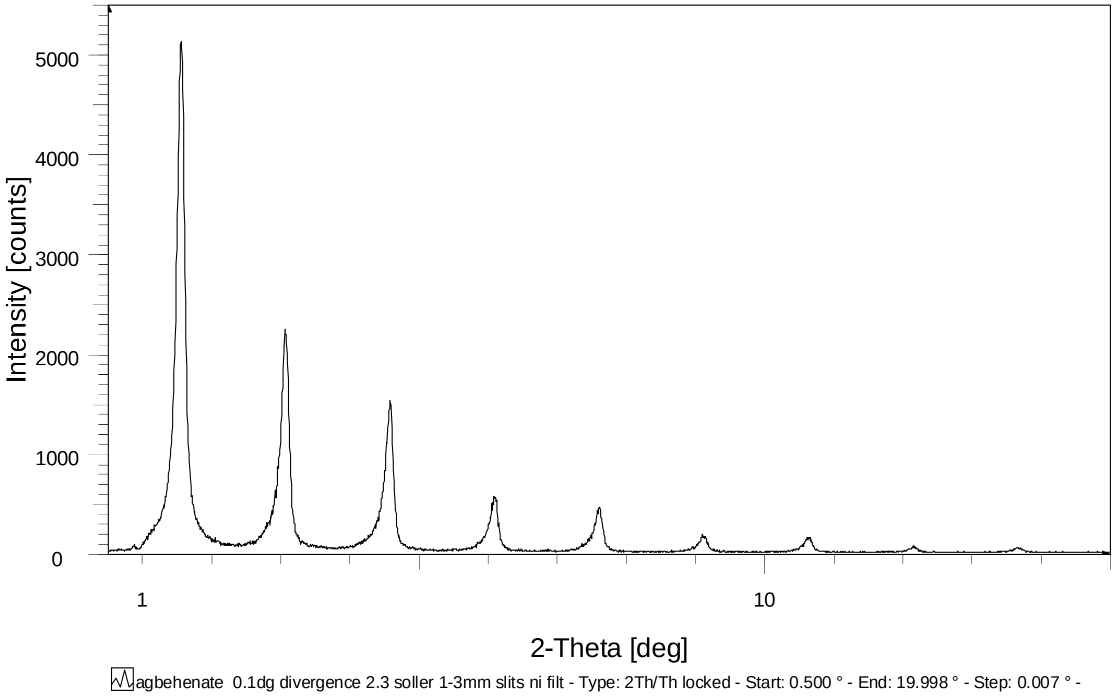
Powder diffractometer (STOE)



Goniometer head

4.3. X-ray powder diffraction (Bragg-Brentano Geometry)

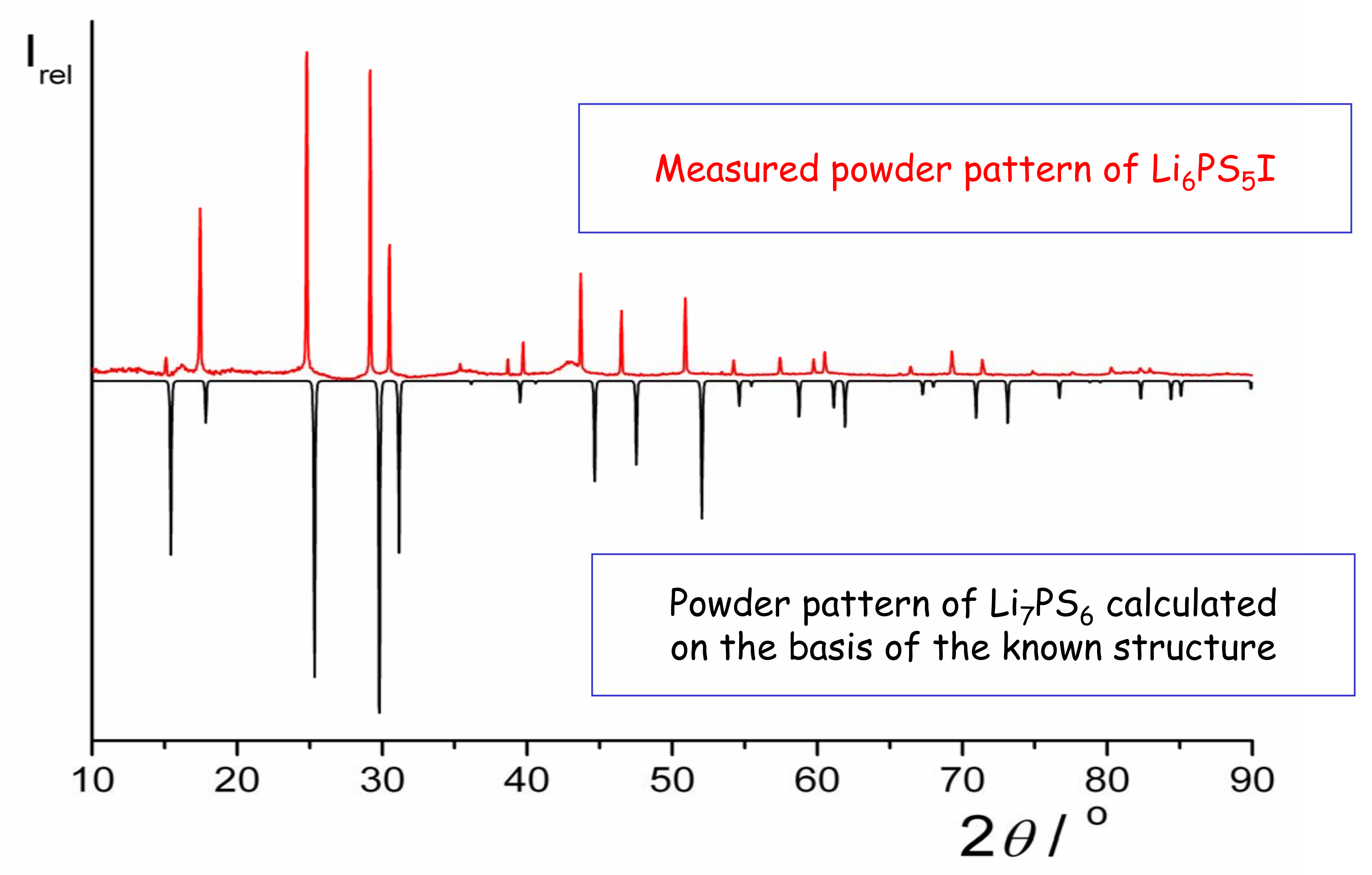
Silver-Behenate



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.**

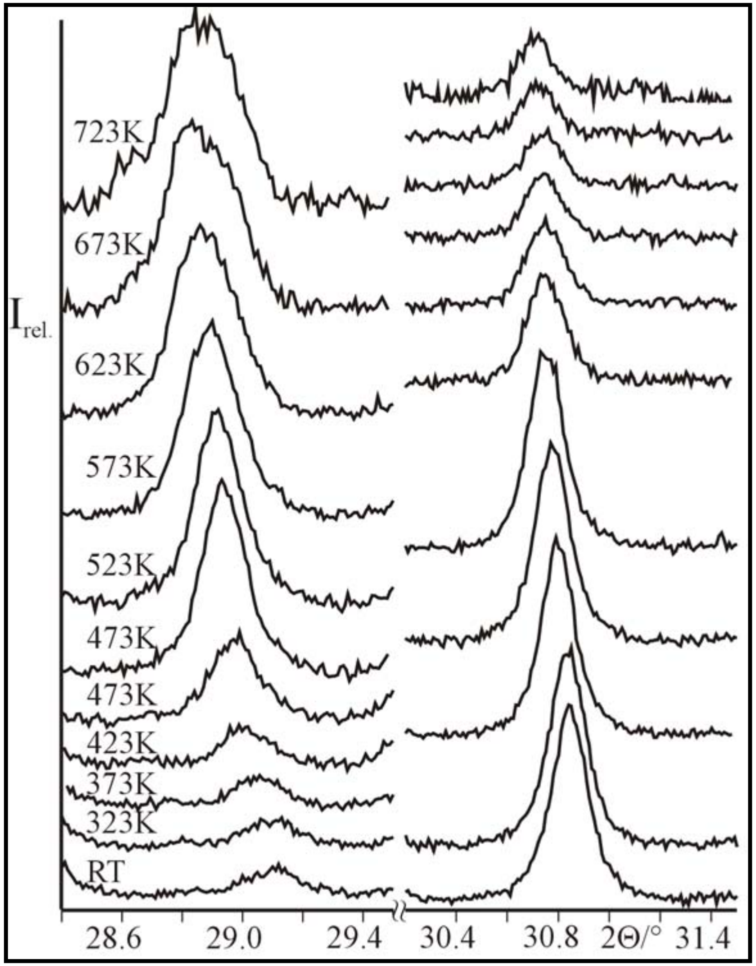
4.3 X-ray powder diffraction (analysis)



Measured powder pattern of Li_6PS_5I

Powder pattern of Li_7PS_6 calculated on the basis of the known structure

4.3 X-ray powder diffraction

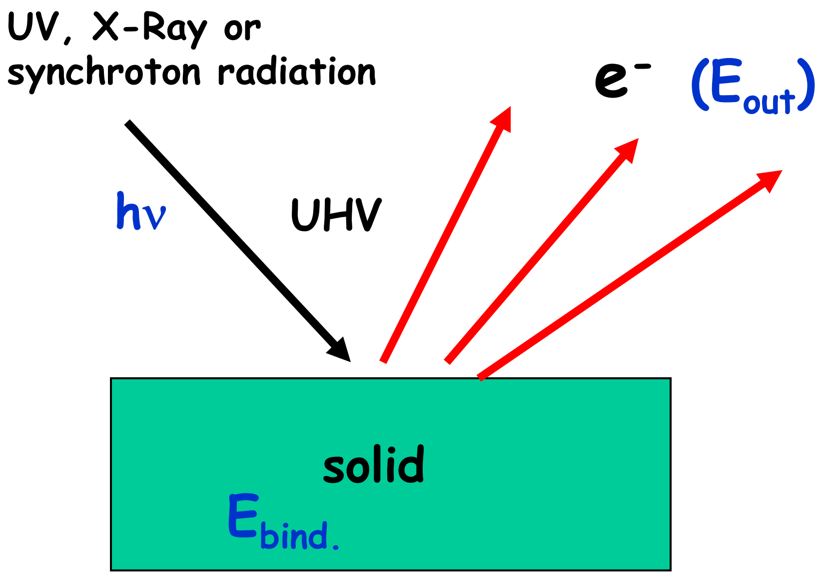


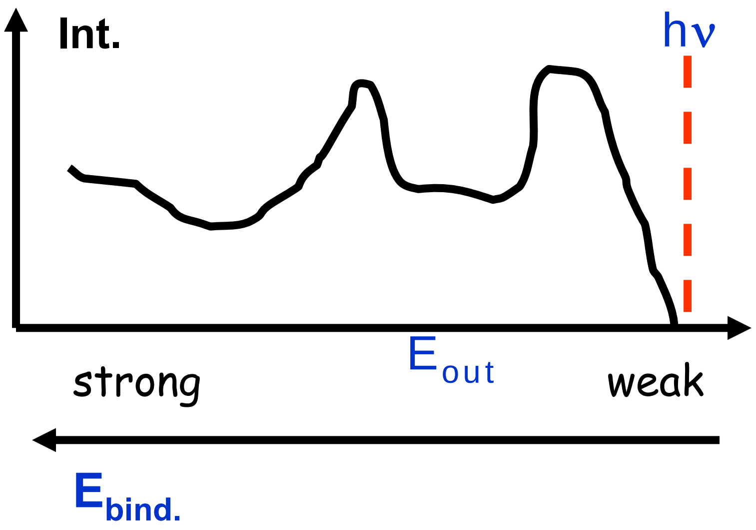
Temperature dependent X-ray powder diffraction diagram

4.4 Photoemission or Photoelectron spectroscopy: ESCA

ESCA = Electron Spectroscopy for Chemical Analysis

Basic equation: $E_{out} = h\nu - E_{bind.}$





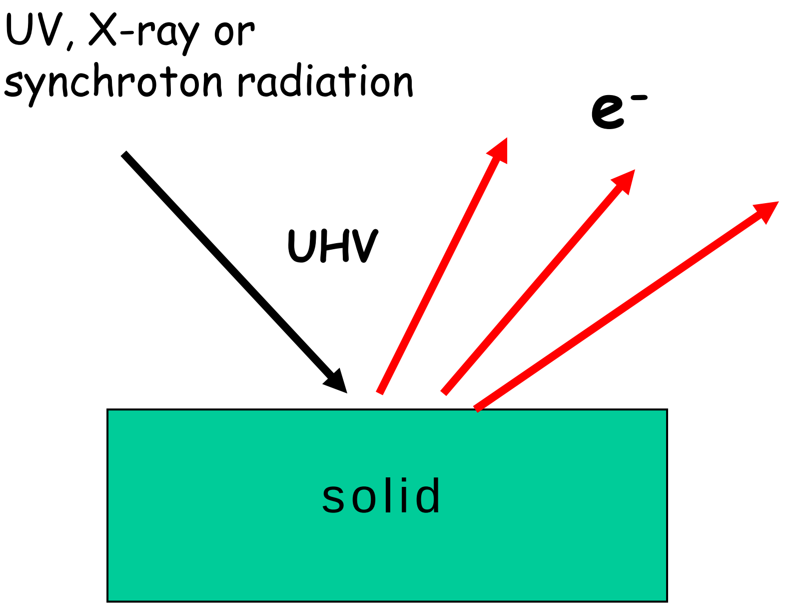
The spectrum of the emitted electrons is analyzed with respect to:

- energy
- momentum
- spin

- the higher the binding energy ($E_{bind.}$) the lower the E_{out} !

- ESCA is particularly a surface sensitive method (UHV !)

4.4 ESCA measurement for solids: band structure

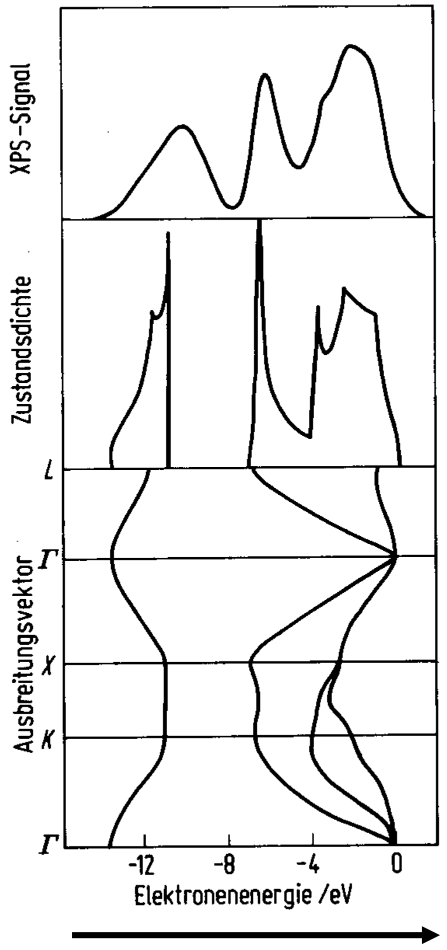


UV, X-ray or
synchroton radiation

e⁻

UHV

solid



energy

UPS spectrum

DOS
(below E_F)

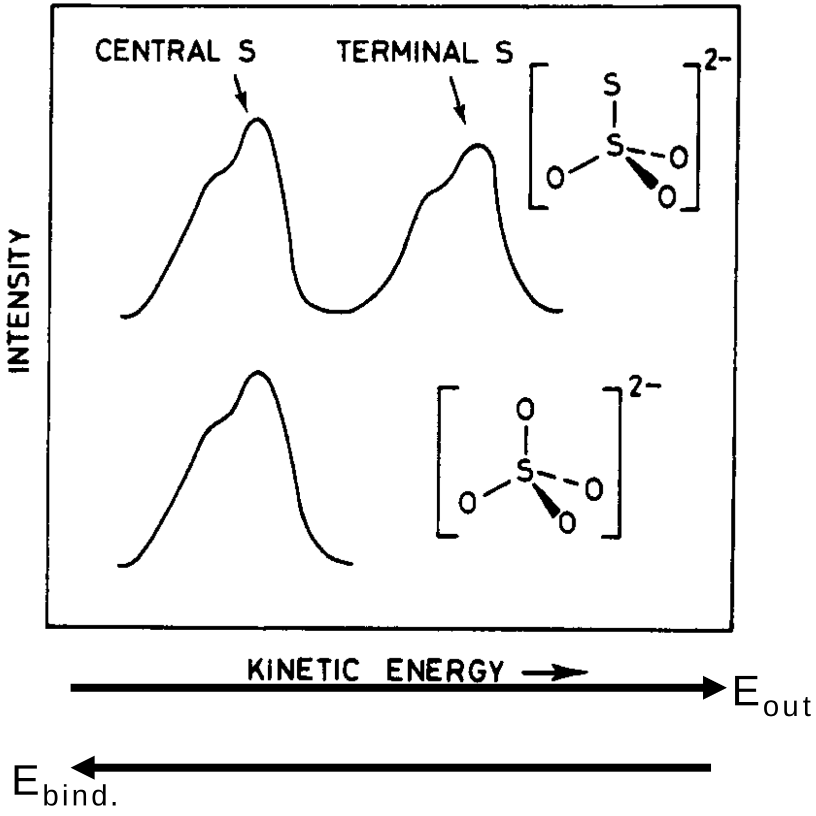
Band structure

(chemical bonding in
different directions of a
crystalline solid)

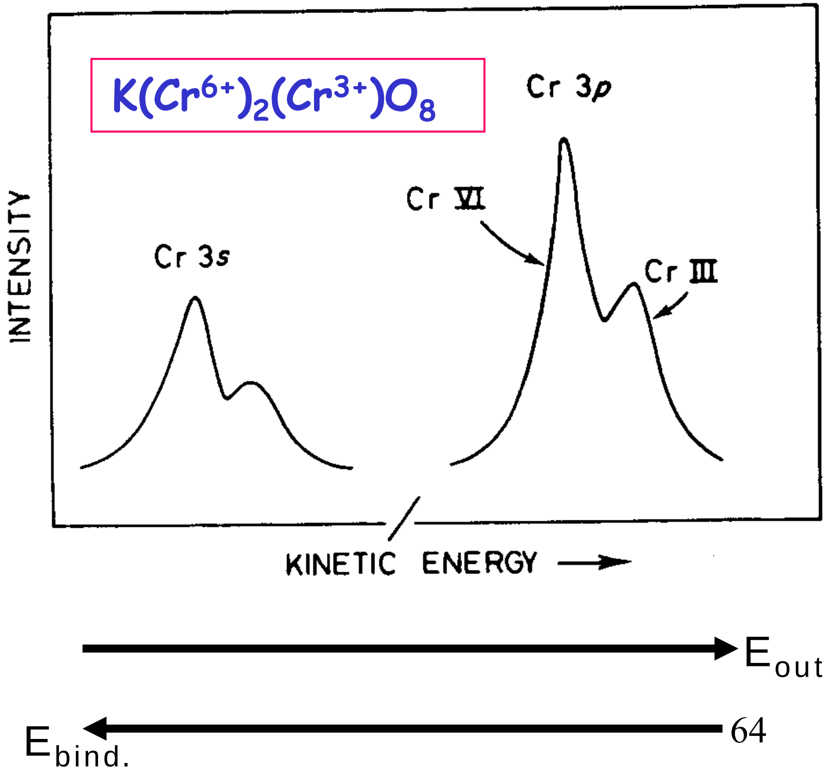
4.4 Typical ESCA spectra for molecules: functionality of atoms in molecules

- Analysis of the energy levels of electrons in molecules („chemical shift“)

$S_2O_3^{2-}$



KCr_3O_8

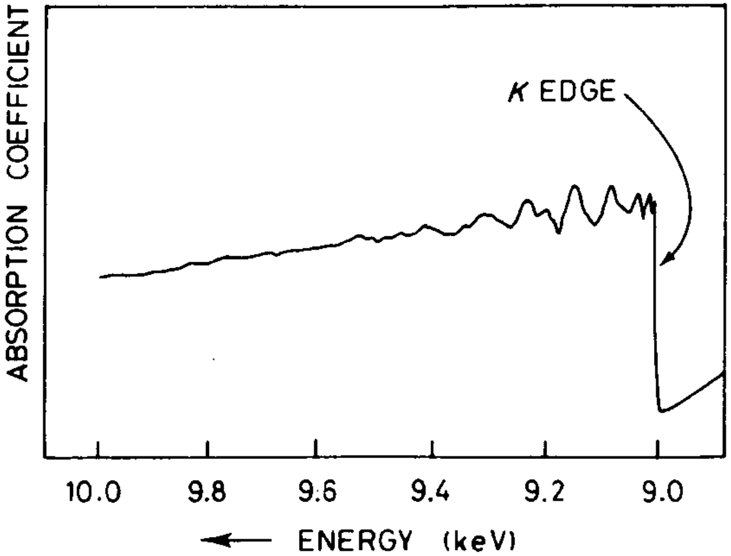


$K(Cr^{6+})_2(Cr^{3+})O_8$

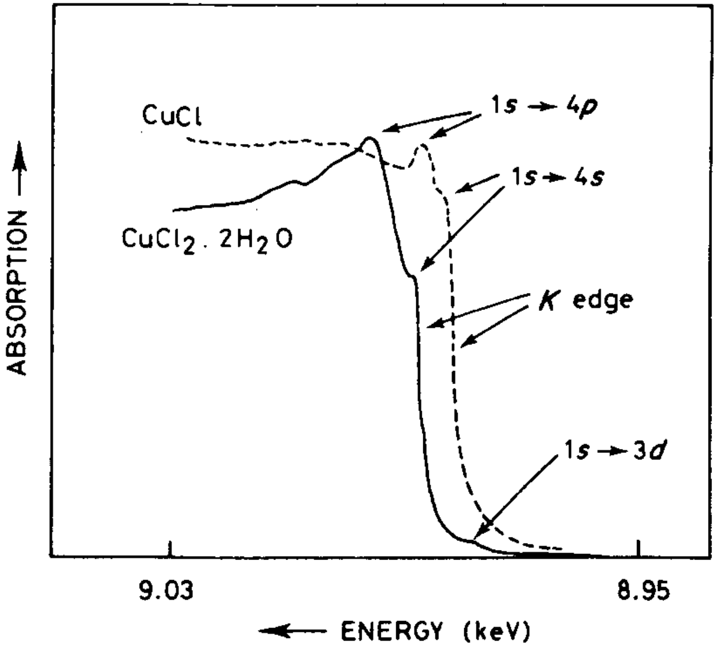
4.5 X-ray absorption spectroscopy: EXAFS, XANES

Spectroscopical methods associated with specific physical effects at/near characteristical X-ray absorption edges:

EXAFS: Extended X-Ray Absorption Fine Structure
XANES: X-Ray Absorption Near Edge Structure
- tunable synchroton radiation in the X-Ray region necessary



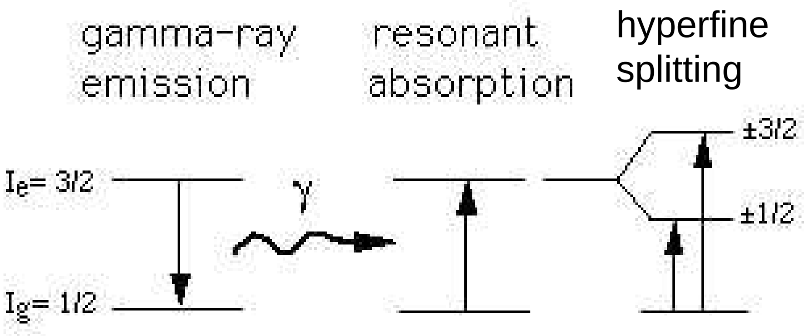
EXAFS spectrum of Cu (K edge)
(information about the coordination of Cu)



Near K edge structure of Cu in two Cu compounds (information about the oxidation state)

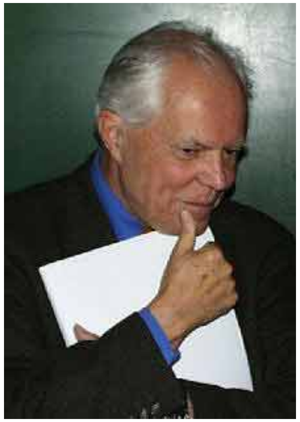
4.6 Moessbauer Spectroscopy

→ The nucleus of the specific isotope of an atom embdedded in a solid (e.g. ^{57}Fe = absorber) is excited by γ-rays emitted by an instable isotope of a neighbor element (e.g. ^{57}Co = source). Slow mechanical movement of the source modifies the emission energy (Doppler effect) and allows resonance absorption in the absorber. The resonance energy depends significantly on the chemical surrounding of the absorber atom



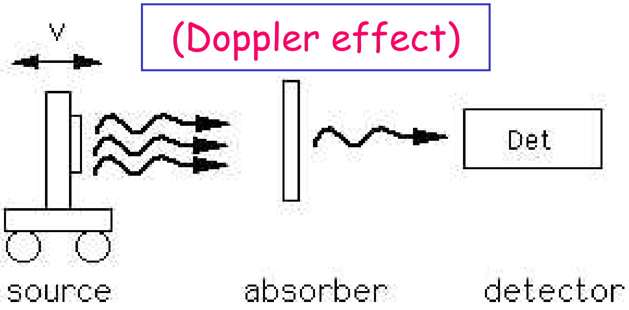
source:
e.g. ^{57}Co
(tunable)

absorber:
e.g. ^{57}Fe



R. Moessbauer
N.P. 1961

(Doppler effect)



frequently applied for
→ ^{57}Fe, ^{119}Sn, ^{127}J ...

→ chemical surrounding (symmetry, coordination number, oxidation state, magnetism) of atoms with these nuclei in a solid can be probed in a highly sensitive way (~10^{-8} eV)

4.6 Moessbauer Spectroscopy

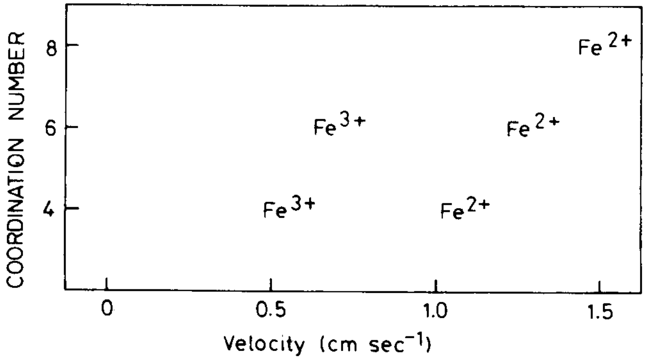


Fig. 4.27 Chemical shifts in iron-containing compounds. (From Bancroft, *Mössbauer Spectroscopy*, McGraw-Hill, 1973)

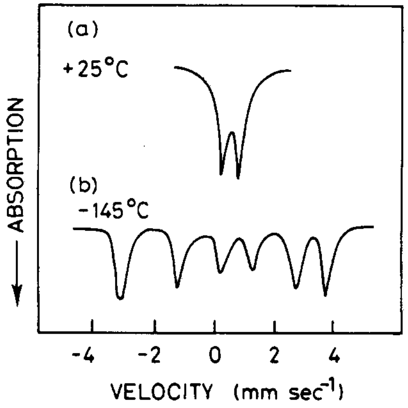


Fig. 4.28 Mössbauer spectrum of $KFeS_2$ (a) above and (b) below the Néel temperature. (From Greenwood, *Chem. Brit.*, **3**, 56, 1967)

Two major informations from Moessbauer spectra:

a) „Chemical Shift"

(not to be confused with the same term in NMR and ESCA)

→ oxidation state

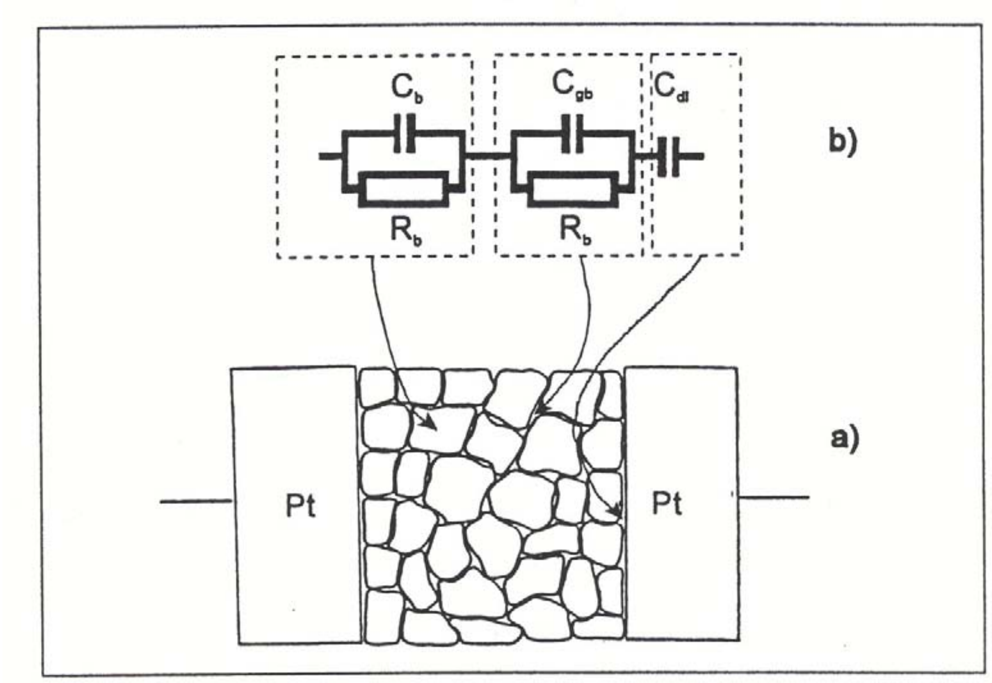
b) Hyperfine Splitting

→ magnetic interactions, symmetry

4.7 Impedance spectroscopy (basic aspects)

Purpose: Exploring the electrical behavior of a microcrystalline solid sample as function of an alternating current (ac) with a variable frequency.

(note: difference between ac-/dc- and ionic/electronic conduction !!!)



Three basically different regions for the exchange interactions between current and sample:

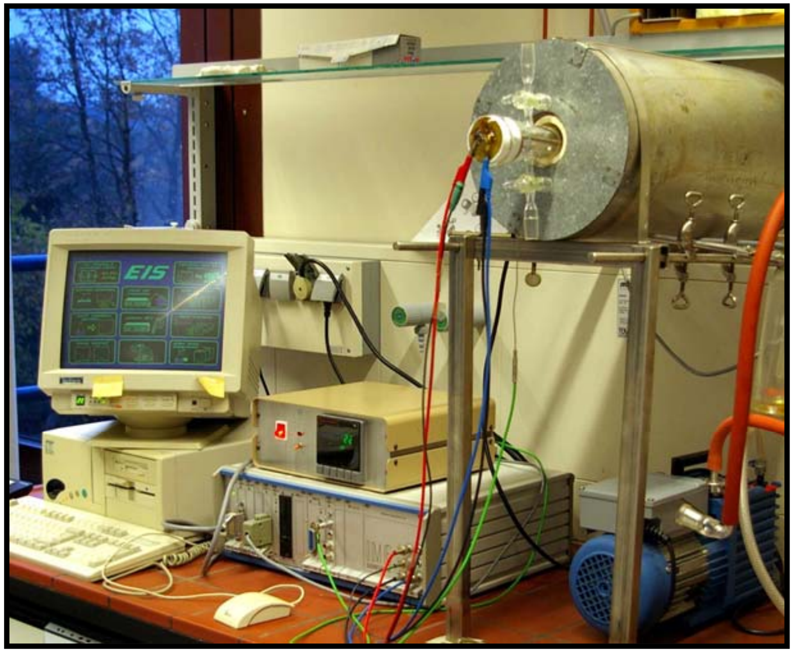
a) inside the grains („bulk“)

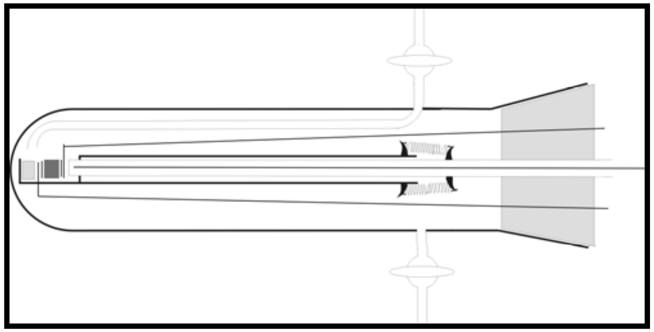
b) at grain boundaries

c) surface of the electrodes

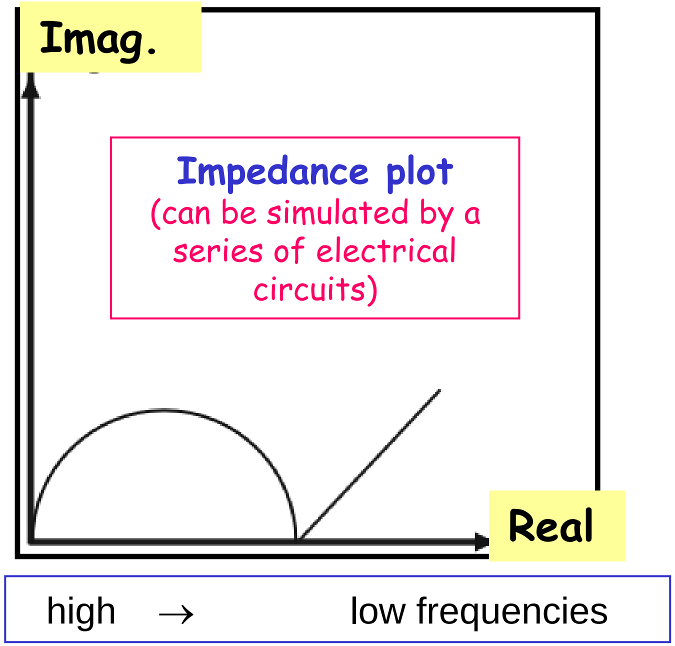
The electrical behavior is simulated by a suitable combination of RC circuits: R = resistivity, C = capacity

4.7 Impedance device and impedance plot for an ionic conductor





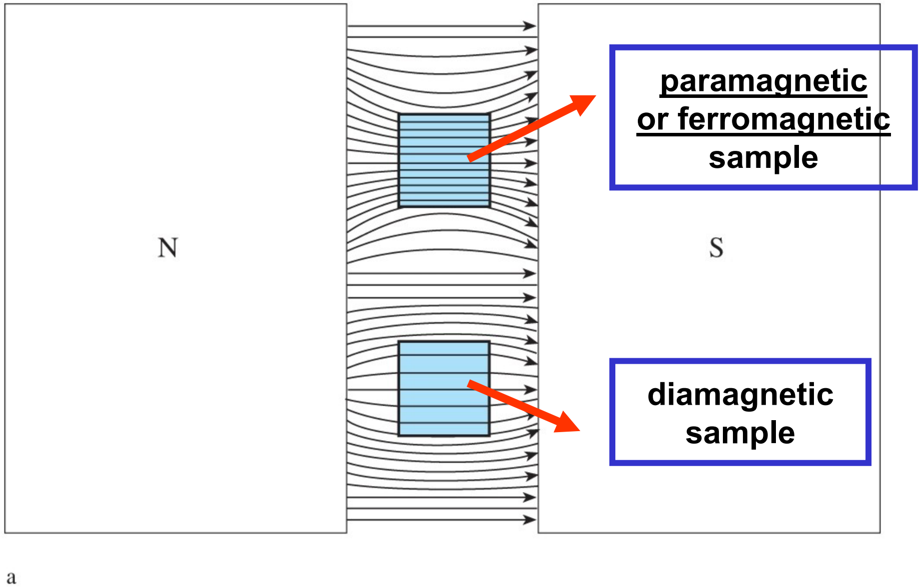
Idealized impedance plot (Nyquist diagram) for an ionic conductor



Impedance plot
(can be simulated by a series of electrical circuits)

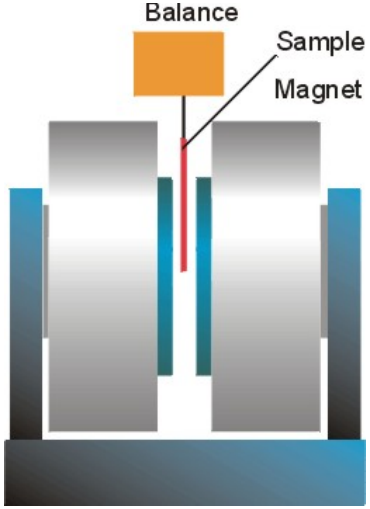
high → low frequencies

4.8 Magnetic measurements: Gouy-balance and squid magnetometer



paramagnetic or ferromagnetic sample

diamagnetic sample



Gouy balance

SQUID: Superconducting Quantum Interference Device

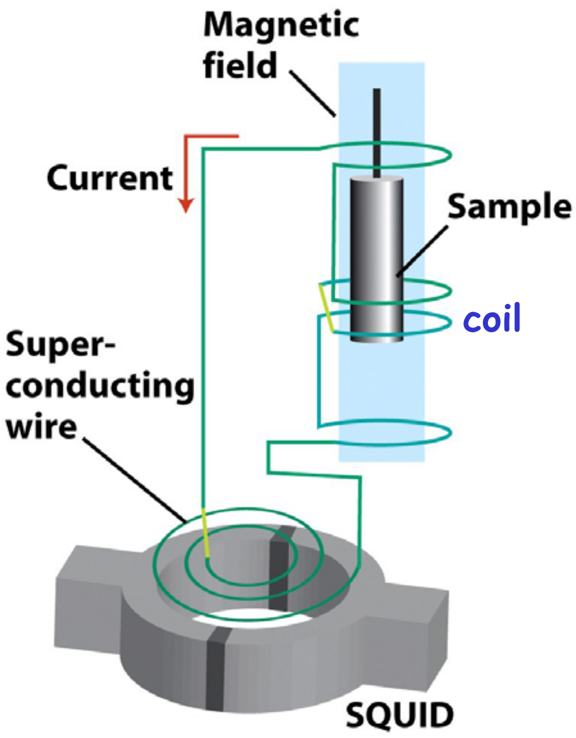


Figure 6-29
Shriver & Atkins Inorganic Chemistry, Fourth Edition
© 2006 by D. F. Shriver, P. W. Atkins, T. L. Overton, J. P. Rourke, M. T. Weller, and F. A. Armstrong

Based on the **quantization of magnetic flux** by a „weak link" (**Josephson contact**) in a superconducting wire (loop) that allows the tunneling of **„Cooper pairs"**.

4.9 Thermal Analysis: DTA (Differential Thermal Analysis)

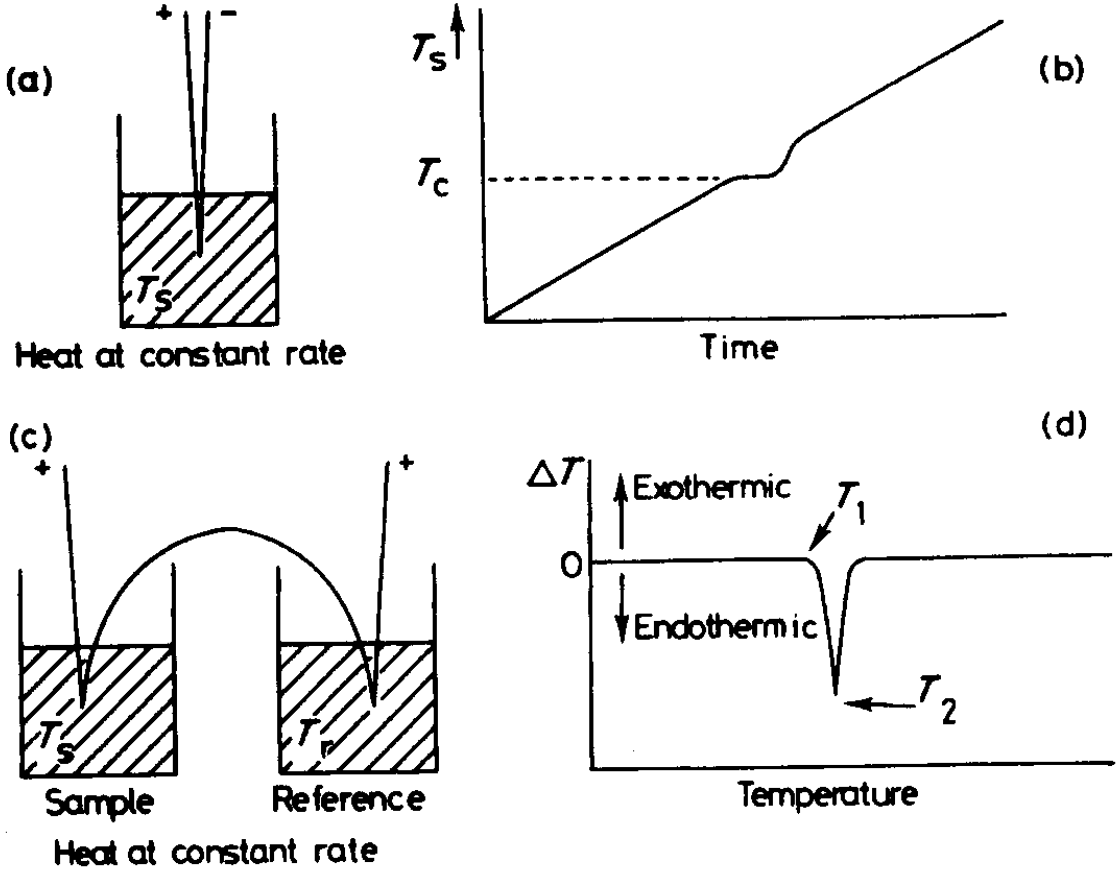
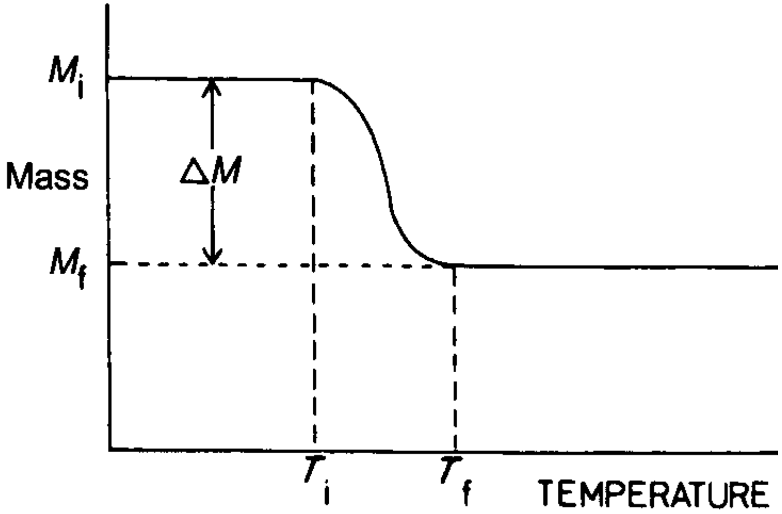
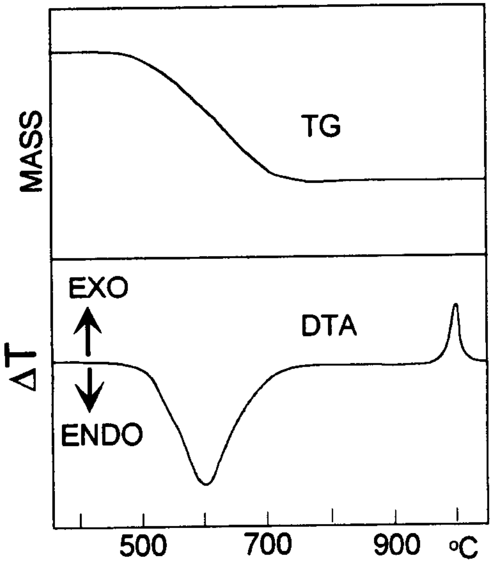


Fig. 4.31 The DTA method. Graph (b) results from the set-up shown in (a) and graph (d), a typical DTA trace, results from the arrangement shown in (c)

4.9 Thermal analysis: TG (Thermogravimetry)

(Mass change during heating or cooling, combinable with DTA)





Other variants of thermal analysis

:

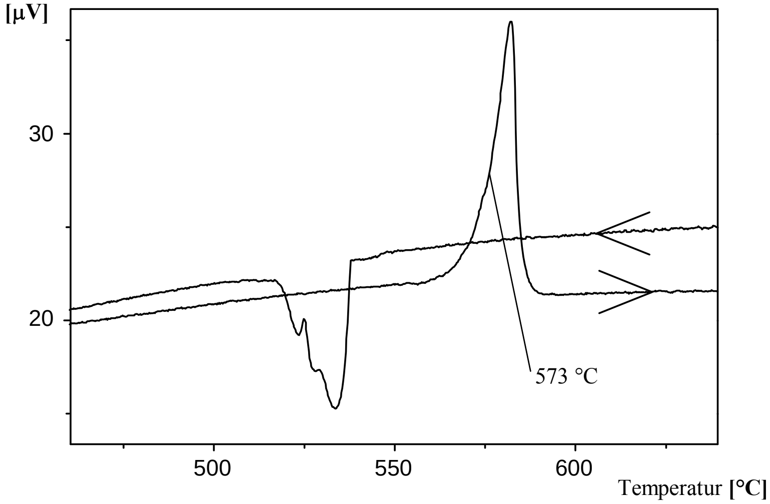
DSC: <u>D</u>ifferential <u>S</u>canning <u>C</u>alorimetry

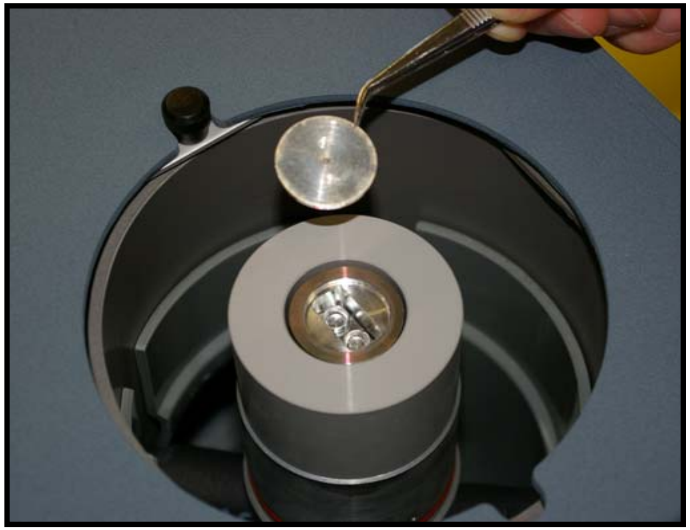
- Quantitative measurement of enthalpy changes

TMA: <u>T</u>hermo <u>M</u>echanical <u>A</u>nalysis (e.g. dilatometry)

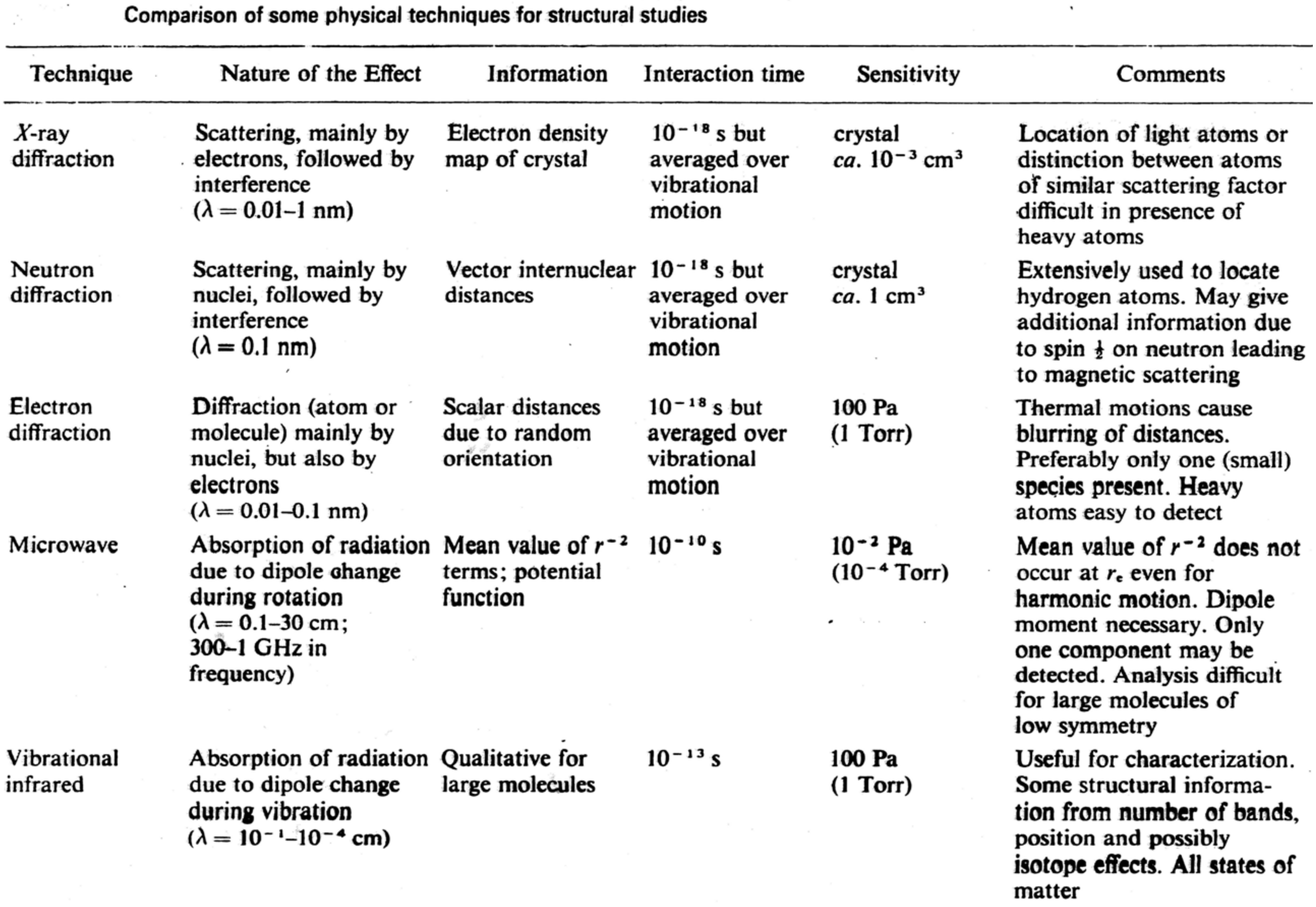
- Mechanical changes that occur upon temperature changes

4.9 Thermal analysis: DSC (Differential Scanning Calorimetry) (-170 °C to 700°C)





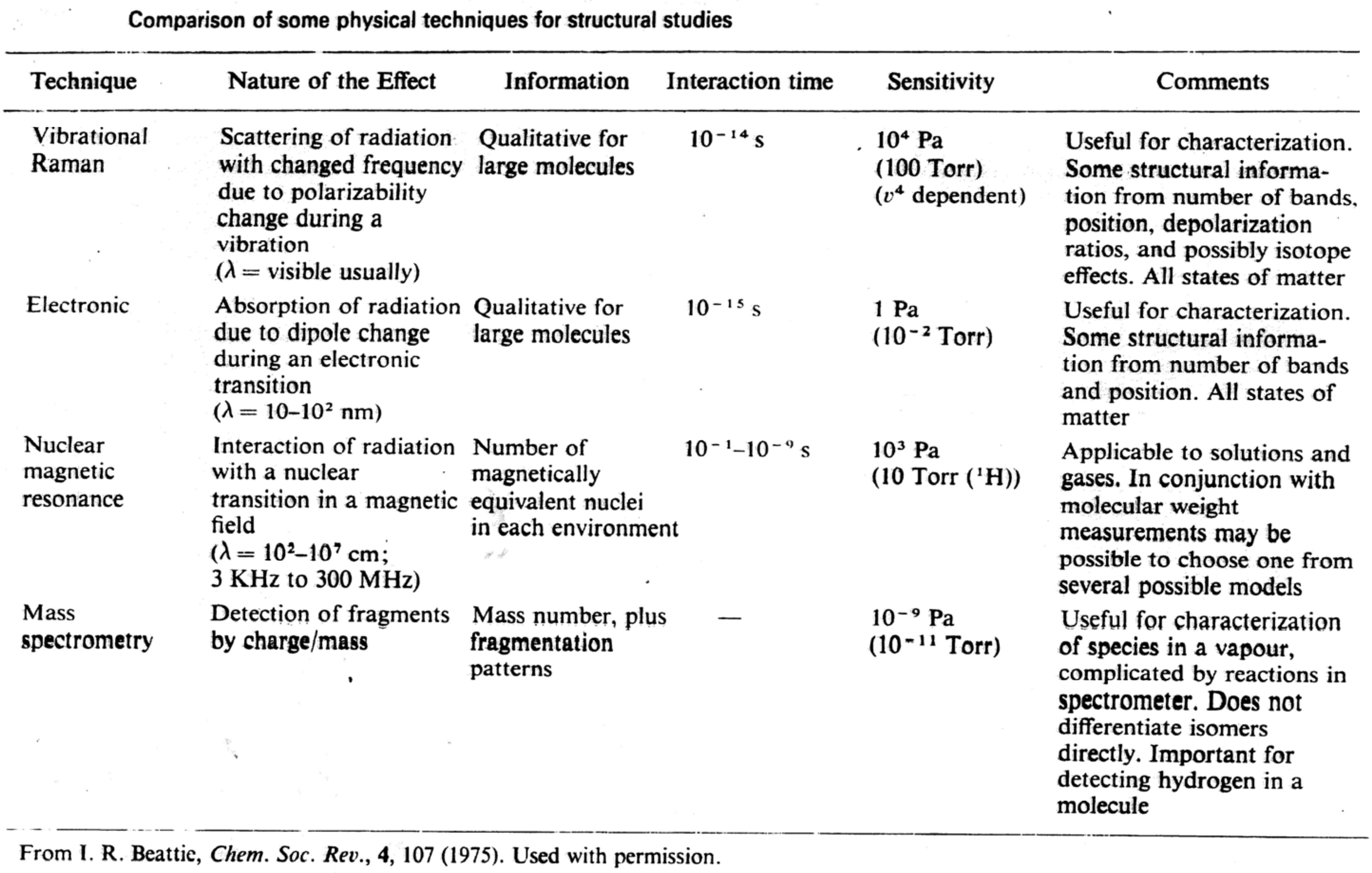
4.10 Comparison of some techniques for structural studies



Comparison of some physical techniques for structural studies

Technique	Nature of the Effect	Information	Interaction time	Sensitivity	Comments
X-ray diffraction	Scattering, mainly by electrons, followed by interference ($\lambda = 0.01–1$ nm)	Electron density map of crystal	10^{-18} s but averaged over vibrational motion	crystal *ca.* 10^{-3} cm^3	Location of light atoms or distinction between atoms of similar scattering factor difficult in presence of heavy atoms
Neutron diffraction	Scattering, mainly by nuclei, followed by interference ($\lambda = 0.1$ nm)	Vector internuclear distances	10^{-18} s but averaged over vibrational motion	crystal *ca.* 1 cm^3	Extensively used to locate hydrogen atoms. May give additional information due to spin $\frac{1}{2}$ on neutron leading to magnetic scattering
Electron diffraction	Diffraction (atom or molecule) mainly by nuclei, but also by electrons ($\lambda = 0.01–0.1$ nm)	Scalar distances due to random orientation	10^{-18} s but averaged over vibrational motion	100 Pa (1 Torr)	Thermal motions cause blurring of distances. Preferably only one (small) species present. Heavy atoms easy to detect
Microwave	Absorption of radiation due to dipole change during rotation ($\lambda = 0.1–30$ cm; 300–1 GHz in frequency)	Mean value of r^{-2} terms; potential function	10^{-10} s	10^{-2} Pa (10^{-4} Torr)	Mean value of r^{-2} does not occur at r_e even for harmonic motion. Dipole moment necessary. Only one component may be detected. Analysis difficult for large molecules of low symmetry
Vibrational infrared	Absorption of radiation due to dipole change during vibration ($\lambda = 10^{-1}–10^{-4}$ cm)	Qualitative for large molecules	10^{-13} s	100 Pa (1 Torr)	Useful for characterization. Some structural information from number of bands, position and possibly isotope effects. All states of matter

4.10 Comparison of some techniques for structural studies

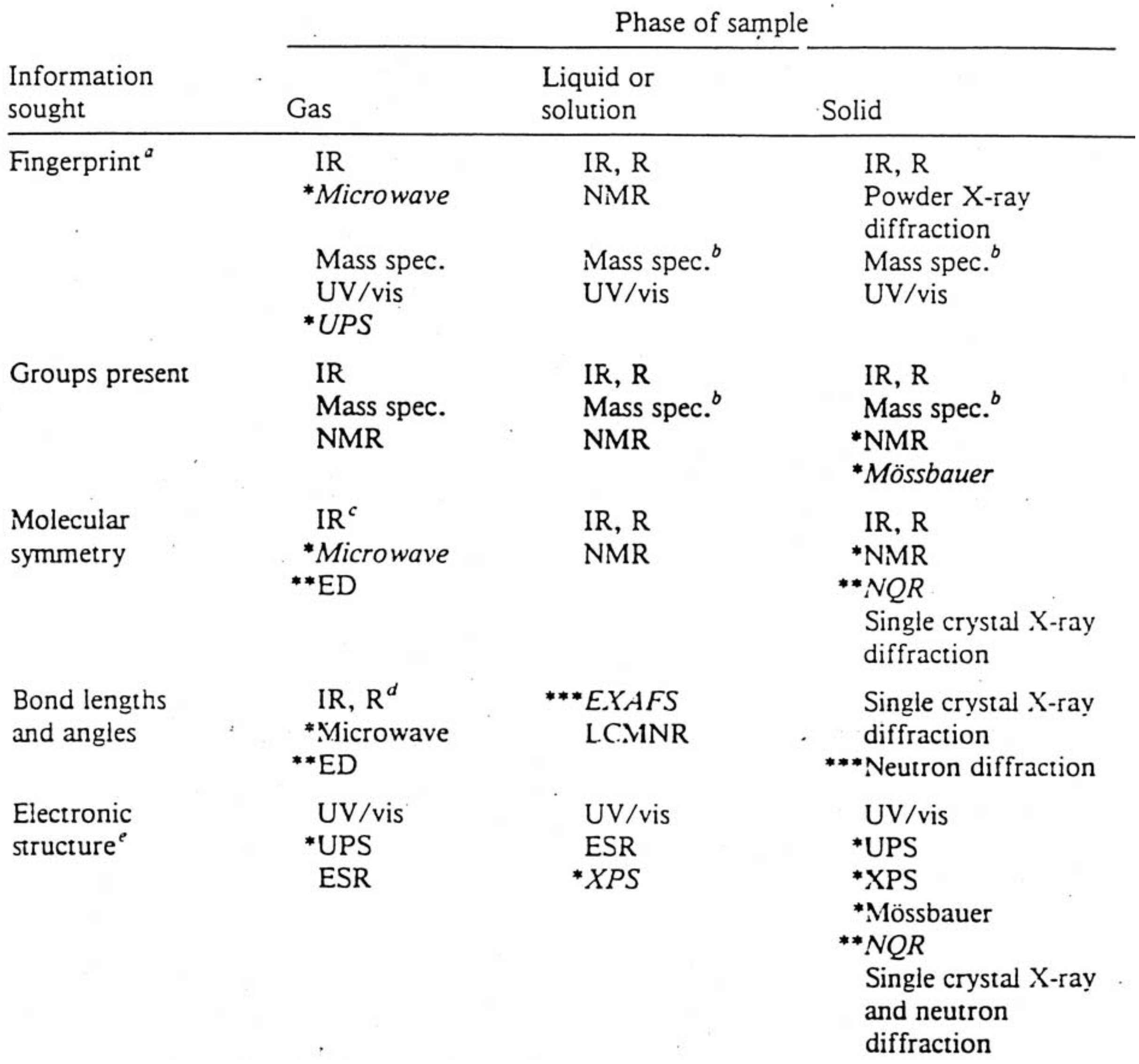


Comparison of some physical techniques for structural studies

Technique	Nature of the Effect	Information	Interaction time	Sensitivity	Comments
Vibrational Raman	Scattering of radiation with changed frequency due to polarizability change during a vibration (λ = visible usually)	Qualitative for large molecules	10^{-14} s	10^4 Pa (100 Torr) (v^4 dependent)	Useful for characterization. Some structural information from number of bands, position, depolarization ratios, and possibly isotope effects. All states of matter
Electronic	Absorption of radiation due to dipole change during an electronic transition ($\lambda = 10$–10^2 nm)	Qualitative for large molecules	10^{-15} s	1 Pa (10^{-2} Torr)	Useful for characterization. Some structural information from number of bands and position. All states of matter
Nuclear magnetic resonance	Interaction of radiation with a nuclear transition in a magnetic field ($\lambda = 10^2$–10^7 cm; 3 KHz to 300 MHz)	Number of magnetically equivalent nuclei in each environment	10^{-1}–10^{-9} s	10^3 Pa (10 Torr (^{1}H))	Applicable to solutions and gases. In conjunction with molecular weight measurements may be possible to choose one from several possible models
Mass spectrometry	Detection of fragments by charge/mass	Mass number, plus fragmentation patterns	—	10^{-9} Pa (10^{-11} Torr)	Useful for characterization of species in a vapour, complicated by reactions in spectrometer. Does not differentiate isomers directly. Important for detecting hydrogen in a molecule

From I. R. Beattie, *Chem. Soc. Rev.*, **4**, 107 (1975). Used with permission.

4.10 Comparison of some techniques for structural studies



Information sought	Phase of sample		
	Gas	Liquid or solution	Solid
Fingerprint[a]	IR *_Microwave_ Mass spec. UV/vis *_UPS_	IR, R NMR Mass spec.[b] UV/vis	IR, R Powder X-ray diffraction Mass spec.[b] UV/vis
Groups present	IR Mass spec. NMR	IR, R Mass spec.[b] NMR	IR, R Mass spec.[b] *NMR *_Mössbauer_
Molecular symmetry	IR[c] *_Microwave_ **ED	IR, R NMR	IR, R *NMR **_NQR_ Single crystal X-ray diffraction
Bond lengths and angles	IR, R[d] *Microwave **ED	***_EXAFS_ LCMNR	Single crystal X-ray diffraction ***Neutron diffraction
Electronic structure[e]	UV/vis *UPS ESR	UV/vis ESR *_XPS_	UV/vis *UPS *XPS *Mössbauer **_NQR_ Single crystal X-ray and neutron diffraction