Systematics of crystals: symmetry groups

circular dichroism

chiral crystals and molecules

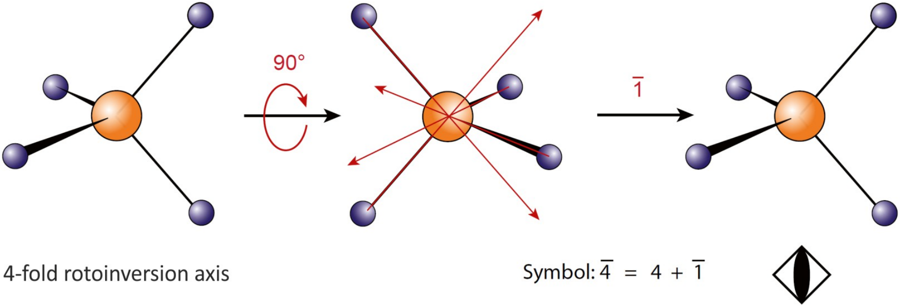
Evgraf Fedorov

by Alexander Tsirlin, Leipzig University

Lecture 3: October 18, 2023

Lecture notes

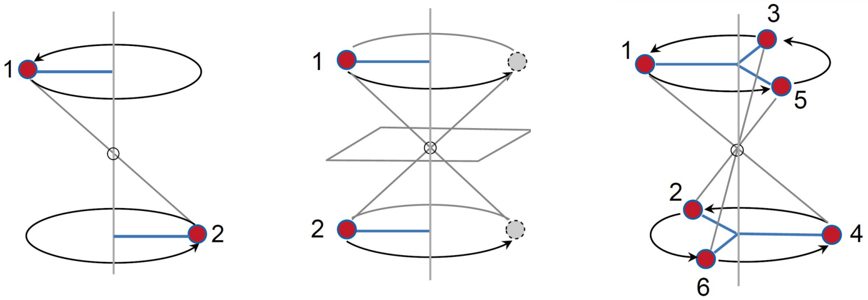
- are now available on the web page
  https://research.uni-leipzig.de/sum/ssp.html
- work in progress, especially figures
  check lecture slides
- not sure if it continues on the weekly basis
  no guarantee whatsoever
- comments, suggestions, corrections welcome
  alexander.tsirlin@uni-leipzig.de
- additional content compared to lectures
  links for further reading (blue color)



Schönflies notation:	*none*
Hermann-Mauguin notation:	$\bar{3}$, $\bar{4}$, $\bar{6}$
Example ($\bar{4} \parallel c$):	$x, y, z \longrightarrow \bar{y}, x, \bar{z}$

Image credit: F. Hoffmann, Faszination Kristalle und Symmetrie

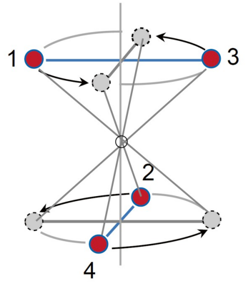
Rotoinversion axes



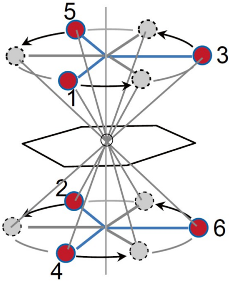
$\bar{1} = i$ $\bar{2} = m$ $\bar{3} = 3 + \bar{1}$

Only $\bar{3}$ is an independent symmetry element here

Image credit: F. Hoffmann, Faszination Kristalle und Symmetrie



$\bar{4} = 4 + \bar{1}$

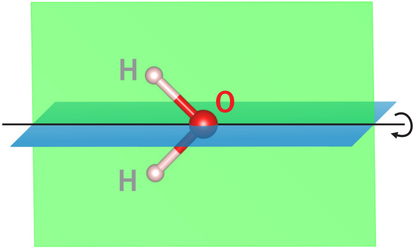


$\bar{6} = 6 + \bar{1} = 3 \perp m$

$\bar{4}$ is an independent symmetry element

$\bar{6}$ is a simpler notation for $3 \perp m$

Image credit: F. Hoffmann, Faszination Kristalle und Symmetrie

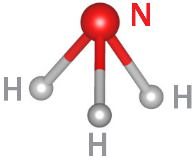


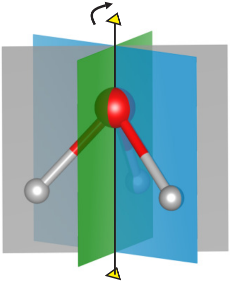
Water

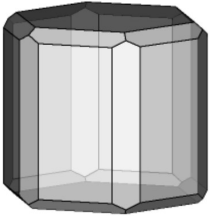
point group: *mm*2

Ammonia

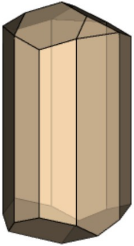
point group: 3*m*



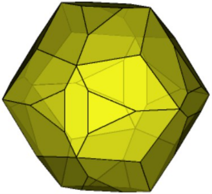




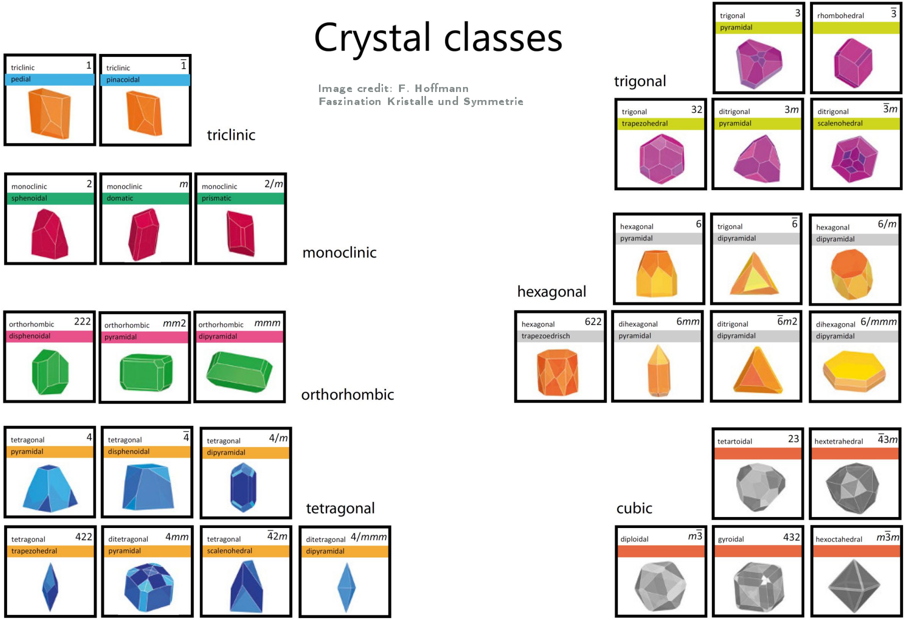

vanadinite ($6/m$)
hexagonal dipyramidal



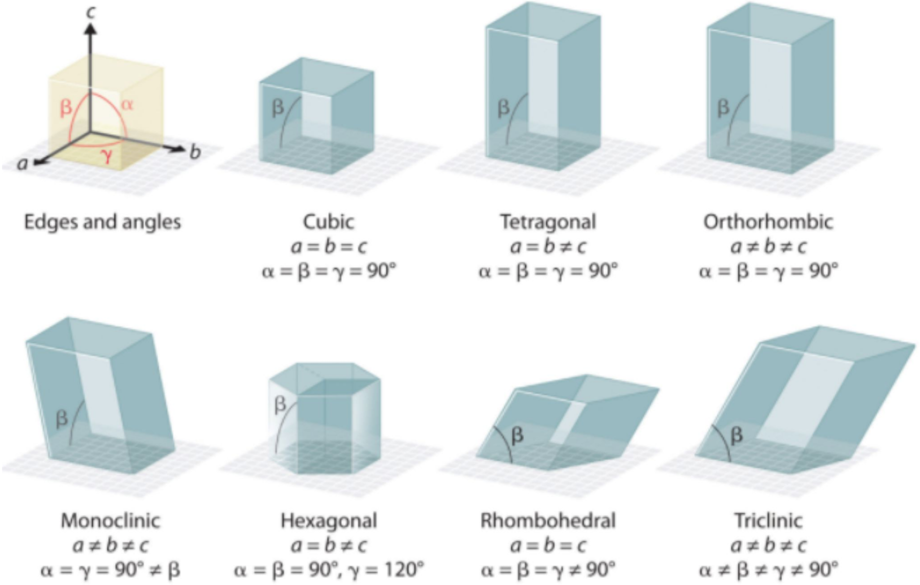

spangolite ($3m$)
ditrigonal pyramidal




skutterudite ($m\bar{3}$)
diploidal


Crystal classes
Image credit: F. Hoffmann
Faszination Kristalle und Symmetrie
triclinic
triclinic 1 pedial
triclinic $\bar{1}$ pinacoidal
monoclinic
monoclinic 2 sphenoidal
monoclinic m domatic
monoclinic $2/m$ prismatic
orthorhombic
orthorhombic 222 disphenoidal
orthorhombic $mm2$ pyramidal
orthorhombic mmm dipyramidal
tetragonal
tetragonal 4 pyramidal
tetragonal $\bar{4}$ disphenoidal
tetragonal $4/m$ dipyramidal
tetragonal 422 trapezohedral
ditetragonal $4mm$ pyramidal
tetragonal $\bar{4}2m$ scalenohedral
ditetragonal $4/mmm$ dipyramidal
trigonal
trigonal 3 pyramidal
rhombohedral $\bar{3}$
trigonal 32 trapezohedral
ditrigonal $3m$ pyramidal
ditrigonal $\bar{3}m$ scalenohedral
hexagonal
hexagonal 6 pyramidal
trigonal $\bar{6}$ dipyramidal
hexagonal $6/m$ dipyramidal
hexagonal 622 trapezoedrisch
dihexagonal $6mm$ pyramidal
ditrigonal $\bar{6}m2$ dipyramidal
dihexagonal $6/mmm$ dipyramidal
cubic
tetartoidal 23
hextetrahedral $\bar{4}3m$
diploidal $m\bar{3}$
gyroidal 432
hexoctahedral $m\bar{3}m$

Crystal systems

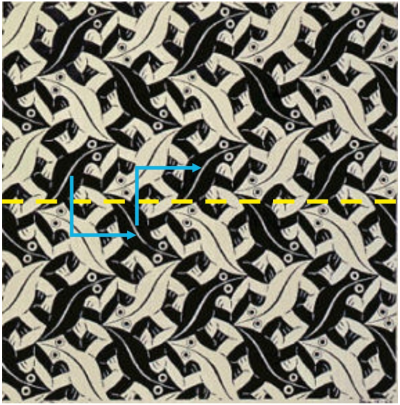


M.C. Escher
Study of the regular division of the plane with reptiles

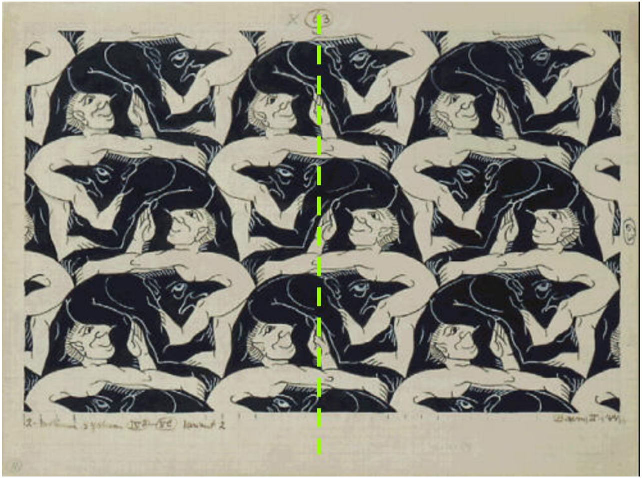
M.C. Escher
Study of the regular division of the plane with reptiles

M.C. Escher
Lizard

M.C. Escher
Study of the regular division of the plane with reptiles



M.C. Escher
Lizard



M.C. Escher, *Pessimist-optimist*

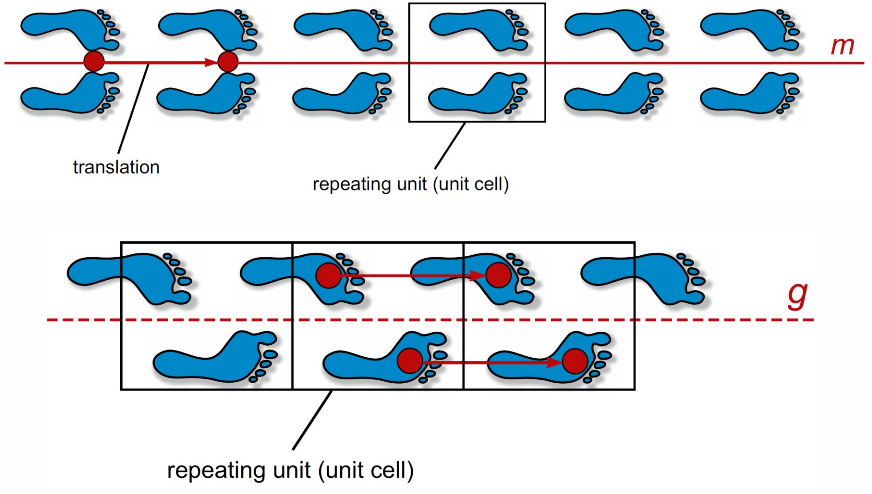
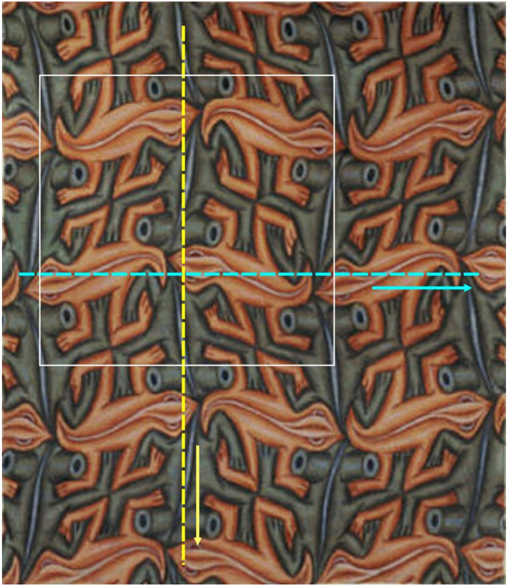


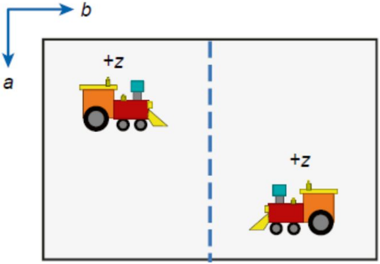
Image credit: F. Hoffmann, Faszination Kristalle und Symmetrie

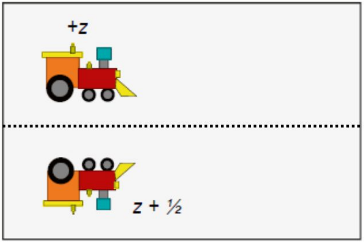


M.C. Escher

Two lizards

Two types of glide planes

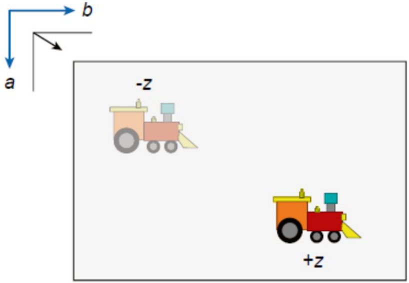


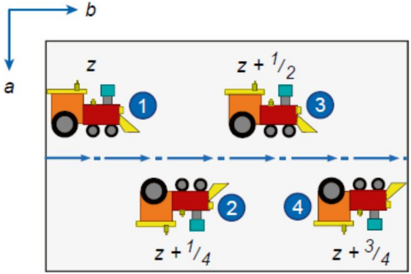


Glide plane $a \perp \boldsymbol{b}$
translation by $\boldsymbol{a}/2$

Glide plane $c \perp \boldsymbol{a}$
translation by $\boldsymbol{c}/2$

Image credit: F. Hoffmann, Faszination Kristalle und Symmetrie





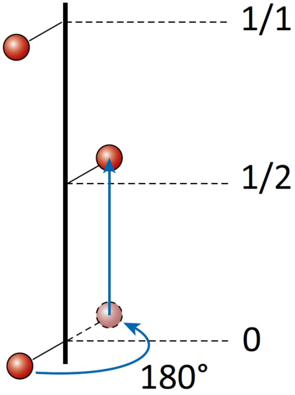
Glide plane $n \perp \boldsymbol{c}$

translation by $(\boldsymbol{a} + \boldsymbol{b})/2$

Glide plane $d \perp \boldsymbol{a}$

translation by $(\boldsymbol{b} + \boldsymbol{c})/4$

Image credit: F. Hoffmann, Faszination Kristalle und Symmetrie



Screw axis
rotation + translation

Image credit: F. Hoffmann, Faszination Kristalle und Symmetrie

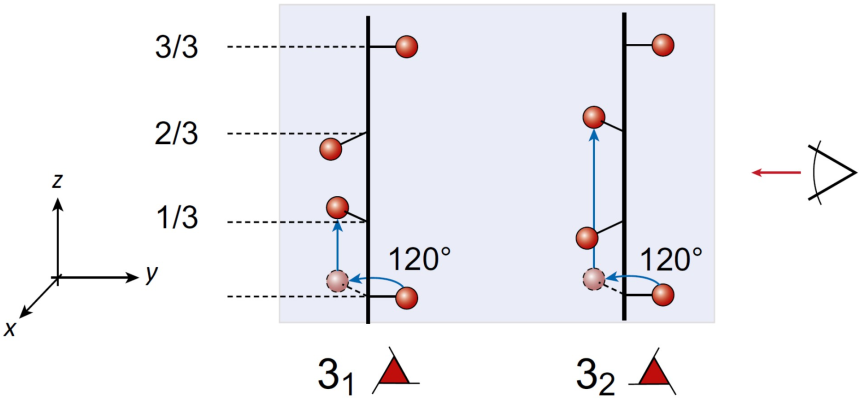


Image credit: F. Hoffmann, Faszination Kristalle und Symmetrie

3_1 and 3_2 imply
opposite rotations

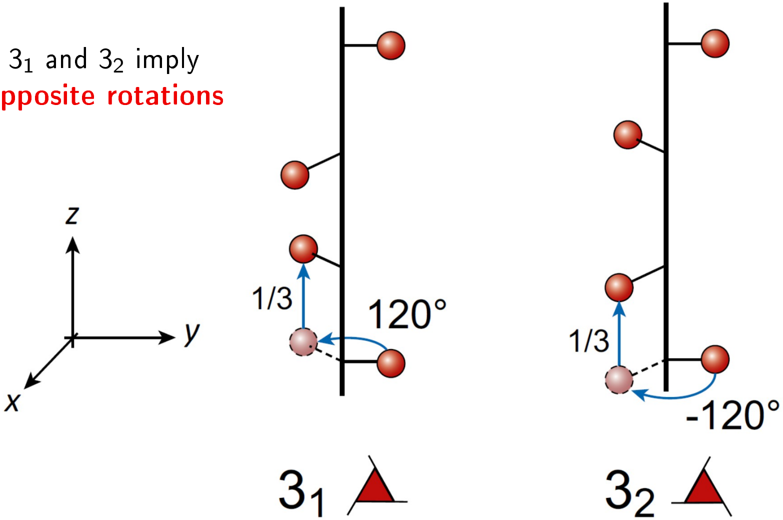
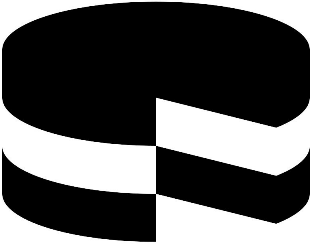


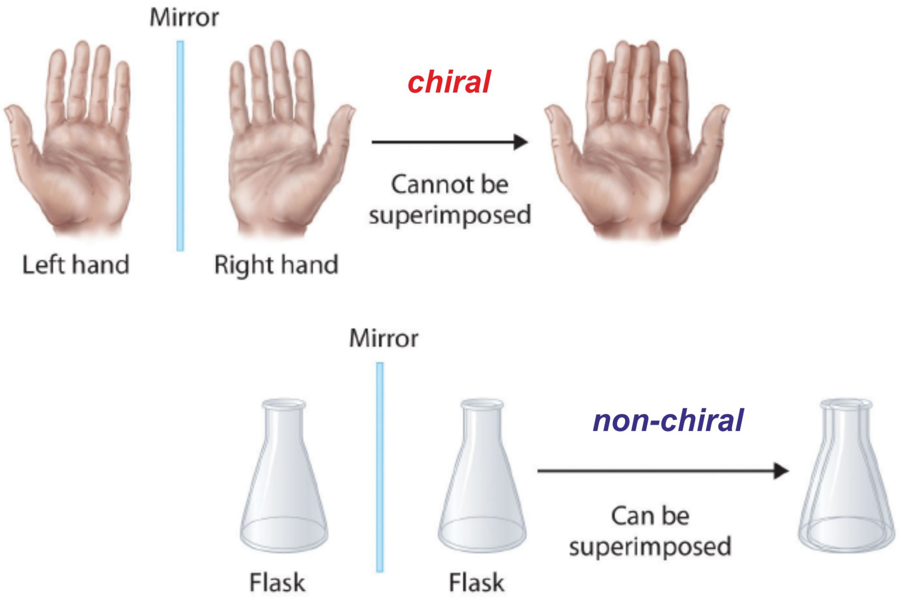
Image credit: F. Hoffmann, Faszination Kristalle und Symmetrie



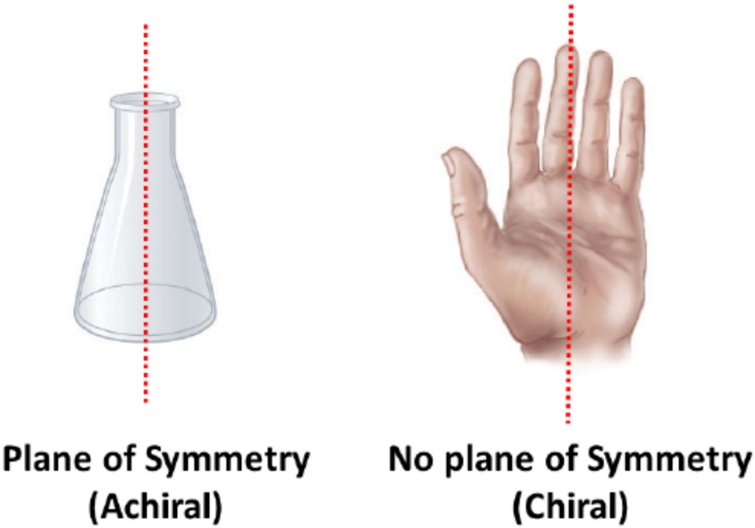
Material

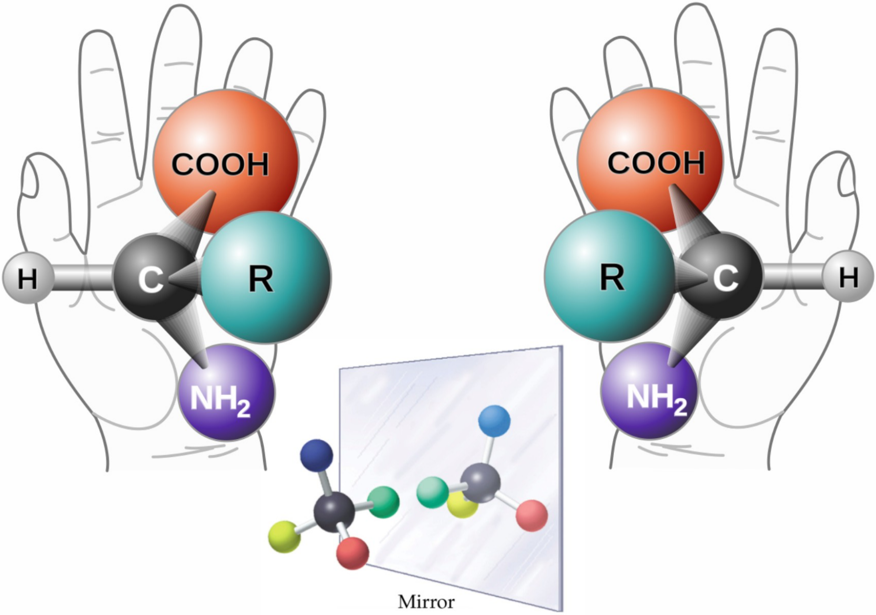
chiral molecules and crystals

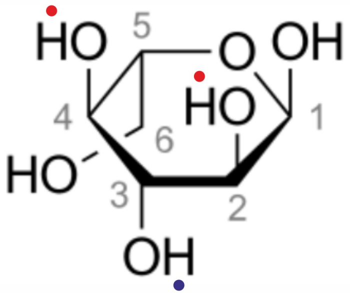

Mirror
Left hand
Right hand
chiral
Cannot be superimposed


Mirror
Left hand
Right hand
chiral
Cannot be superimposed
Mirror
Flask
Flask
non-chiral
Can be superimposed

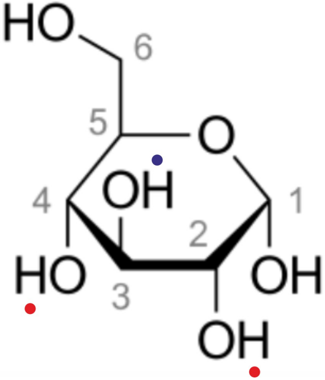
Chirality vs. symmetry




COOH
R
C
H
NH2
Mirror
COOH
R
C
H
NH2

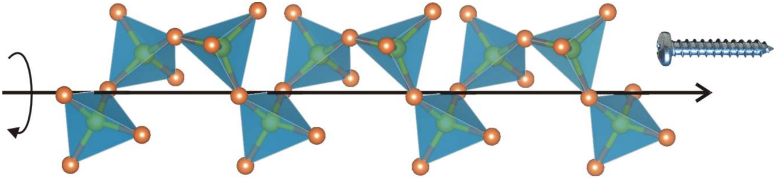


L-glucose
levo

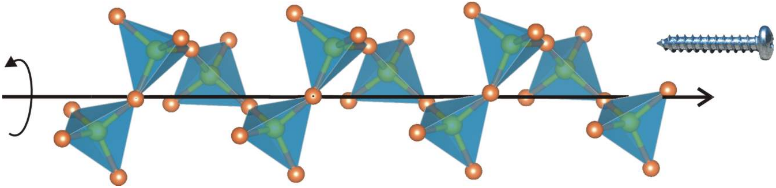


D-glucose
dextro

- same chemical composition
- same bonds
- different **absolute configuration**



right ($P3_221$)

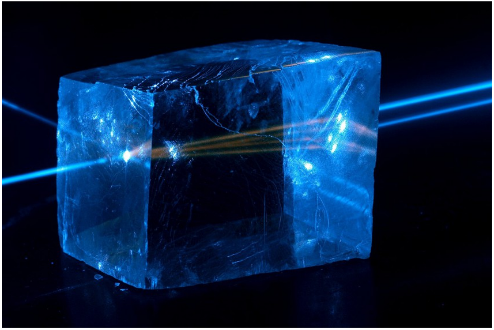


left ($P3_121$)

Many of the symmetry groups are **chiral**

Experimental technique

circular dichroism

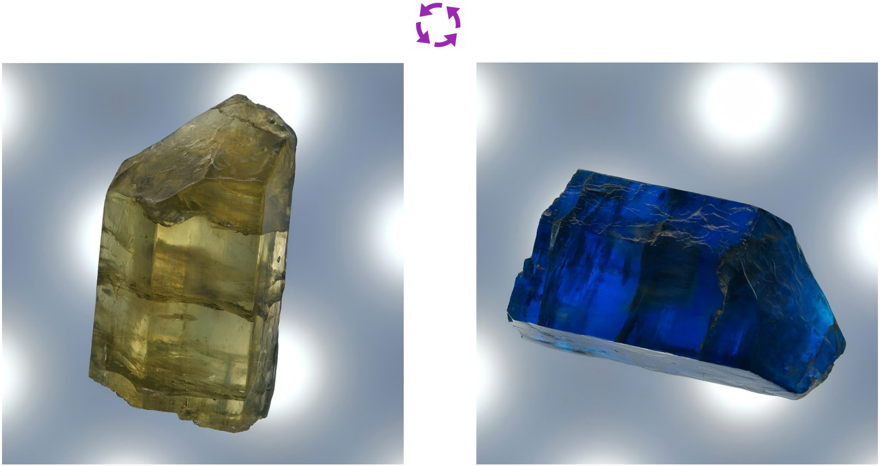


Birefringence

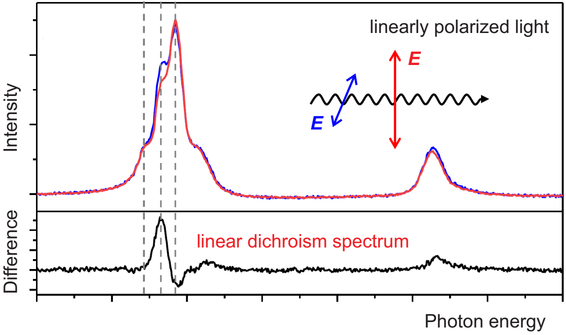
splits light into two beams
typically without affecting color

Dichroic mirror

reflects one color
transmits another



Apatite crystal shows different colors in **polarized light** depending on the orientation

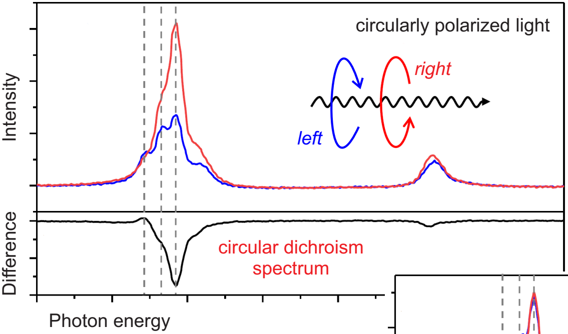


Linear dichroism

different absorption
for two polarizations

crystals with rotation axis

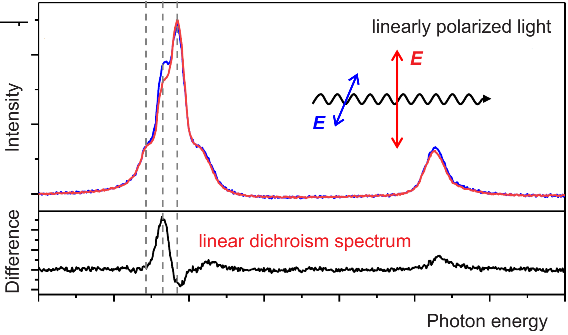
Image credit: Sci. Reports 9, 18169 (2019)



Circular dichroism

different absorption for left and right

chiral crystals

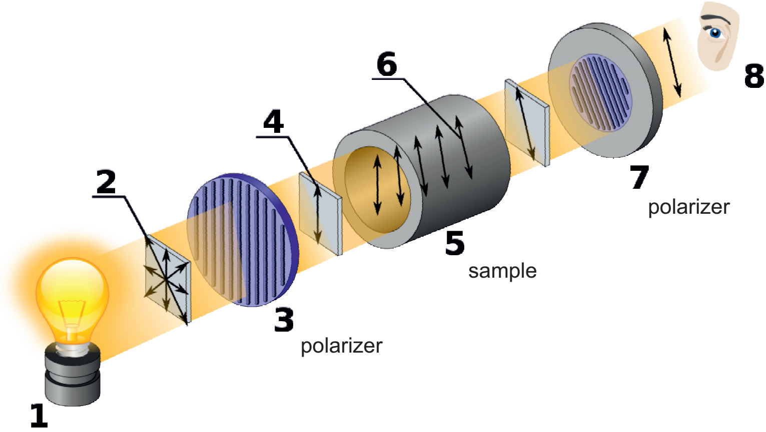


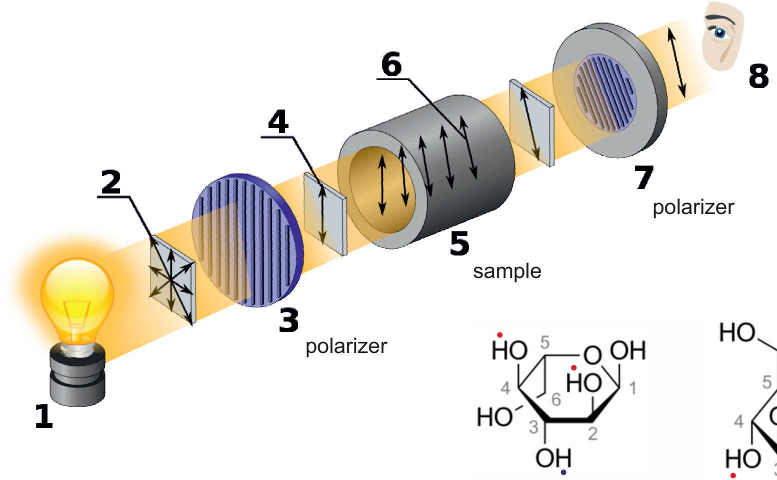
Linear dichroism

different absorption for two polarizations

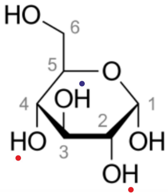
crystals with rotation axis

Image credit: Sci. Reports 9, 18169 (2019)

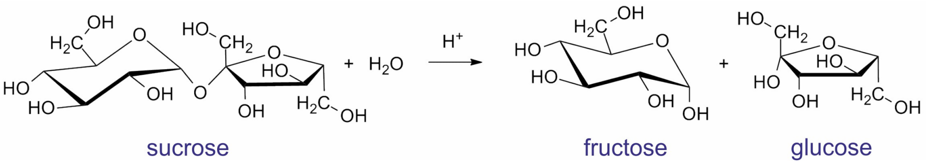

6
4
2
8
7
polarizer
5
sample
3
polarizer
1



L-form
rotation to left

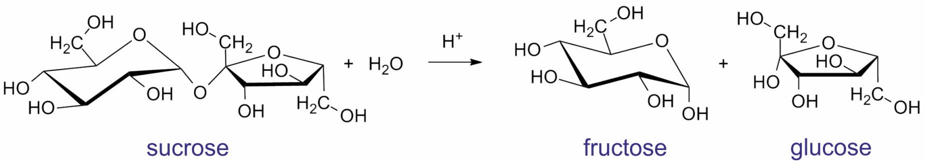


D-form
rotation to right



rotation angles

Sugar	[α] (°)
Sucrose	+66.5
Glucose	+52.7
Fructose	−92.0



rotation angles

Sugar	[α] (°)
Sucrose	+66.5
Glucose	+52.7
Fructose	−92.0

normal syrup
positive rotation

inverted syrup
negative rotation

"Generators"

symmetry elements *with respect to three given viewing directions*

$P\,c\,a\,2_1$ (orthorhombic)

- 2_1 srew axis || **c**
- glide plane *a* ⊥ **b**
- glide plane *c* ⊥ **a**
- Bravais type (kind of centering)

Image credit: F. Hoffmann, Faszination Kristalle und Symmetrie

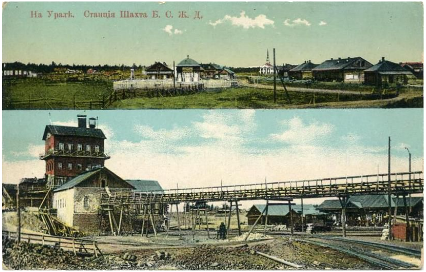
Crystal system	Required symmetries of the point group	Point groups	Space groups	Bravais lattices
Triclinic	None	2	2	1
Monoclinic	1 twofold axis of rotation or 1 mirror plane	3	13	2
Orthorhombic	3 twofold axes of rotation or 1 twofold axis of rotation and 2 mirror planes	3	59	4
Tetragonal	1 fourfold axis of rotation	7	68	2
Trigonal	1 threefold axis of rotation	5	7	1
			18	1
Hexagonal	1 sixfold axis of rotation	7	27	
Cubic	4 threefold axes of rotation	5	36	3
7	**Total**	32	230	14

Source: Wikipedia

Person

Evgraf Fedorov

- 1864–1874: study in a military school, work for the military
- 1874–1880: study at the Saint Petersburg Technological Institute, revolutionary activities
- 1880–1883: study at the Mining Institute
- 1884–1894: geologist at the Turyinsky mines (Ural region)



Evgraf Fedorov
1853–1919

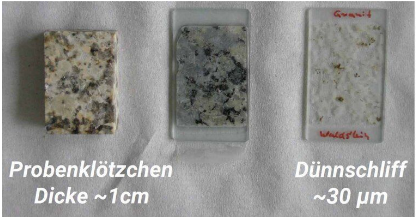
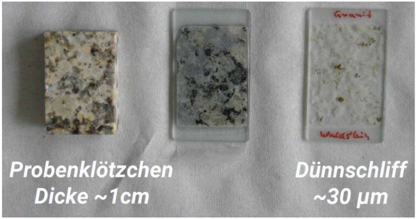


Image credits: Dr. Kilian Pollok (Uni Jena), Vadim Smalkov (CC-BY-SA), musoptin.com (fair use)



All directions probed
on a single thin section
of the mineral

Image credits: Dr. Kilian Pollok (Uni Jena), Vadim Smalkov (CC-BY-SA), musoptin.com (fair use)

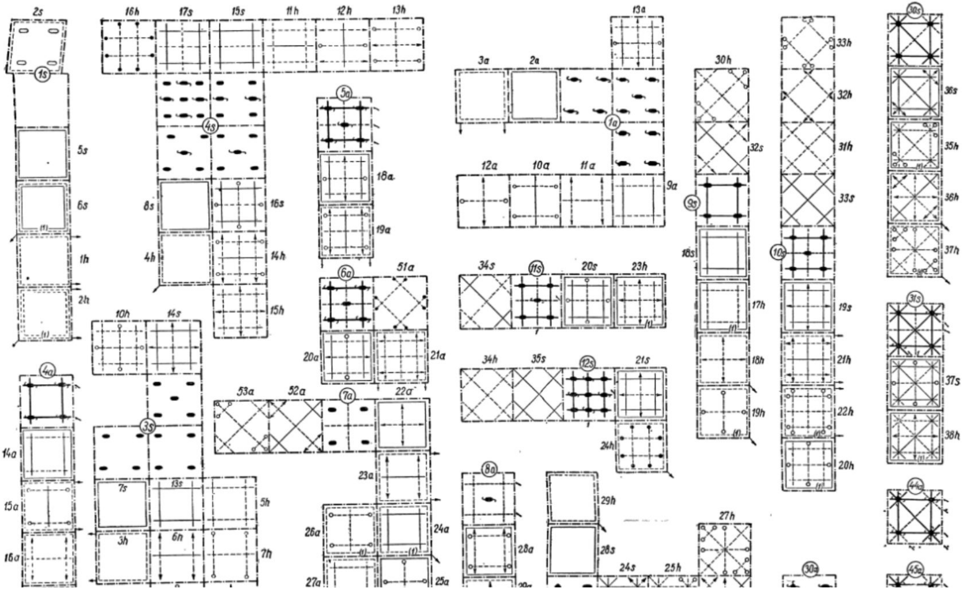


Image credits: Fedorov, International Tables for Crystallography

230 space groups

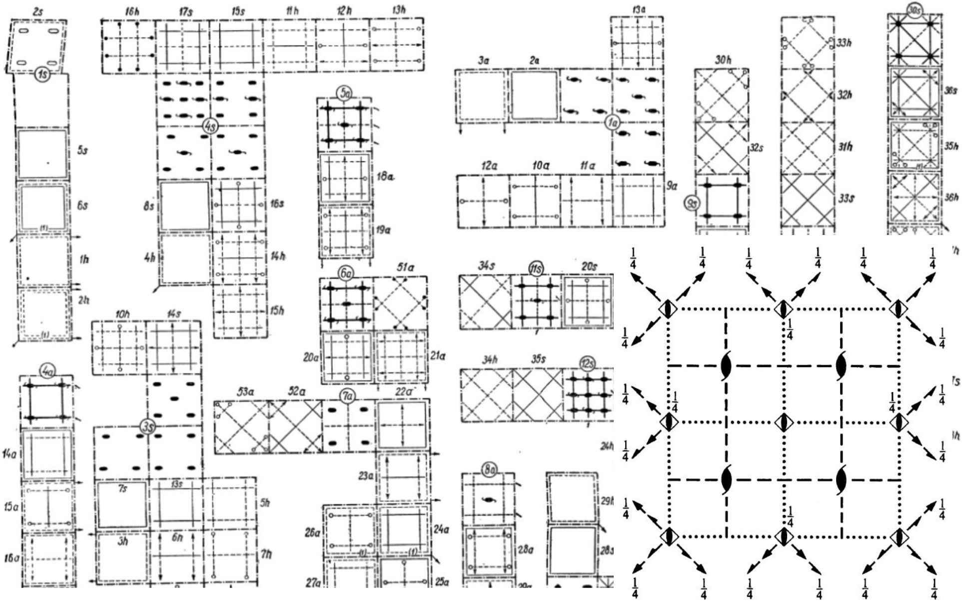


Image credits: Fedorov, International Tables for Crystallography


230
The Space Group List Project
BY NC SA
by Frank Hoffmann
P1 (#1) Gilmarite
P1̄ (#2) Chalcanthite
P2 (#3) Thomasclarkite
P2₁ (#4) Alloclasite
C2 (#5) Dioxo-((S)-N-salicylidene-3-aminopyrrolidine)-vanadium(v)
Pm (#6) BaBe₂Si₂O₇
Pc (#7) Tashelgite
Cm (#8) Gerstleyite
Cc (#9) FeMo₂S₄
P2/m (#10) Muthmannite
P2₁/m (#11) CaSb₂
C2/m (#12) Augelite
P2/c (#13) Ferberite
P2₁/c (#14) B₈S₁₆
C2/c (#15) Jadeite
P222 (#16) Pottasium-L-alaninato-dichloridoplatinate
P222₁ (#17) Cs₂O(B₂O₃)₉
P2₁2₁2 (#18) La₃InS₆
P2₁2₁2₁ (#19) NaAlCl₄
C222₁ (#20) K₂AgS
C222 (#21) Godlevskite
F222 (#22) NaAg(NO₂)₂
I222 (#23) NaFeS₂
I2₁2₁2₁ (#24) (1R,2R)-1,2-Diaminocyclohexane (2R,3R)-2,3-butanediol
Pmm2 (#25) GaAs
Pmc2₁ (#26) Carbocernaite
Pcc2 (#27) 2,5-Bis(5-bromo-2-thienyl)-thiophene
Pma2 (#28) Krennerite
Pca2₁ (#29) Cobaltite
Pnc2 (#30) Terskite
Pmn2₁ (#31) Enargite
Pba2 (#32) Minyulite
Pna2₁ (#33) Wakabayashilite
Pnn2 (#34) Li₂TiTeO₆
Cmm2 (#35) KNbW₂O₉
Cmc2₁ (#36) Spertiniite
Ccc2 (#37) ZP-4
Amm2 (#38) Ca₂Na₂(CO₃)₃
Abm2 (#39) 2,5-bis(4-Bromobenzylidene)-cyclopentanone
Ama2 (#40) LiBH₄ (at 2.4 Gpa)
Abc2 (#41) Si₂CN₄
Fmm2 (#42) CH₂I₂
Fdd2 (#43) Edenharterite
Imm2 (#44) AgNO₂
Iba2 (#45) Banalsite
Ima2 (#46) Batisite
Pmmm (#47) Ta₄O
Pnnn (#48) (μ2-Oxo)-bis(Cl₃- bis(1-H₃C-imidazole)-oxo-rhenium(v))
Pccm (#49) CsPr(MoO₄)₂
Pban (#50) Retzian
Pmma (#51) BaThBr₆
Pnna (#52) SnWO₄
Pmna (#53) FeNbTe₂
Pcca (#54) AgClO₂
Pbam (#55) Reinerite
Pccn (#56) Valentinite
Pbcm (#57) BaTiOF₄
Pnnm (#58) Cu(NH₃)₄(NO₃)₂
Pmmn (#59) Pasavaite
Pbcn (#60) CuNb₂O₆
Pbca (#61) Hambergite
Pnma (#62) Avogadrite
Cmcm (#63) Ferruccite
Cmca (#64) Tuhualite
Cmmm (#65) MgVO₃
Cccm (#66) Cordierite
Cmma (#67) Johachidolite
Ccca (#68) Magnesiocarpholite
Fmmm (#69) La₂NiO₄.₁₅
Fddd (#70) Thenardite
Immm (#71) VNi₂
Ibam (#72) Leningradite
Ibca (#73) Chesnokovite
Imma (#74) Weberite
P4 (#75) Na₀.₁WO₃
P4₁ (#76) Percleveite
P4₂ (#77) Pinnoite
P4₃ (#78) Sr₂As₂O₇
I4 (#79) WOBr₄
I4₁ (#80) NbO₂
P4̄ (#81) Zr(P₂S₆)
I4̄ (#82) In(PS₄)
P4/m (#83) BaLa4Cu₅O₁₃
P4₂/m (#84) Sr₂Fe₀.₉₇Mo₀.₉₄O₅.₈₁
P4/n (#85) PCl₄SbF₆
P4₂/n (#86) NaSb(OH)₆
I4/m (#87) Sr₂Ni(WO₆)
I4₁/a (#88) Na(AlH₄)
P422 (#89) [Pt₂(μ-OCOCH₃)₄-(μ-OCOC₅H₄FeCp)₄]
P42₁2 (#90) Ba(VO)Cu₄(PO₄)₄
P4₁22 (#91) Mg₂(TiO₄)
P4₁2₁2 (#92) Cristobalite
P4₂22 (#93) [AsPh₄][Ce(S₂PMe₂)₄]
P4₂2₁2 (#94) Zinc(II) 4,4'-Bipyridine-2,6,2',6'-tetracarboxylate
P4₃22 (#95) Na₂S
P4₃2₁2 (#96) Li(AlSi₂O₆)
I422 (#97) Ekanite
I4₁22 (#98) CPF-1
P4mm (#99) BaTiO₃
P4bm (#100) Na₀.₅Bi₀.₅TiO₃
P4₂cm (#101) [Me₄N][Cu₂(NCS)₃]
P4₂nm (#102) S₄N₄
P4cc (#103) VOSe₂O₅
P4nc (#104) HgTlBa₂CuOₓ

- 1864–1874: study in a military school, work for the military
- 1874–1880: study at the Saint Petersburg Technological Institute, revolutionary activities
- 1880–1883: study at the Mining Institute
- 1884–1894: geologist at the Turyinsky mines (Ural region)

- 1889: developed the rotation stage
- 1891: classification of 230 space groups
- 1896: elected member of the Bavarian Academy of Sciences
- from 1905: professor at the Mining Institute

William Bragg (1914):

"I have considered your method with great interest. **I find it so difficult to describe a structure in words...** I will try to depict the great lot of crystals I do in your way."

Evgraf Fedorov
1853–1919