X-ray analysis

1. Basic crystallography
2. Basic diffraction physics
3. Experimental methods

Introduction
Noble prizes associated with X-ray diffraction

- 1901 W. C. Roentgen (Physics) for the discovery of X-rays.
- 1914 M. von Laue (Physics) for X-ray diffraction from crystals.
- 1915 W. H. and W. L. Bragg (Physics) for structure derived from X-ray diffraction.
- 1917 C. G. Barkla (Physics) for characteristic radiation of elements.
- 1924 K. M. G. Siegbahn (Physics) for X-ray spectroscopy.
- 1927 A. H. Compton (Physics) for scattering of X-rays by electrons.
- 1936 P. Debye (Chemistry) for diffraction of X-rays and electrons in gases.
- 1962 M. Perutz and J. Kendrew (Chemistry) for the structure of hemoglobin.
- 1962 J. Watson, M. Wilkins, and F. Crick (Medicine) for the structure of DNA.
- 1979 A. Cormack and G. Newbold Hounsfield (Medicine) for computed axial tomography.
- 1981 K. M. Siegbahn (Physics) for high resolution electron spectroscopy.
- 1985 H. Hauptman and J. Karle (Chemistry) for direct methods to determine structures.
- 1988 J. Deisenhofer, R. Huber, and H. Michel (Chemistry) for the structures of proteins that are crucial to photosynthesis.

Introduction
What's the result of X-ray analyses?

Crystal data

Formula sum	Mg_2SiO_4 (Olivine)
Crystal system	orthorhombic
Space group	*P* b n m (no. 62)
Unit cell dimensions	*a* = 4.75(2) Å, *b* = 10.25(4) Å, *c* = 6.00(2) Å
Z	4

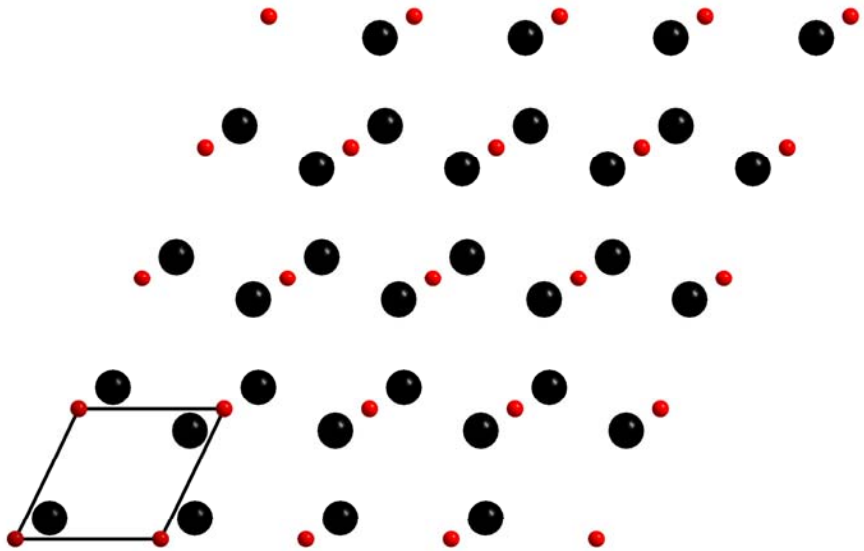
Atomic coordinates

Atom	Ox.	Wyck.	x	y	z
Mg1	+2	4*a*	0.00000	0.00000	0.00000
Mg2	+2	4*c*	0.00995(600)	0.27734(600)	0.75000
Si1	+4	4*c*	0.07373(500)	0.4043(50)	0.25000
O1	-2	4*c*	0.23242(1000)	0.0918(100)	0.75000
O2	-2	4*c*	0.2793(100)	0.05078(1000)	0.25000
O3	-2	8*d*	0.22266(1000)	0.33594(1000)	0.46289(1000)

- **Structure**
- **Chemical information (bonding, composition)**
- **Real structure (defects)**

1. Basic crystallography
Lattice, motif and structure

Example:
structure and lattice
in 2D



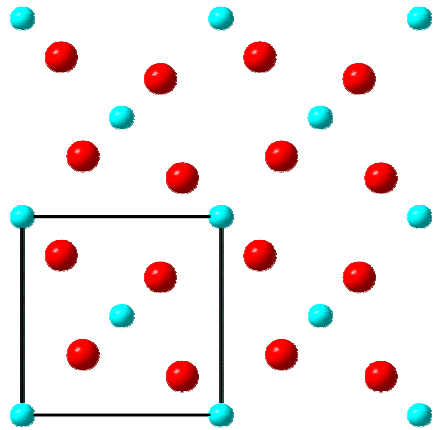
- **Lattice**
  - **pattern of points**
  - **no chemical information, mathematical description**
  - **no atoms, but points and lattice vectors (a, b, c, α, β, γ), unit cell**
- **Motif (characteristic structural feature, atom, group of atoms…)**
- **Structure = Lattice + Motif**
  - **contains chemical information (e. g. environment, bond length…)**
  - **describes the arrangement of atoms (symmetry of the crystal)**

1. Basic crystallography
Unit cell: interconnection of lattice and structure

Definition:

Unit cell = parallel sided region of the lattice from which the entire crystal can be constructed by purely translational displacements

- **contents of unit cell represents chemical composition (multiples of chemical formula)**
- **primitive cell: simplest cell, contains one lattice point**
- **centered cell: more than one point inside unit cell**



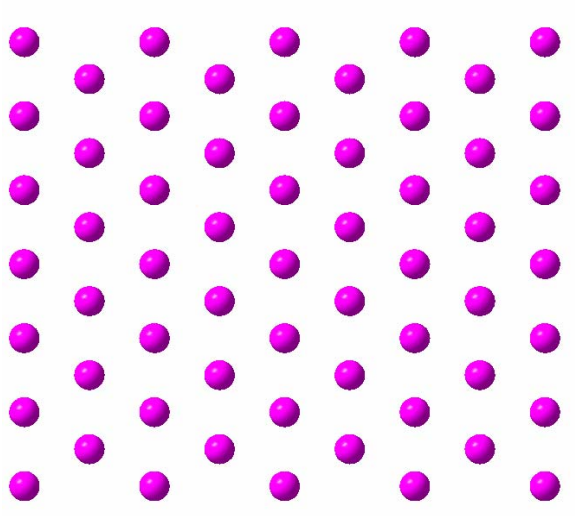
Conventions:

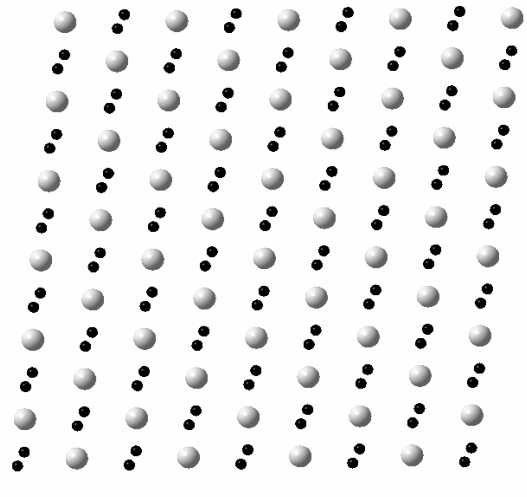
1. Cell edges should coincide with symmetry axes or reflection planes

2. The smallest possible cell which fulfills 1. should be chosen

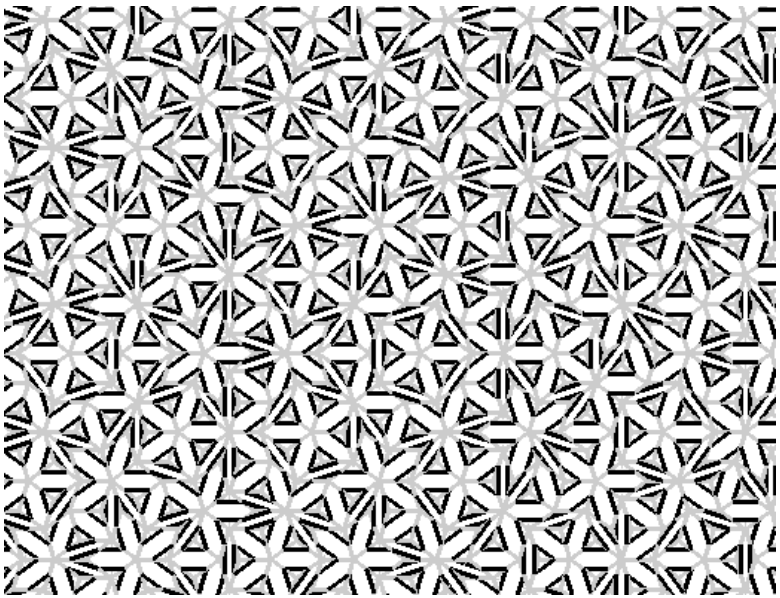
1. Basic crystallography
Unit cell: exercise

Determine the primitive unit cell and one example for a centered setting

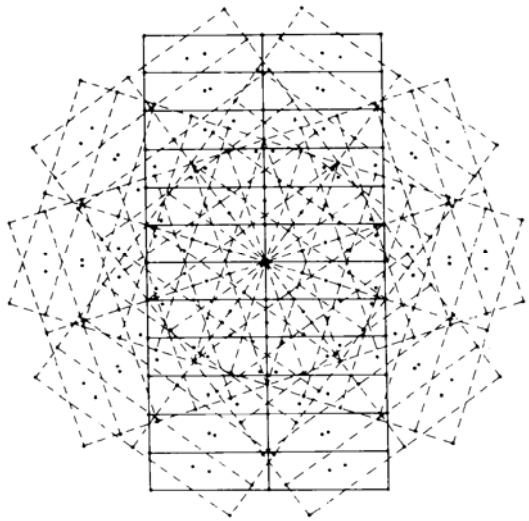


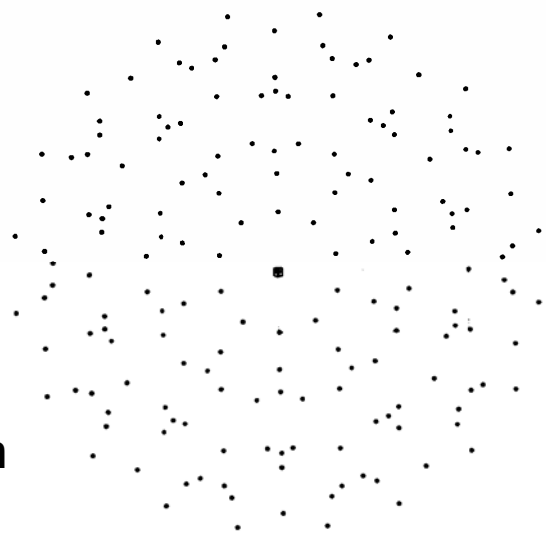


1. Basic crystallography
Aperiodic structures: e. g. quasicrystals



Penrose tiling





Forbidden symmetry
produced by superposition

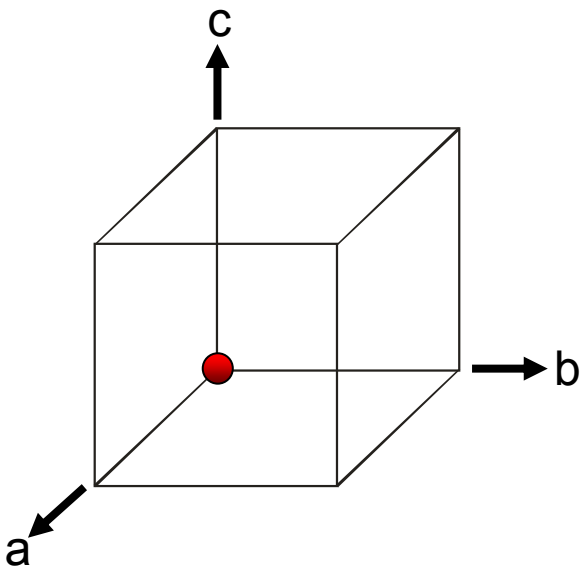
1. Basic crystallography
Unit cells and crystal system

- millions of periodic structures but 7 types of primitive cells (crystal systems)
- crystal system = particular restriction concerning the unit cell
- crystal system = unit cell with characteristic symmetry elements (later)

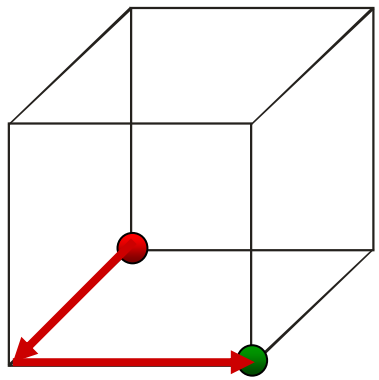
Crystal system	Restrictions axes	Restrictions angles
Triclinic	-	-
Monoclinic	-	$\alpha = \gamma = 90°$
Orthorhombic	-	$\alpha = \beta = \gamma = 90°$
Tetragonal	a = b	$\alpha = \beta = \gamma = 90°$
Trigonal	a = b	$\alpha = \beta = 90°,\ \gamma = 120°$
Hexagonal	a = b	$\alpha = \beta = 90°,\ \gamma = 120°$
Cubic	a = b = c	$\alpha = \beta = \gamma = 90°$

1. Basic crystallography
Indexation of directions in direct space

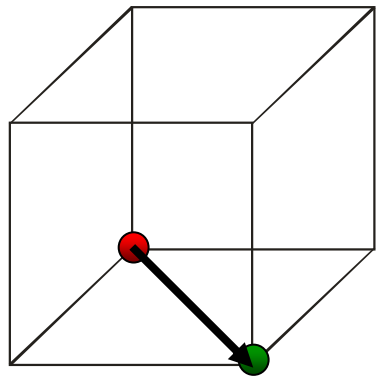
"[uvw] = [110]"
Procedure in three steps



1. Select 000



2. Mark position of second point

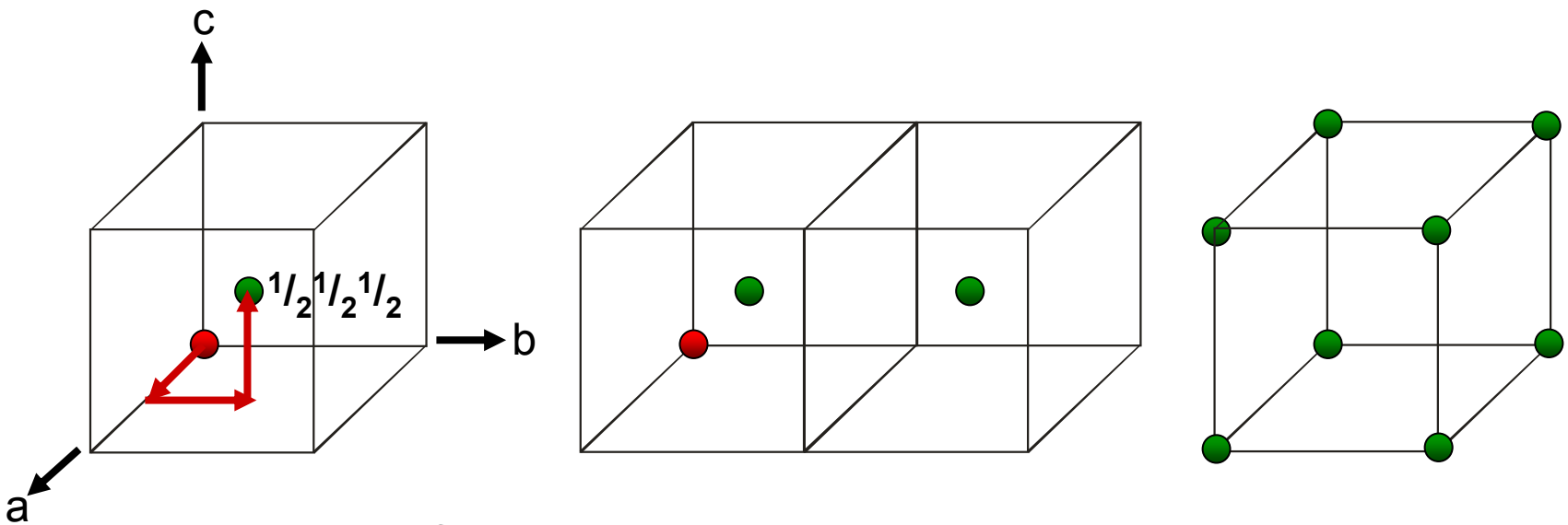


3. Draw vector

Convention: right-handed coordinate system

- **middle finger: a**
- **thumb: b**
- **forefinger: c**

1. Basic crystallography
Fractional coordinates (position of the atoms)



- possible values for x, y, z: [0; 1], atoms are multiplied by translations
- atoms are generated by symmetry elements (later)

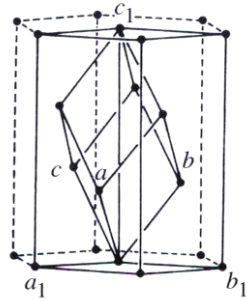
- Example: Sphalerite (ZnS)

- Equivalent points are represented by one triplet only
  - equivalent by translation
  - equivalent by other symmetry elements (later)

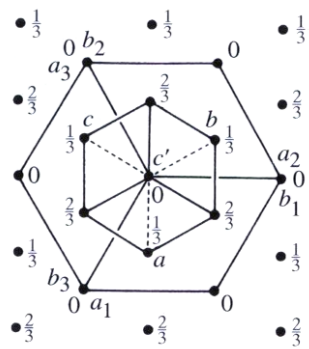
1. Basic crystallography
Centered unit cells- Bravais-type

The Bravais-types P, F, I, C, A, B, R denote centerings of the unit cells

- **Centering of unit cell = Translation**
- **7 crystal systems, 14 characteristic unit cells (i.e. Bravais-type)**
- **7 types of centerings:**
- **P: no centering (0,0,0)**
- **F: translation of each point by (1/2,1/2,0);(0,1/2,1/2);(1/2,0,1/2)**
- **I: translation of each point by (1/2,1/2,1/2)**
- **C: translation of each point by (1/2,1/2,0)**
- **A: translation of each point by (0,1/2,1/2)**
- **B: translation of each point by (1/2,0,1/2)**
- **R: translation of each point by (2/3,1/3,1/3);(1/3,2/3,2/3)**
- **All fractional coordinates are multiplied by centerings**



(a)



1. Basic crystallography
Bravais-type: example

Crystal data

Formula sum	NaCl
Crystal system	cubic
Space group	*F* m -3 m (no. 225)
Unit cell dimensions	*a* = 5.6250(5) Å
Z	4

Halite

Atomic coordinates

Atom	**Ox.**	**Wyck.**	**x**	**y**	**z**
Na	+1	4*a*	0	0	0
Cl	-1	4*b*	1/2	1/2	1/2

1. Basic crystallography
Wyckoff-notation and occupancy factor

Crystal data

Formula sum	$Cu_{0.8}\ In_{2.4}\ Se_4$
Crystal system	tetragonal
Space group	*I* -4 2 *m* (no. 121)
Unit cell dimensions	*a* = 5.7539(3) Å *c* = 11.519(1) Å
Z	2

Atomic coordinates

Molecules

Atom	**Ox.**	**Wyck.**	**Occ.**	**x**	**y**	**z**
Cu1	+1	2*a*	0.8	0	0	0
In1	+3	4*d*	1.0	0	1/2	1/4
In2	+3	2*b*	0.4	0	0	1/2
Se1	-2	8*i*	1.0	1/4	1/4	1/8

Occ. factors × Wyckoff number = no. of atoms/unit cell

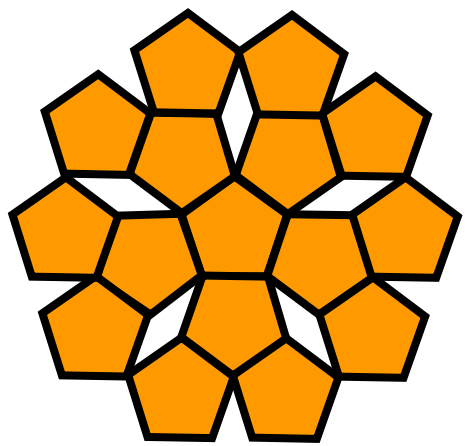
1. Basic crystallography
Crystallographic symmetry elements

SE in crystallography:

- **Inversion**
- **Mirror**
- **Rotation axes: 1,2,3,4,6**
- **Translations**

} **Coupling and combination**

Question:
Why is e. g. 5 forbidden in crystal structures?

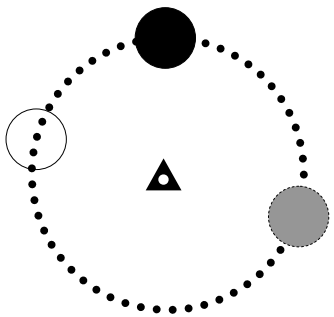


1. Basic crystallography
Coupling- rotation and inversions

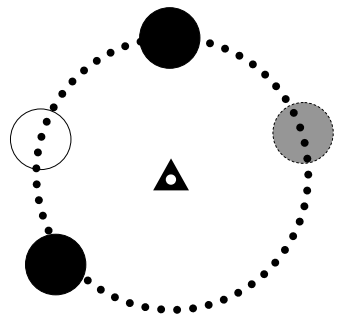
Coupling:

- **both SE are applied in one step**
- **one of the two coupled SE is an intermedium**

$\bar{3}$

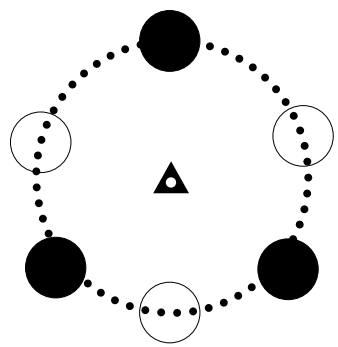


intermedium



intermedium

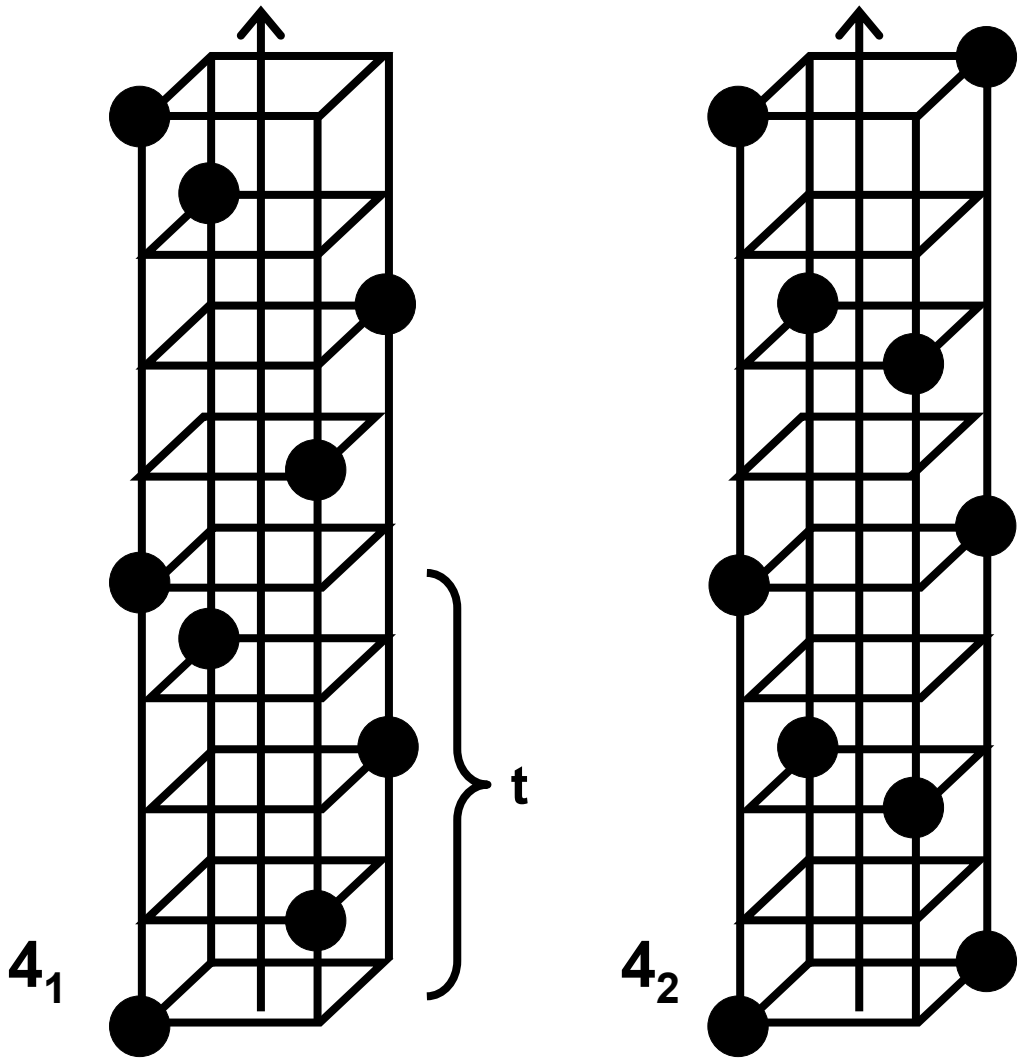
What about $\bar{2}$?



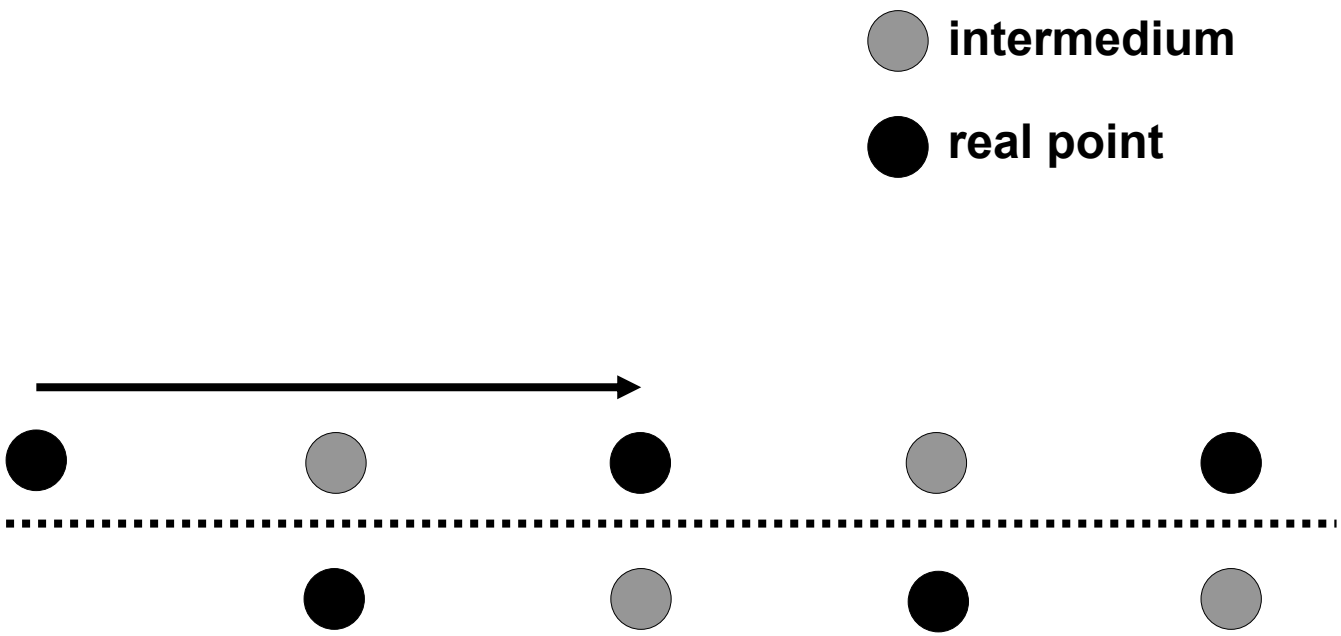
1. Basic crystallography
Coupling- rotation and translation- Screw axes X_n

Strategy: X-fold rotation after translation of n/X along the screw axis

2_1
$3_1\ 3_2$
$4_1\ 4_3\ 4_2$
$6_1\ 6_5\ 6_2\ 6_4\ 6_3$



1. Basic crystallography
Coupling- mirror and translation – Gilde planes

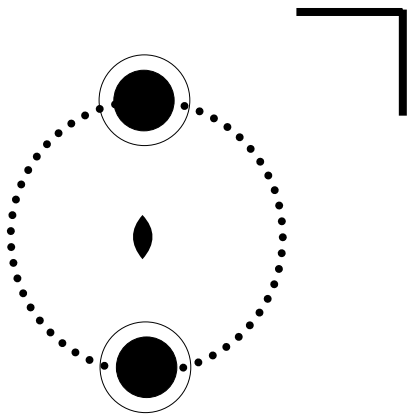


a, b, c, n, d, e

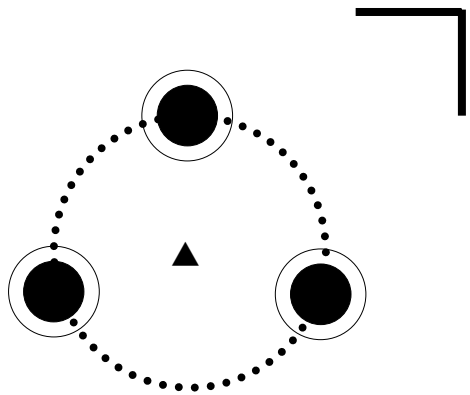
a, b, c: ½ a, ½ b, ½ c
n: ½ (a + b), ½ (a + c), ½ (b + c)
d: ½ n

1. Basic crystallography
Combination of mirror and rotation

Combination:
- **both SE are applied (two steps)**
- **no intermedium**



2/m



3/m

1. Basic crystallography
Directions of characteristic symmetry elements

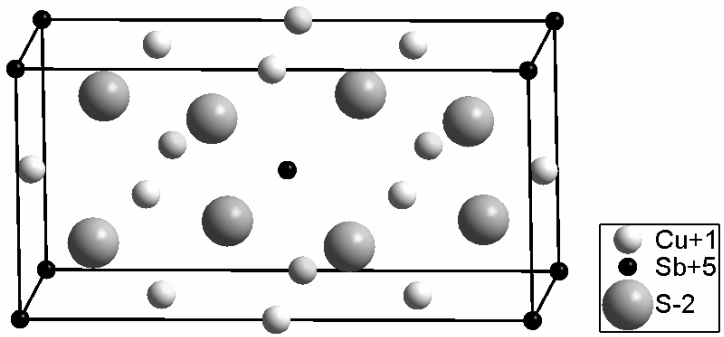
Crystal system	Characteristic SE	Char. direction / sequence
Triclinic	1, $\bar{1}$	-
Monoclinic	2 and/or m	b
Orthorhombic	2 (3×) and/or m(3×)	a, b, c
Trigonal	3 (1×)	c, a, [210]
Tetragonal	4 (1×)	c, a, [110]
Hexagonal	6	c, a, [210]
Cubic	3 (4×)	[111], a, [110]

What can we learn from this table?

- **The knowledge of the characteristic SE allows to determine the crystal system**
- **Pseudometrics possible, e. g. monoclinic with $\beta = 90°$**
- **Systematization of SE in space group symbols**

Repetition
Basic terms of 3D crystallography

- Lattice, motif and structure
- Unit cell (primitive and centered)
- Wyckoff notation, occupancy factor, composition of crystals
- Crystal system
- Bravais type
- Crystallographic SE



- Coupling of SE: rotoinversion, screw axes, glide planes
- Combination of SE
- Characteristic SE of the crystal casses

1. Basic crystallography
Crystal class

32 Crystal classes: Combination of SE without translations

Crystal system	Restriction	Crystal Class
Triclinic	-	1,$\bar{1}$
Monoclinic	- $\alpha = \gamma = 90°$	2, m, 2/m
Orthorhombic	a = b $\alpha = \beta = \gamma = 90°$	222, mm2, 2/m 2/m 2/m
Trigonal	a = b $\alpha = \beta = 90°,\ \gamma = 120°$	3, $\bar{3}$, 32, 3m, $\bar{3}$2/m
Tetragonal	a = b $\alpha = \beta = \gamma = 90°$	4, $\bar{4}$, 4/m, 422, 4mm, $\bar{4}$2m, 4/m 2/m 2/m
Hexagonal	a = b $\alpha = \beta = 90°,\ \gamma = 120°$	6, $\bar{6}$, 6/m, 622, 6mm, $\bar{6}$m2, 6/m 2/m 2/m
Cubic	a = b = c $\alpha = \beta = \gamma = 90°$	23, 2/m $\bar{3}$, 432, $\bar{4}$3m, 4/m $\bar{3}$ 2/m

1. Basic crystallography
Characteristic symmetry elements: example

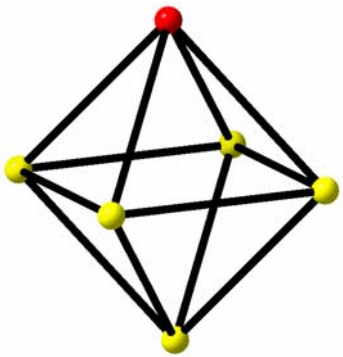
The atoms (A, B and C) of a tetragonal structure are located on: $0\,^1/_2\,0$ (A), $^1/_2\,^1/_2\,0$ (B) and 000 (C). Assume low symmetry

- **Sketch the unit cell along [001]**
- **Determine the composition of a crystal with this structure**
- **Describe the environment of A, B and C**

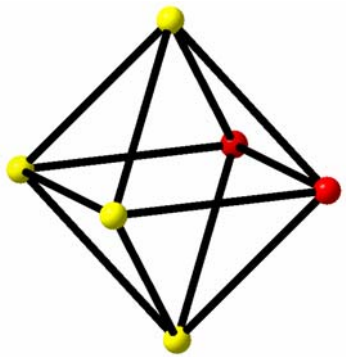
Repeat the exercise for a cubic structure!

1. Basic crystallography
Crystal Classes- examples

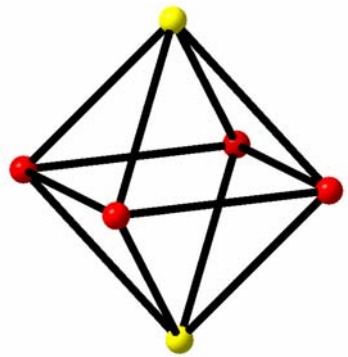
4mm



mm2



4/mmm



Crystal System	Charact. SE	Direction / Sequence
Triklin	1, $\bar{1}$	-
Monoklin	2 and/or m	b
Orthorhombisch	2 (3×) und/oder m(3×)	a, b, c
Trigonal	3 (1×)	c, a, [210]
Tetragonal	4 (1×)	c, a, [110]
Hexagonal	6	c, a, [210]
Kubisch	3 (4×)	a, [111], [110]

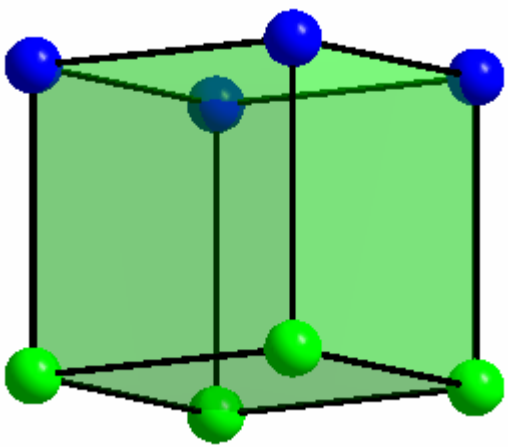
1. Basic crystallography
Exercise: restrictions of the crystal systems

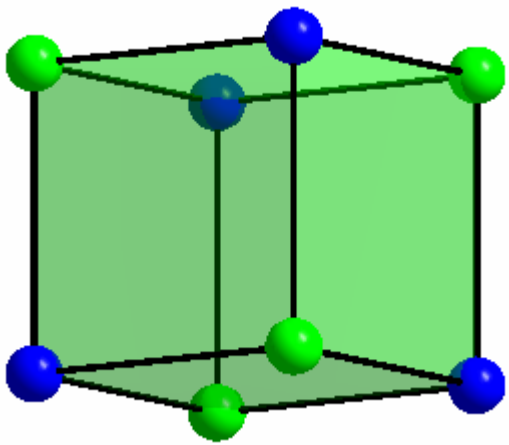
1	In tetragonal crystals, the restriction $\alpha = \beta = \gamma = 90°$ can not be violated	Right	Wrong
2	The characteristic symmetry element of cubic crystals is the fourfold axis	Right	Wrong
3	For monoclinic crystals β must be $\neq 90°$	Right	Wrong
4	$\alpha = \beta = \gamma = 90°$ is not possible for triclinic crystals	Right	Wrong
5	A crystal system with $\alpha = \beta = \gamma = 90°$ and $a = b = c$ must be denominated “cubic”	Right	Wrong
6	A crystal system with $\alpha = \beta = \gamma = 90°$ and $a \neq b \neq c$ can be denominated “orthorhombic”	Right	Wrong

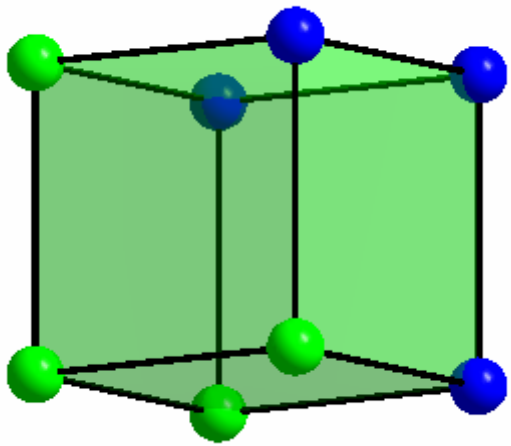
1. Basic crystallography
Crystal Classes- exercises

Determine the SE of following arrangements

Specify the crystal system and the crystal class







1. Basic crystallography
Space groups: Introduction

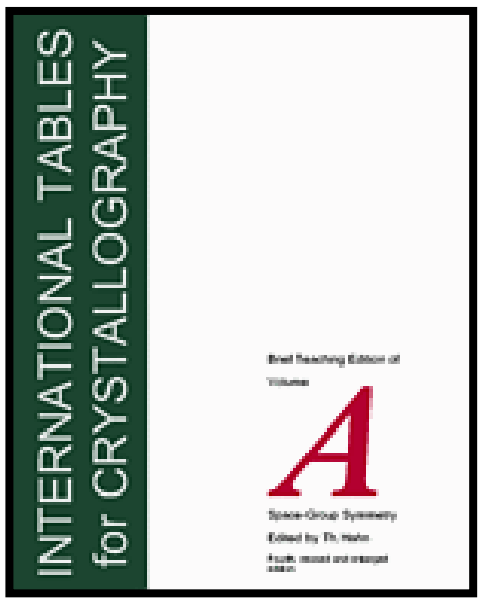
A crystallographic space group is a set of symmetry operations which describes all periodic patterns (230, 3D) in 3D space

Space group notations (H.-M.-notation)

- **first letter: Bravais-type (lattice centering)**
- **second and subsequent numbers and letters: symmetry elements along characteristic directions**
- **caution: some notations are reduced**

$$P\,3_1\,2\,1$$

1. Basic crystallography
Space group tables



Generators selected (1); $t(1,0,0)$; $t(0,1,0)$; $t(0,0,1)$; (2); (4)

Positions

Multiplicity, Wyckoff letter, Site symmetry	Coordinates		
6 c 1	(1) x,y,z	(2) $\bar{y},x-y,z+\frac{1}{3}$	(3) $\bar{x}+y,\bar{x},z+\frac{2}{3}$
	(4) $y,x,\bar{z}$	(5) $x-y,\bar{y},\bar{z}+\frac{2}{3}$	(6) $\bar{x},\bar{x}+y,\bar{z}+\frac{1}{3}$
3 b .2.	$x,0,\frac{5}{6}$	$0,x,\frac{1}{6}$	$\bar{x},\bar{x},\frac{1}{2}$
3 a .2.	$x,0,\frac{1}{3}$	$0,x,\frac{2}{3}$	$\bar{x},\bar{x},0$

Symmetry of special projections

Along [001] $p31m$
$\mathbf{a}' = \mathbf{a}$ $\mathbf{b}' = \mathbf{b}$
Origin at $0,0,z$

Along [100] $p2$
$\mathbf{a}' = \frac{1}{2}(\mathbf{a}+2\mathbf{b})$ $\mathbf{b}' = \mathbf{c}$
Origin at $x,0,\frac{1}{3}$

Along [210] $p11m$
$\mathbf{a}' = \frac{1}{2}\mathbf{b}$ $\mathbf{b}' = \mathbf{c}$
Origin at $x,\frac{1}{2}x,\frac{1}{6}$

Maximal non-isomorphic subgroups

I [2] $P3_111$ ($P3_1$, 144) 1; 2; 3
[3] $P121$ ($C2$, 5) 1; 4
[3] $P121$ ($C2$, 5) 1; 5
[3] $P121$ ($C2$, 5) 1; 6

IIa none

IIb [3] $H3_121$ ($\mathbf{a}' = 3\mathbf{a}, \mathbf{b}' = 3\mathbf{b}$) ($P3_112$, 151)

Maximal isomorphic subgroups of lowest index

IIc [2] $P3_221$ ($\mathbf{c}' = 2\mathbf{c}$) (154); [4] $P3_121$ ($\mathbf{a}' = 2\mathbf{a}, \mathbf{b}' = 2\mathbf{b}$) (152); [7] $P3_121$ ($\mathbf{c}' = 7\mathbf{c}$) (152)

Minimal non-isomorphic supergroups

I [2] $P6_122$ (178); [2] $P6_422$ (181)

II [3] $H3_121$ ($P3_112$, 151); [3] $R32$ (obverse) (155); [3] $R32$ (reverse) (155); [3] $P321$ ($\mathbf{c}' = \frac{1}{3}\mathbf{c}$) (150)

reciprocal space

Reflection conditions

General:

$000l$: $l = 3n$

Special: no extra conditions

direct space

1. Basic crystallography
Space group: Examples (H.M. notation)

Example 1: *Pm* (full notation)

- P means primitive (no centering)
- characteristic SE: m → monoclinic
- m perpendicular to [010]

Example 2: *C*2/*c* (full notation)

- C means ab-plane (001) is centered
- characteristic SE: 2 or c → monoclinic.
- 2 along b, c perpendicular to b

Example 3: $P6_3/mmc = P6_3/m\ 2/m\ 2/c$ (full notation)

- P means primitive (no centering)
- characteristic SE: 6_3 → hexagonal
- 6_3 along c, m perpendicular c, 2 along a, m perpendicular a, 2 along [210], c perpendicular [210]

Information derived from H.M. notation

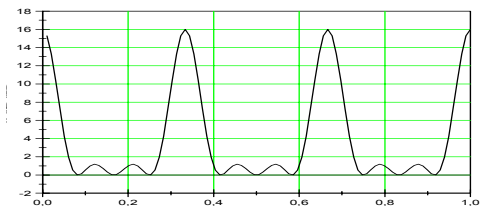
- Crystal system, Crystal class
- Centrosymmetric / non centrosymmetric
- Reflection conditions (“Extinctions”)

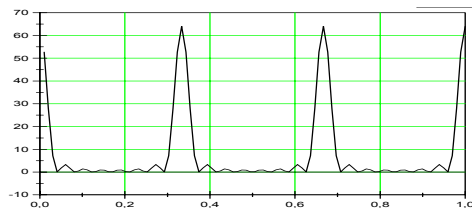
2. Basic diffraction physics
Model for X-ray diffraction (XRD)

Scattering can be separated into:

- **scattering by all electrons of the distinct atoms of the structure (atomic form factor)**
- **scattering by all atoms of the structure (structure factor, convolution lattice and unit cell)**
- **scattering by the whole crystal (finite size effects: broadening of FT)**

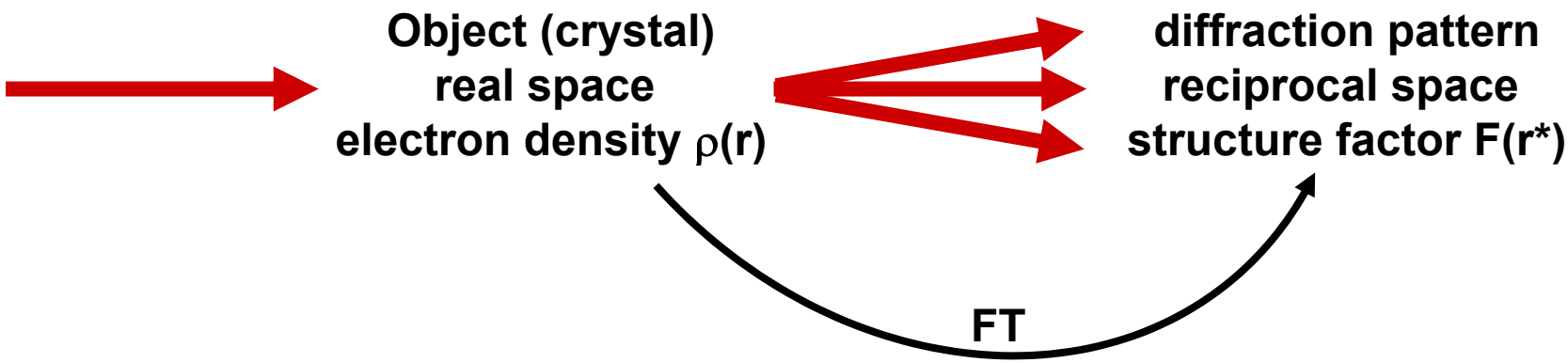
4 atoms



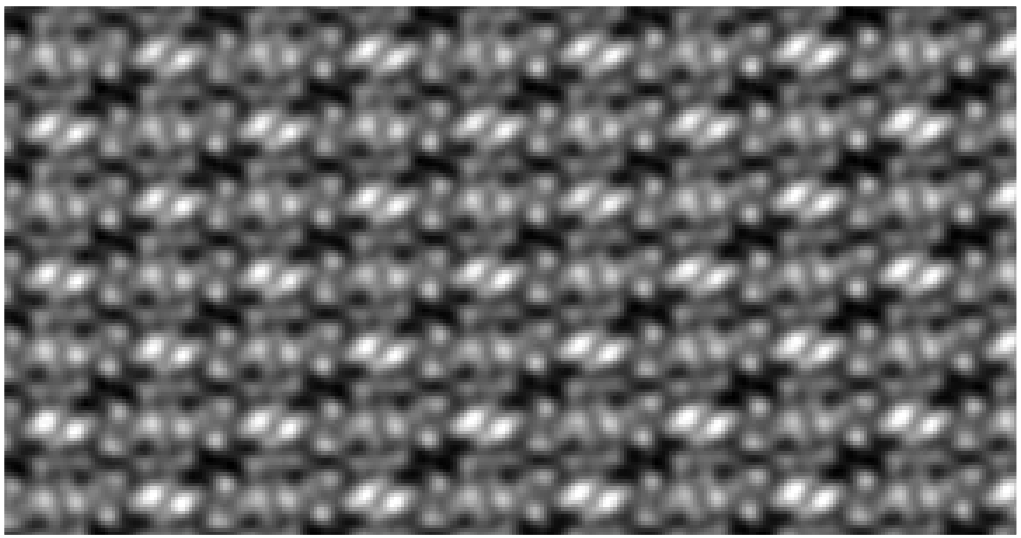


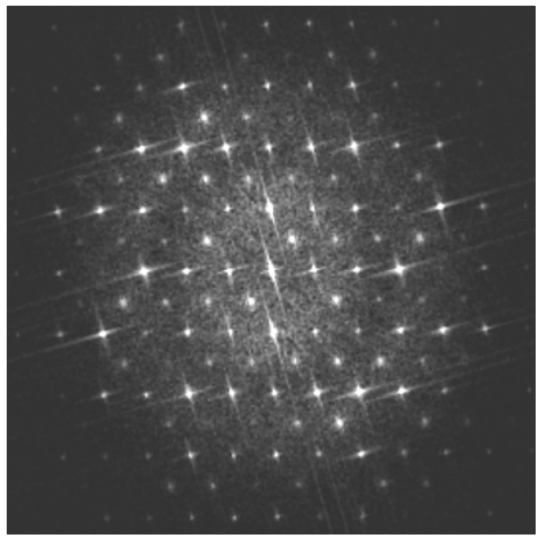
8 atoms

Mathematical description: Fourier transformation

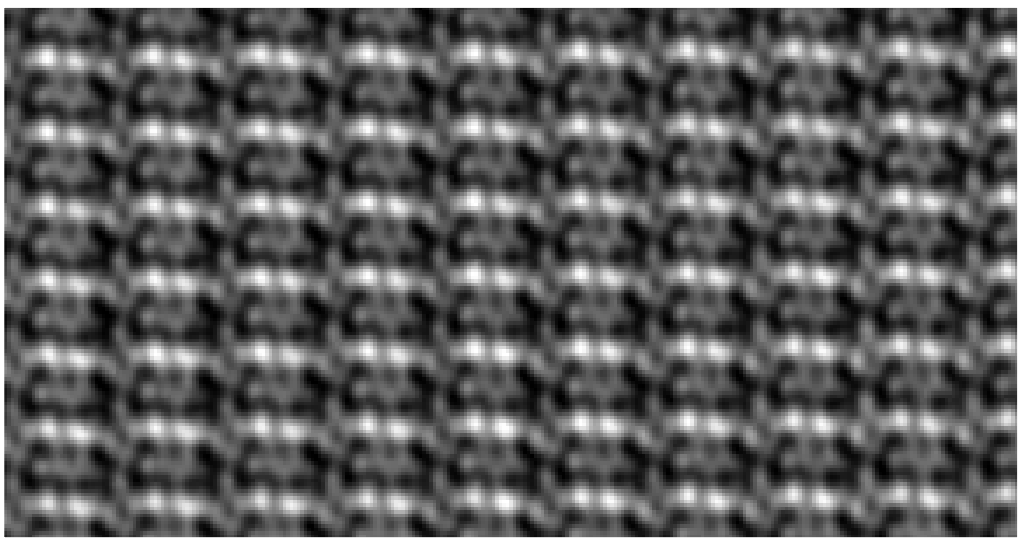


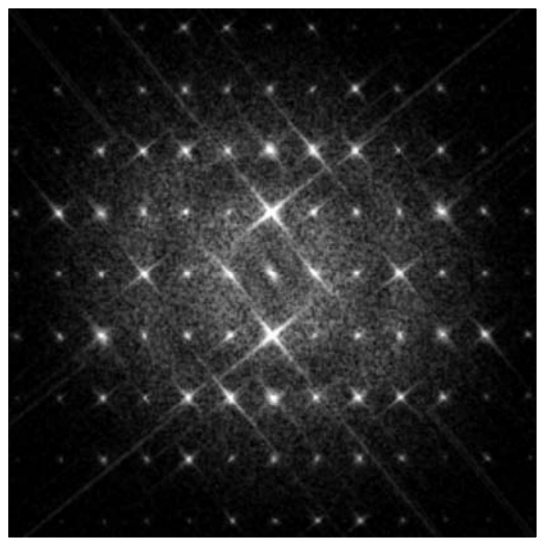
2. Basic diffraction physics
Example: FFTs in electron microscopy





1 nm





2. Basic diffraction physics
Basic FTs in XRD I: Atomic scattering factor

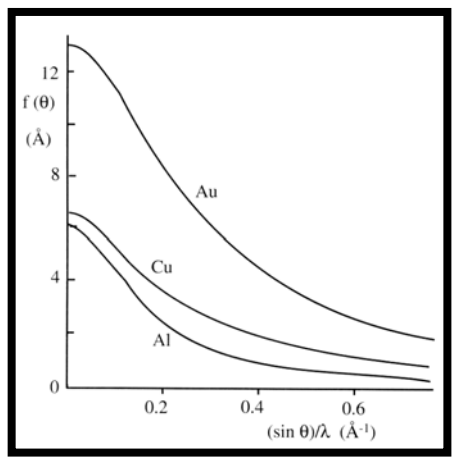
$$\rho(r) = \int_{V^*} F(r^*) \exp(-2i\pi(rr^*))\, dr^* \qquad F(r^*) = \int_{V} \rho(r) \exp(2i\pi(rr^*))\, dr$$

- **Scattering by atoms (FT of $U_a(r)$)**

$$f_a(r^*) = \int_{V} U_a(r)\, (\sin(2\pi rr^*))/2\pi rr^*\, dr \sim \sum f_{el}.(r^*), \text{ with: } U_a(r) = 4\pi r^2\, \rho_a(r)$$

Experimental consequences

- high diffracted intensity at low θ, e.g. left side of powder DP
- "light atoms problem", consequence: alternative methods



2. Basic diffraction physics
Basic FTs in XRD II: periodic and infinite crystals

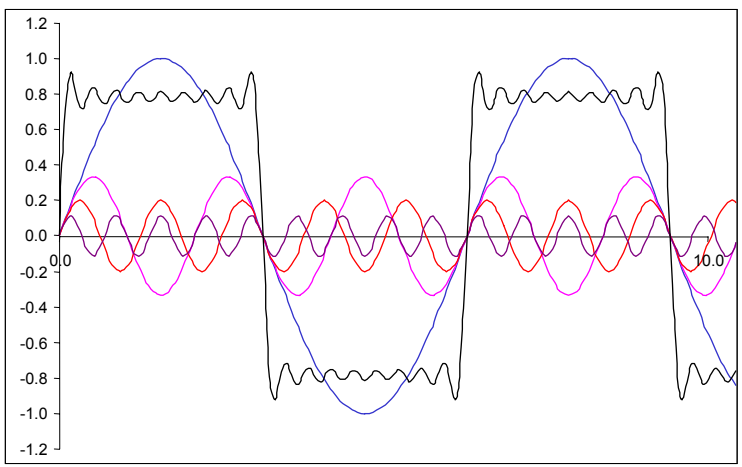
$$\rho(r) = \int_{V^*} F(r^*) \exp(-2i\pi(rr^*))\, dr^* \qquad F(r^*) = \int_{V} \rho(r) \exp(2i\pi(rr^*))\, dr$$

- $\rho(r)$ exhibits the periodicity of the crystal: Fourier series

$\rho(r) = \sum C_g \exp(2i\pi(r^*r))$, C_g: Fourier coefficient

$= 1/V \sum F_{hkl} \exp(2i\pi(hx + ky + lz))$, hkl: rec. space, xyz: dir. space

$F_{hkl} = \sum f_i \exp(2\pi i(hx + ky + lz))$, summing up the contributions of all atoms



Example: graph of a rectangular

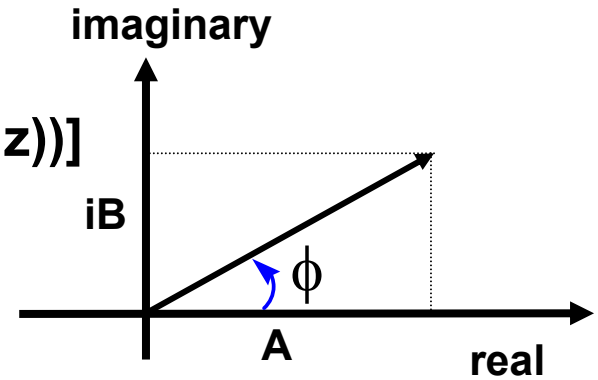
f(x) = sinx + sin3x/3 + sin5x/5 + sin7x/7 +…

2. Basic diffraction physics
Scattered intensity: Structure factor F_{hkl}

$$F_{hkl} = \Sigma f_i \exp(2\pi i(hx + ky + lz))$$

$$= \Sigma f_i [\cos(2\pi(hx + ky + lz)) + i \sin(2\pi(hx + ky + lz))]$$

$$= \Sigma A_i + i B_i$$



Remarks

- F_{hkl}: summing up the contributions from all atoms
- "All structural information is in one reflection"
- ϕ: phase of F_{hkl} contains structure information, $\phi = \arctan B/A$
- $|F_{hkl}| = (A^2 + B^2)^{1/2} \sim I = :$ phase problem, i.e. phase is lost
- Friedel's law: $I_{hkl} = I_{-h-k-l}$
- Symmetry of DP: centrosymmetric (first approximation)

2. Basic diffraction physics
Calculations of structure factors: examples

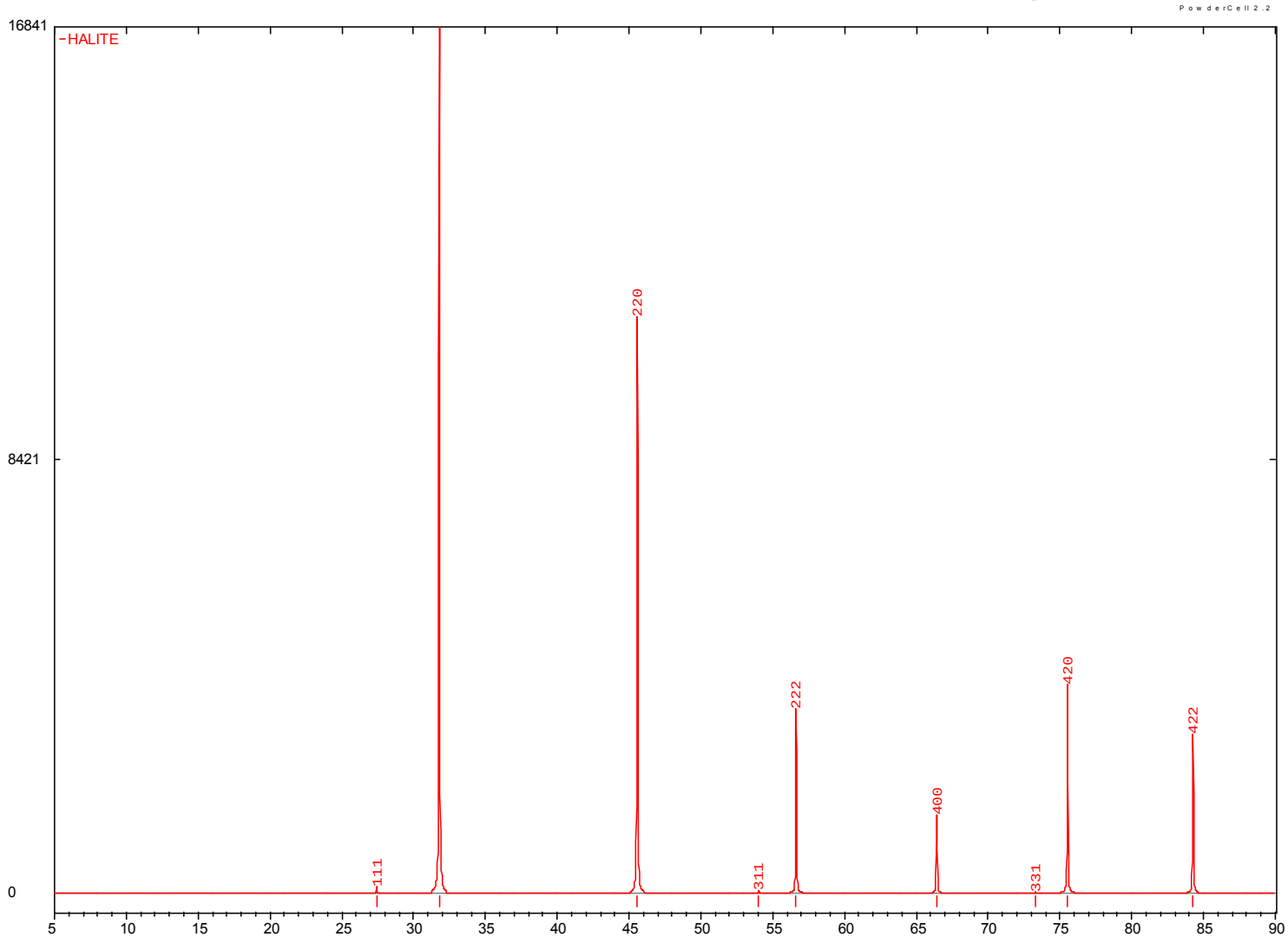
$$F_{hkl} = \sum f_i \exp(2\pi i(hx + ky + lz))$$

$$= \sum f_i [\cos(2\pi(hx + ky + lz)) + i \sin(2\pi(hx + ky + lz))]$$

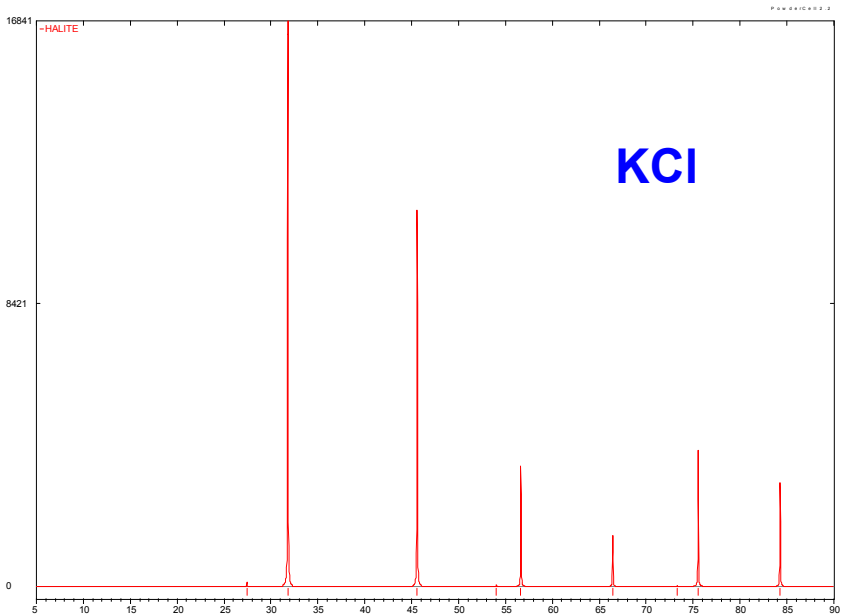
- Primitive (one atom type)
- Calculation for CsCl
- BCC (one atom type)
- Calculation for NaCl

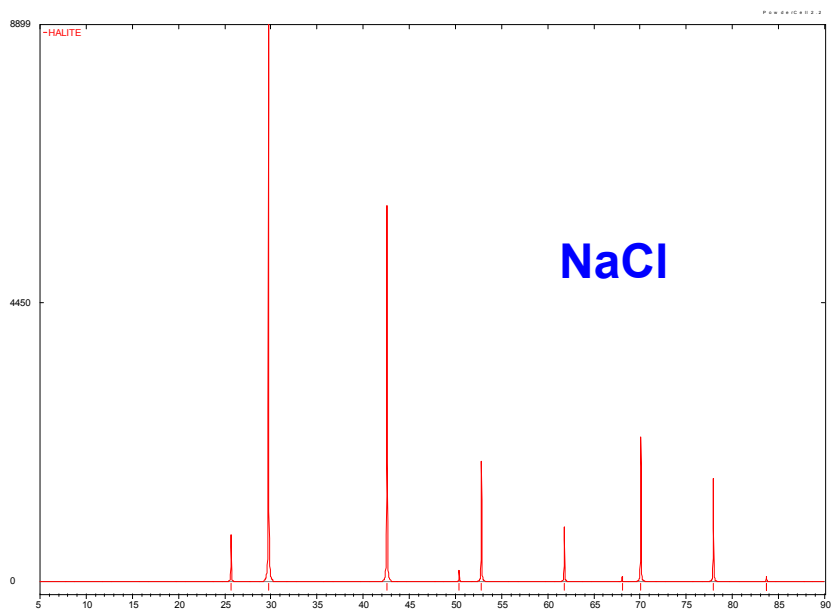
2. Basic diffraction physics
Example NaCl

Each peak corresponds to one set of hkl planes (or equivalent plane)



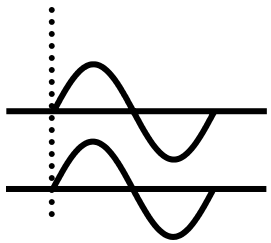
2. Basic diffraction physics
NaCl vs. KCl



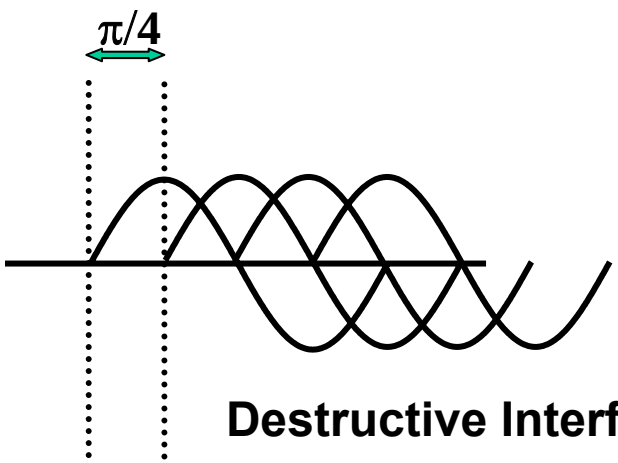


2. Basic diffraction physics
Geometrical approach, Bragg's law (BL)

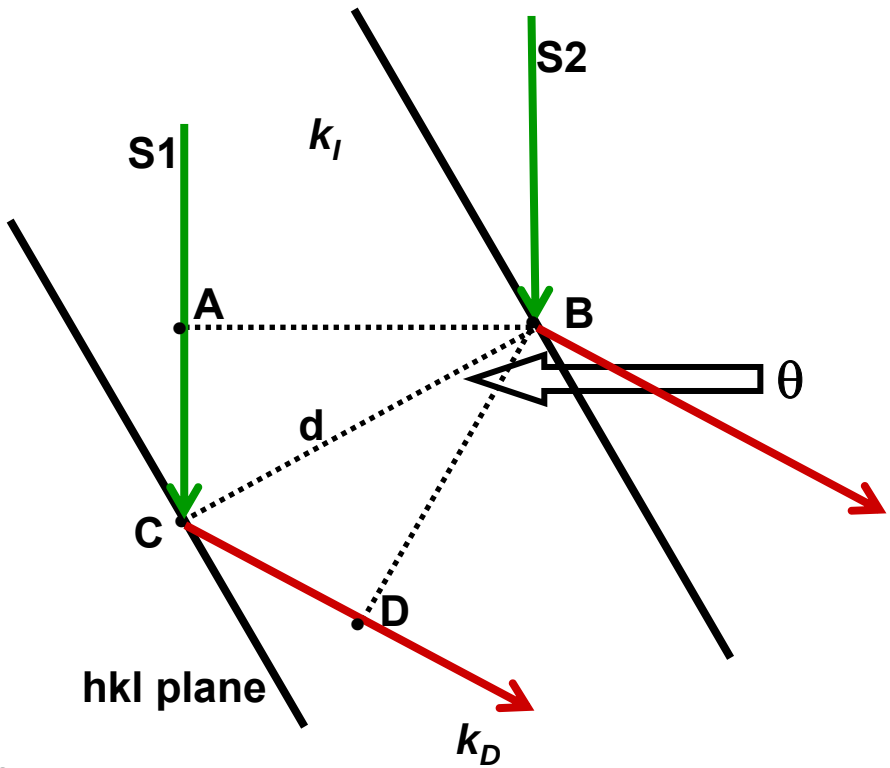
Description by wave vector: k_I: incident beam, k_D: diffracted beam; $|k_I| = |k_D| = 1/\lambda$



Constructive Interference



Destructive Interference

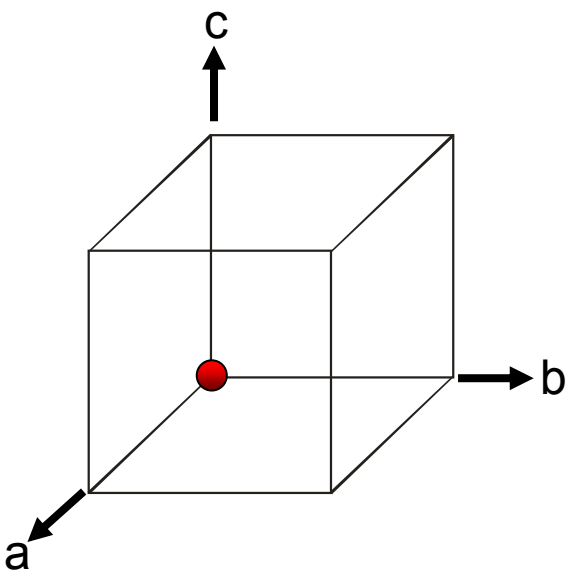


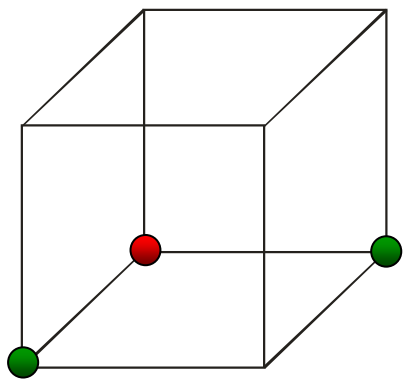
$$AC + CD = n\lambda = 2d\sin\theta_B$$

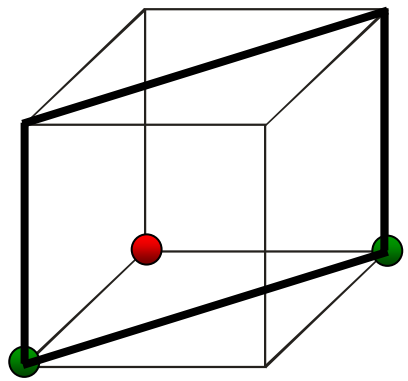
$$2\sin\theta_B/\lambda = n/d = n|d^*|$$

2. Basic diffraction physics
hkl: indices of planes in direct space

“(hkl) = (110)”
Procedure in three steps







1. Select 000

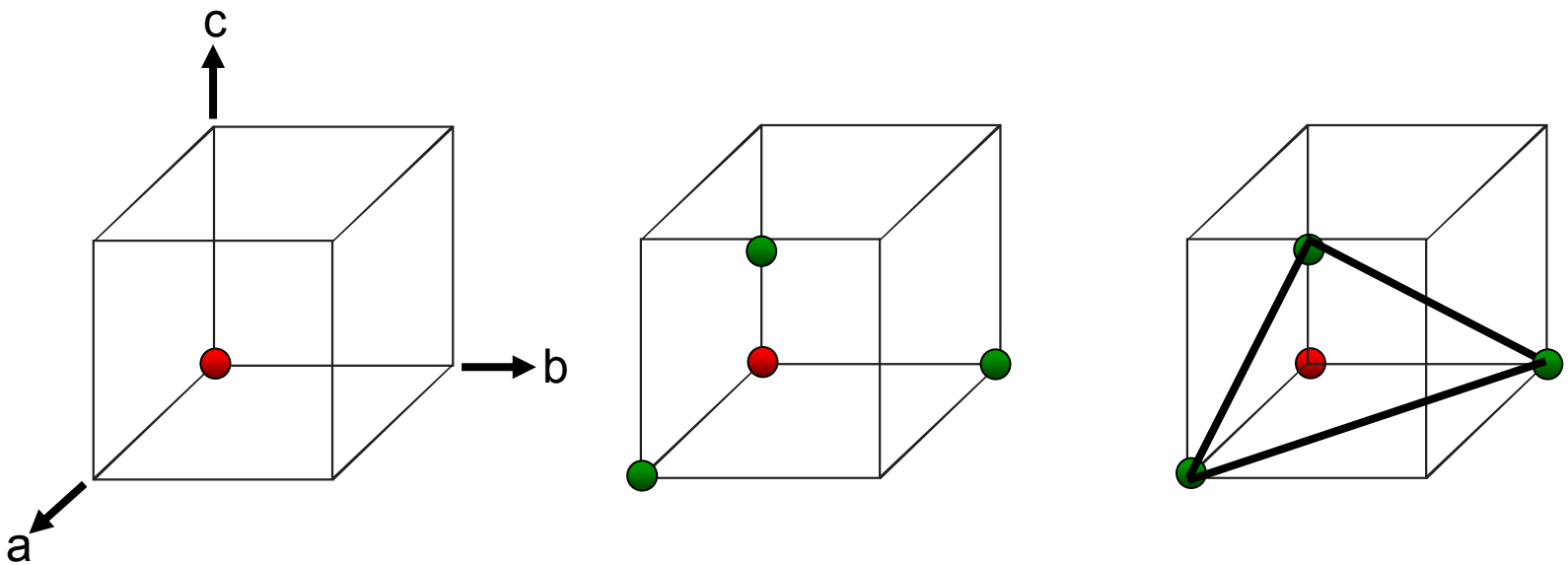
2. Mark intercept of the plane, i. e. reciprocal values 1/h on a, 1/k on b, 1/l on c
Three points, l = 0 means: plane || c

3. Draw plane

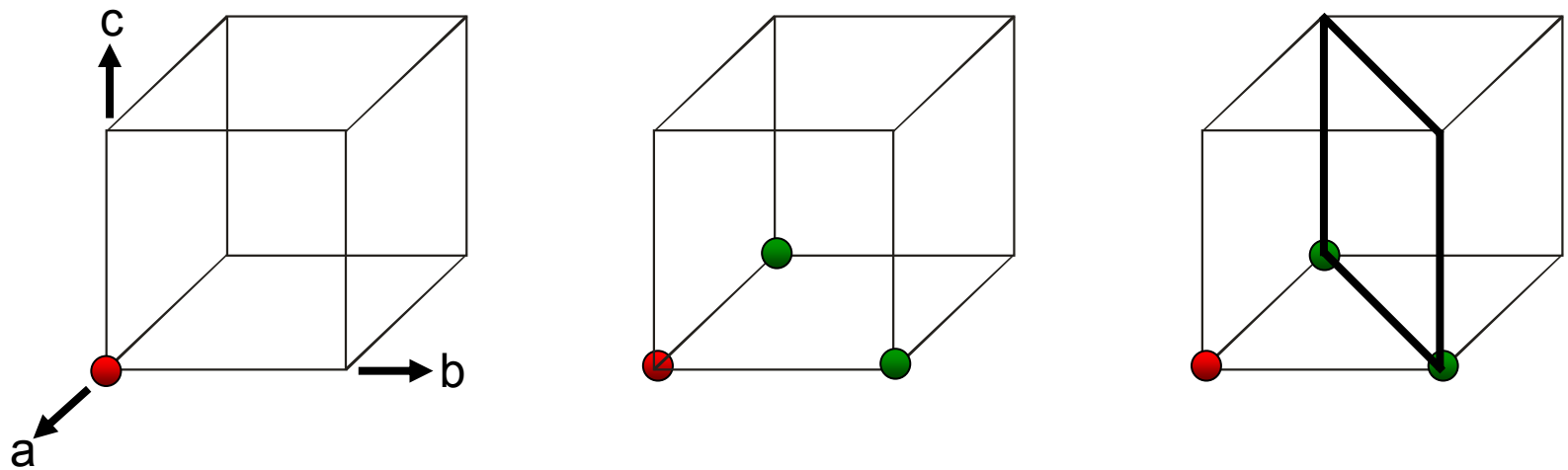
Convention: right-handed coordinate system

2. Basic diffraction physics
hkl planes: examples

(112)



($\bar{1}$10)



2. Basic diffraction physics
Properties / Applications of d/d*

- d ~ to the normal vector of an hkl plane
- |d| ~ distance of two individual hkl planes of the same type

Square form of BL (e.g. orthorhombic)

- $1/d^2 = h^2/a^2 + k^2/b^2 + l^2/c^2$
- $\sin^2\theta = \lambda^2/4\ (h^2/a^2 + k^2/b^2 + l^2/c^2)$
- Application: indexing of DP

Example for manual indexing

- (e.g. cubic): $(1/d)^2 = (1/a)^2\ (h^2 + k^2 + l^2)$, $d = \lambda/(2\sin\theta)$
- Determine d-spacing of each peak from its 2θ value (using Bragg's Law)
- Create a table of $1/d^2$ values for each peak
- Look for a common factor ($1/a^2$) that can be divided into each of the $(1/d)^2$ values

2. Basic diffraction physics
Manual indexation: example 1

2-theta	d	$1000/d^2$		hkl
22.21	4.000	62.5	62.5/62.5=1	100
31.61	2.828	125.0	125.0/62.5=2	110
38.97	2.309	187.6	187.6/62.5=3	111
45.31	2.000	250.0	250.0/62.5=4	200
51.01	1.789	312.4	312.4/62.5=5	210
56.29	1.633	375.0	375.0/62.5=6	211
66.00	1.414	500.2	500.2/62.5=8	220
70.58	1.333	562.8	562.8/62.5=9	221
75.03	1.265	624.9	624.9/62.5=10	310

2. Basic diffraction physics
Manual indexation: example 2 (extinctions)

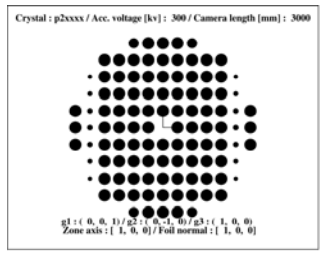
2-theta	d	1000/d2		hkl
28.077	3.175	99.2	99.2/33=3	111
32.533	2.750	132.2	132.2/33=4	200
46.672	1.945	264.3	264.3/33=8	220
55.355	1.658	363.8	363.8/33=11	311
58.045	1.588	396.6	396.6/33=12	222
68.140	1.375	528.9	528.9/33=16	400
75.247	1.262	627.9	627.9/33=19	331
77.559	1.230	661.0	661.0/33=20	420

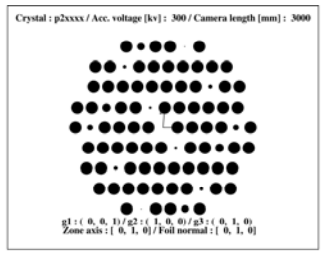
Systematic of extinctions (general reflection conditions): translation

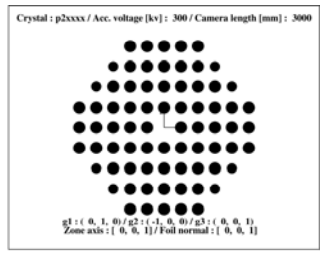
- **Integral reflection conditions: unit cell translations (centers)**
- **Zonal reflection conditions: glide planes**
- **Serial reflection conditions: screw axes**

2. Basic diffraction physics
Extinctions: examples

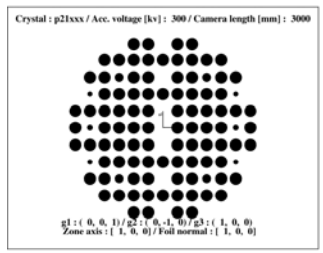
P2

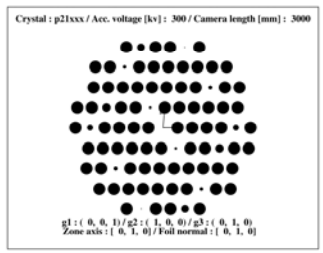


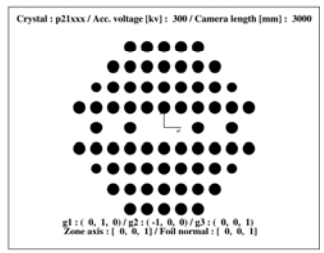




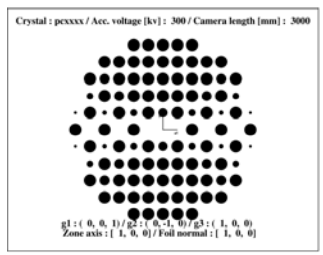
$P2_1$: 0k0 : k = 2n

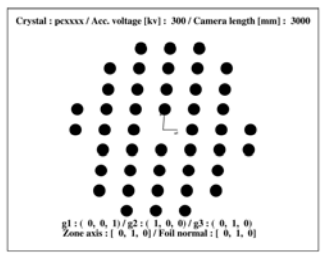


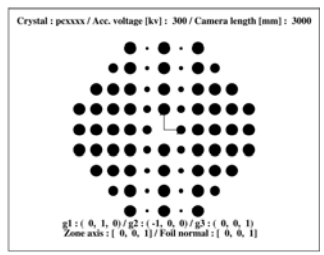




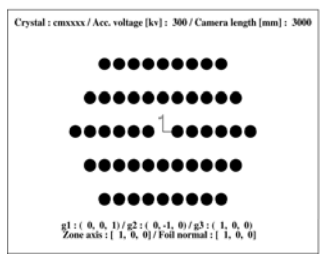
Pc: h0l : l = 2n, 00l : l = 2n

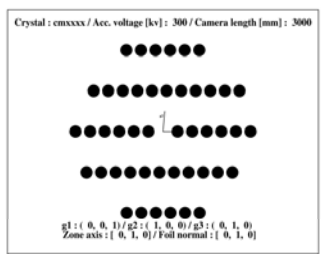


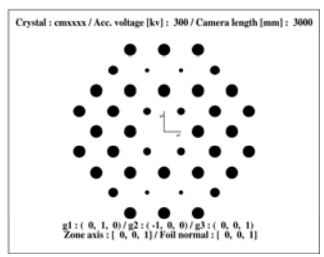




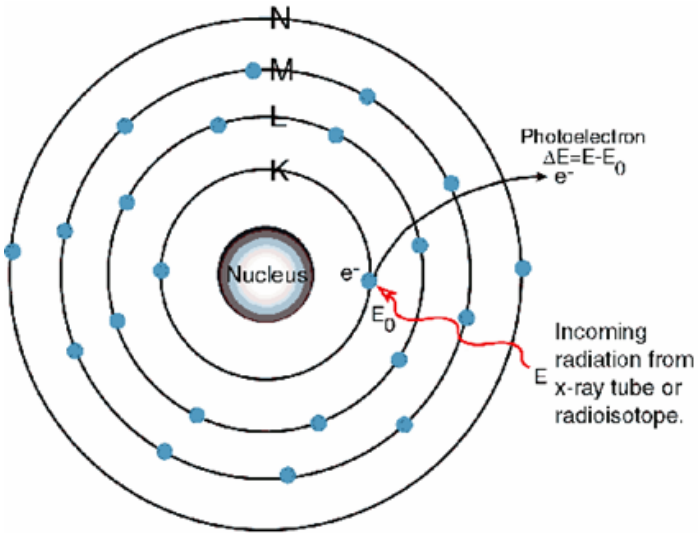
C2: hkl : h + k = 2n…

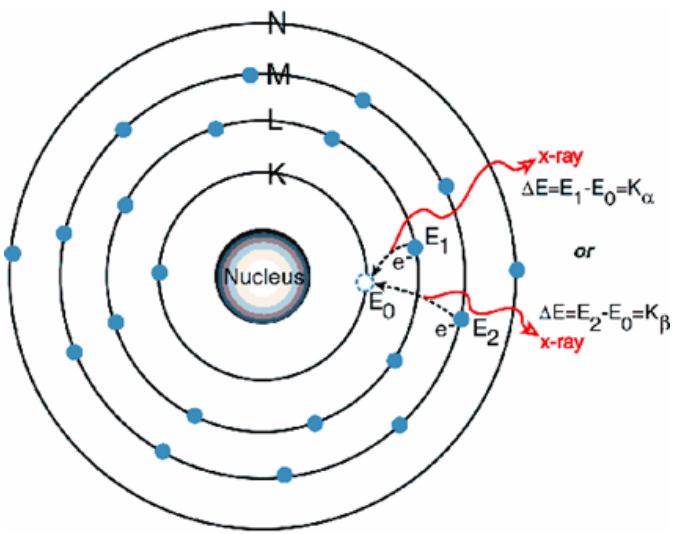






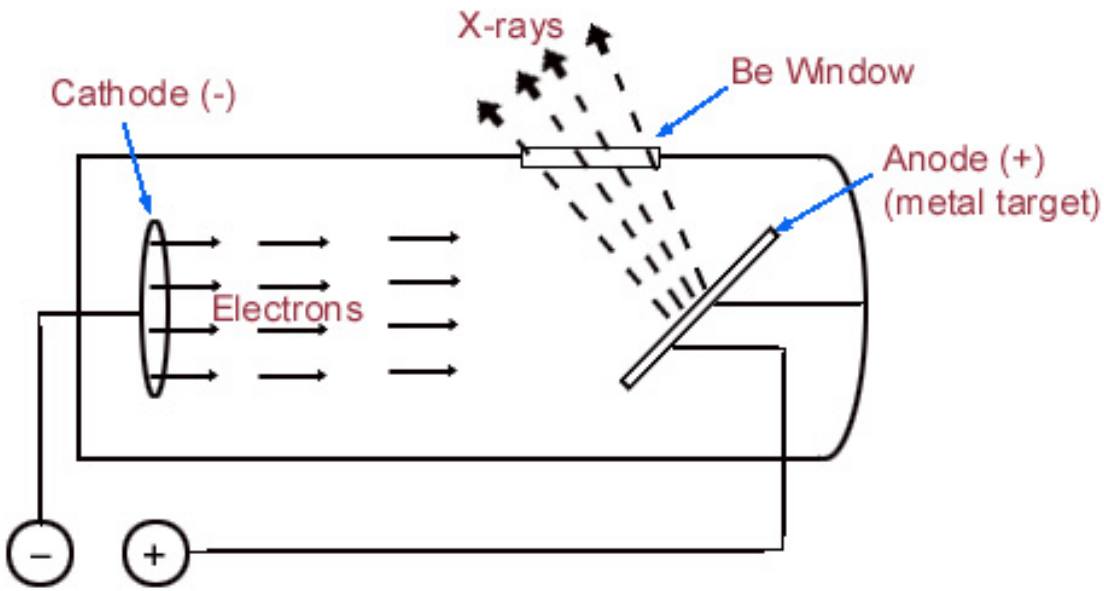
3. Experimental methods
Generation of X-rays





Atomic scale scenario:

- **inner shell electrons are striked out**
- **outer shell electrons fill hole**
- **production of X-rays due to energy difference between inner and outer shell electron**



X-ray tube

3. Determination of 3D structures
Practical work- Essentials

1. Selection of "good" samples:

- Single crystals: diameter < 0.2 mm
- Homogeneous powders: small crystals of one compound

2. Determination of symmetry and unit cell

3. Measurement of diffracted intensities (automatic procedure)

4. Calculation of possible atomic parameters (structure solution)

5. Refinement of the structure model (PC)

- Comparison of experimental and calculated data
- Atomic parameters are optimized until refinement converges

6. Interpretation of the resulting refinement results

- R-values, convergence, thermal parameters

7. Interpretation of the resulting structure (does it make sense?)

- Interatomic distances, occupancy factors (reasonable values?)
- Ionic compounds: compensation of all charges

3. Determination of 3D structures
Results of diffraction studies- Overview

a) Position of the reflections (Bragg's law): Lattice parameters

$(1/d)^2 = (1/a)^2 [h^2 + k^2 + l^2]$

b) Intensity of reflections

- **Symmetry of the structure: Space group**
- **Structure (fractional coordinates)**

c) Profile of the reflections

- **Crystal size and perfection**
  cf. Scherrer formula: $\Delta(2\theta) = \lambda/L\cos\theta$
- **Indications for structural disorder**