Handout 2: Symmetry in Crystallography

Chem 4850/6850/8850

X-ray Crystallography

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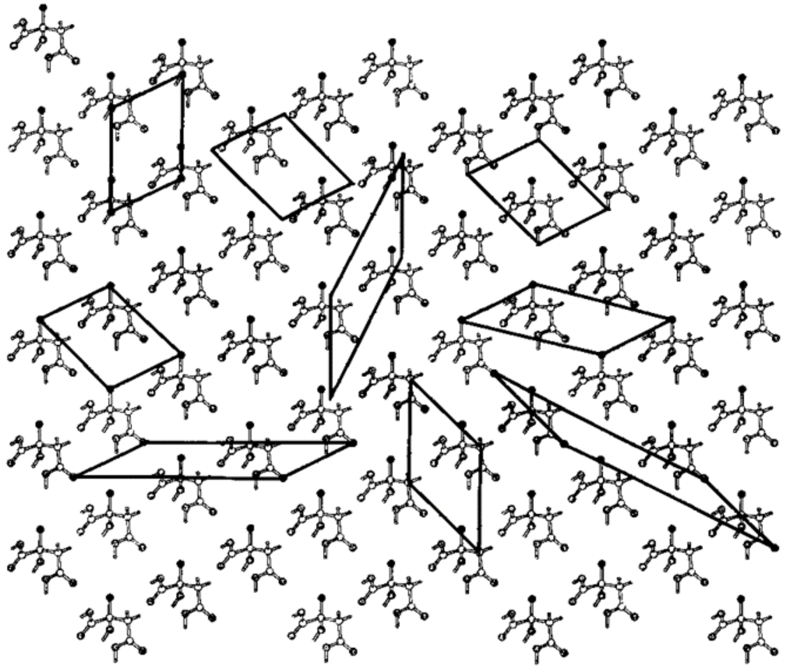
Symmetry and crystals

- **Imagine…**
  - having to describe an infinite crystal with an infinite number of atoms
  - or even a finite crystal, with some 10^{20} atoms
- **Sounds horrible? Well, there's symmetry to help you out! Instead of an infinite number of atoms, you only need to describe the contents of one unit cell, the structural repeating motif…**
  - and life could be even easier, if there are symmetry elements present inside the unit cell!
  - you only need to describe the asymmetric unit if this is the case

Lattice symmetry

- Lattice symmetry refers to the unit cell size and shape
- Without rules, there would be an infinite number of different unit cells to describe any given lattice



"Crystal Structure Analysis for Chemists and Biologists", Glusker, Lewis and Rossi, VCH, 1994.

Unit cell choice

- **By convention, a unit cell is chosen as**
  - the smallest possible repeat unit
  - which has the highest symmetry
- **This can result in *primitive* unit cells or *centered* unit cells**
  - not all crystal systems can be centered by this definition
  - the seven crystal systems in combination with the centering operations give rise to the 14 Bravais lattices

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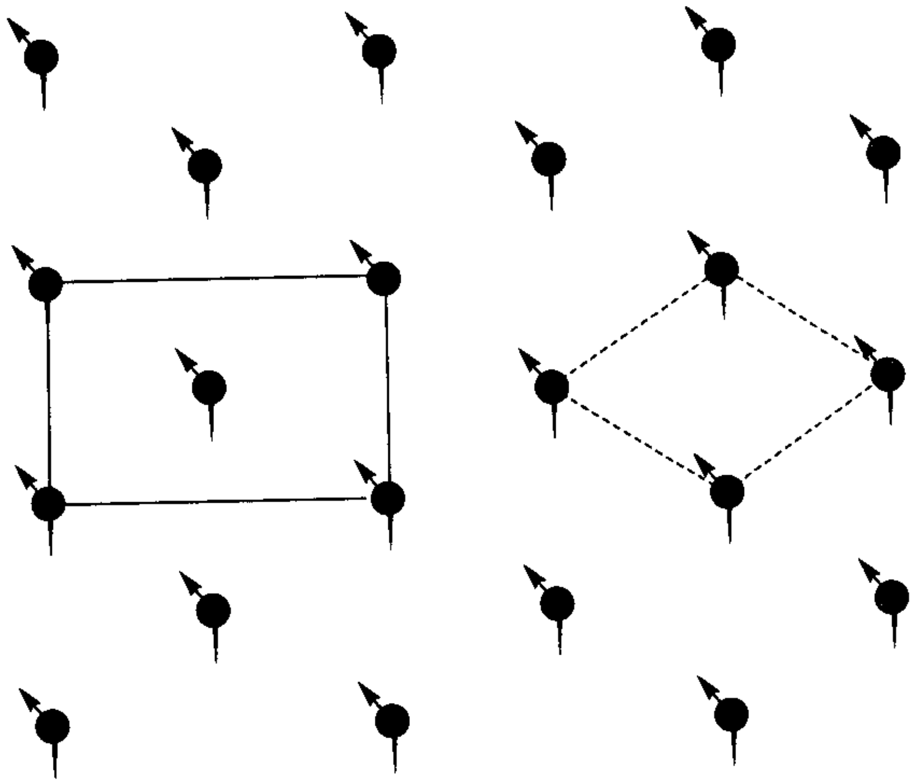
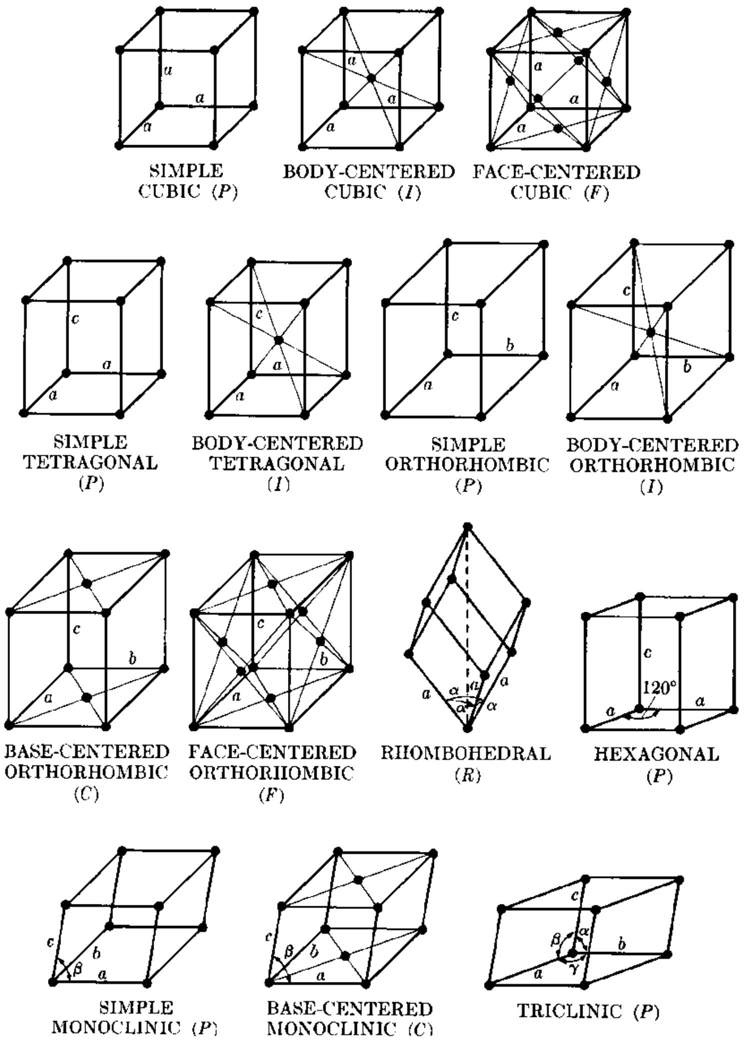
An example of unit cell choice

- **According to our definitions, the centered cell would be preferred**



"Crystal Structure Analysis for Chemists and Biologists", Glusker, Lewis and Rossi, VCH, 1994.

The 14 Bravais lattices



"Elements of X-ray Diffraction", Cullity and Stock, Prentice Hall College Div., 3rd edition, 2001.

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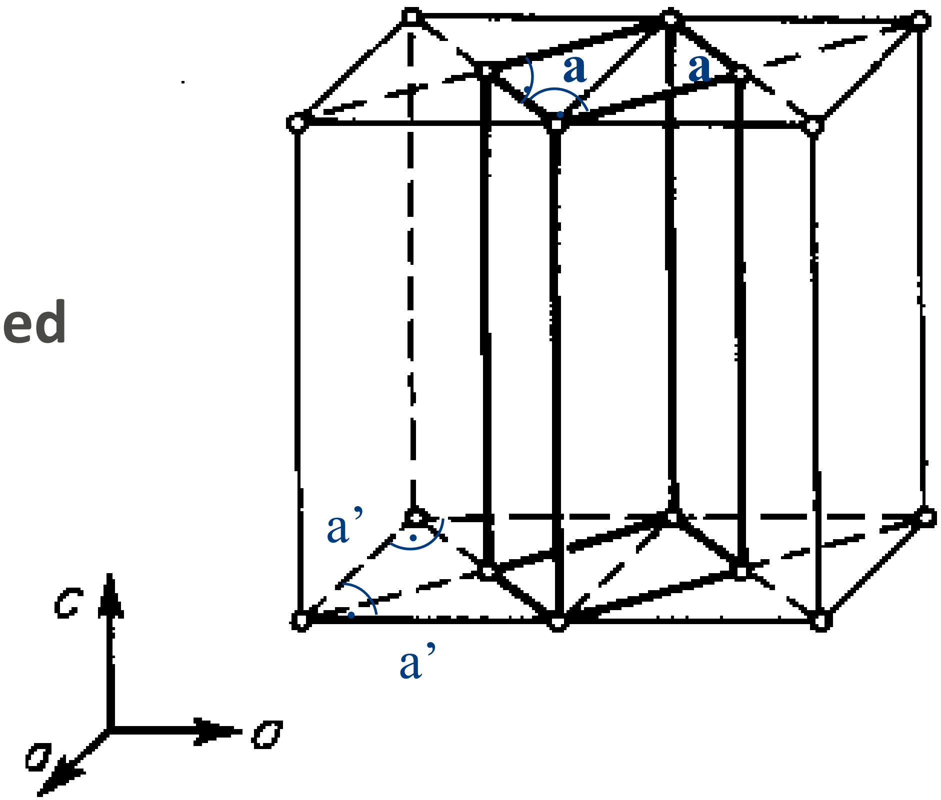
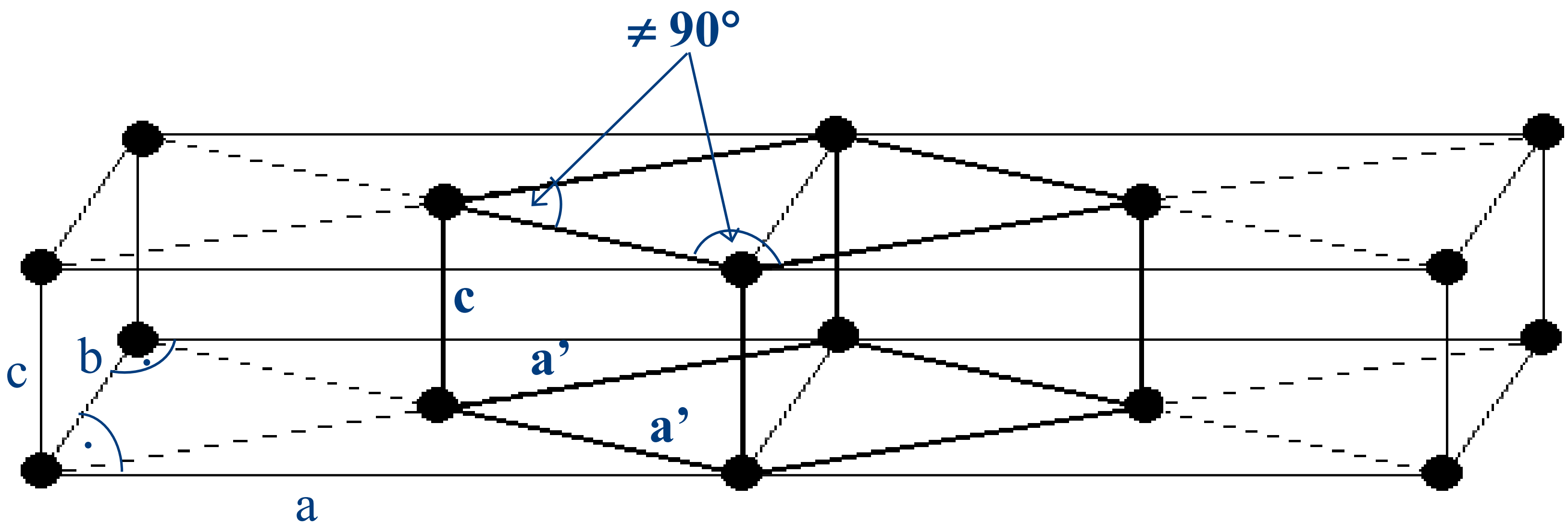
Why can only some lattices be centered?

- A tetragonal base centered cell can always be transformed into a tetragonal primitive cell



Why can only some lattices be centered? (2)



- An orthorhombic base centered cell cannot be transformed into a primitive cell without losing the orthorhombic symmetry

Symmetry elements

- **When talking about symmetry operations, we must distinguish**
  - point symmetry elements
  - translational symmetry
- **Point symmetry elements will always leave at least one point unchanged**
  - rotation axes
  - mirror planes
  - rotation-inversion axes

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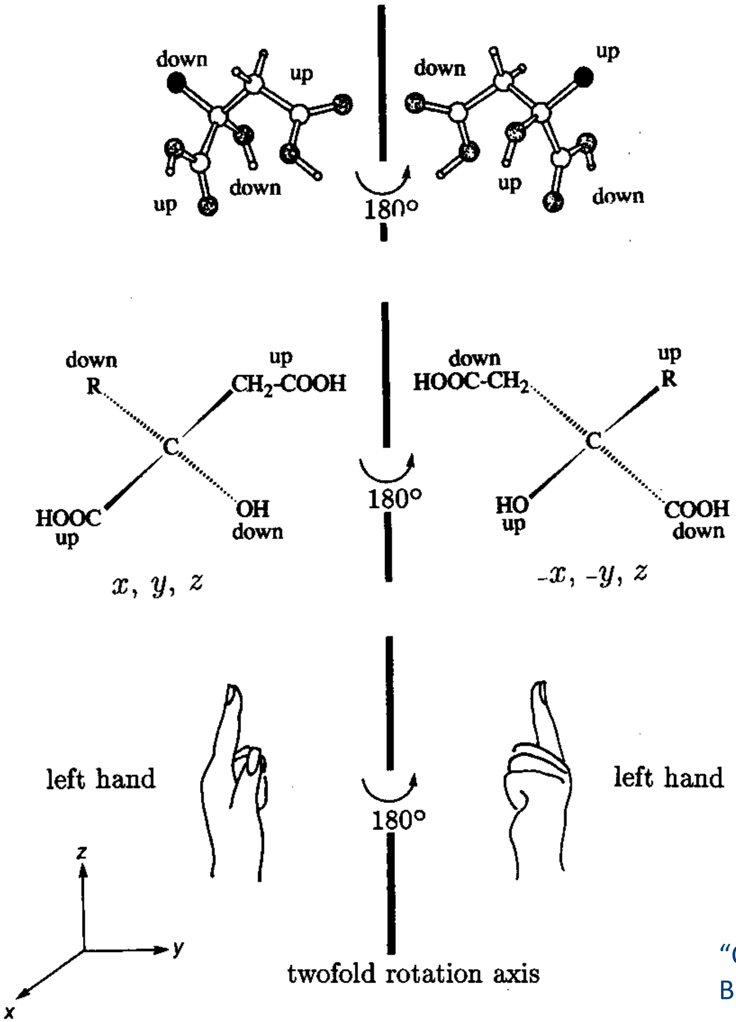
Rotation axes



- **Example: A two-fold rotation axis**
  - no change in handedness
  - referred to as "proper symmetry operation"
- **An *n*-fold rotation axis will rotate the object by 360/*n*°**
- **Symbol: *n* (e.g., 2, 3, 4, 6)**

"Crystal Structure Analysis for Chemists and Biologists", Glusker, Lewis and Rossi, VCH, 1994.

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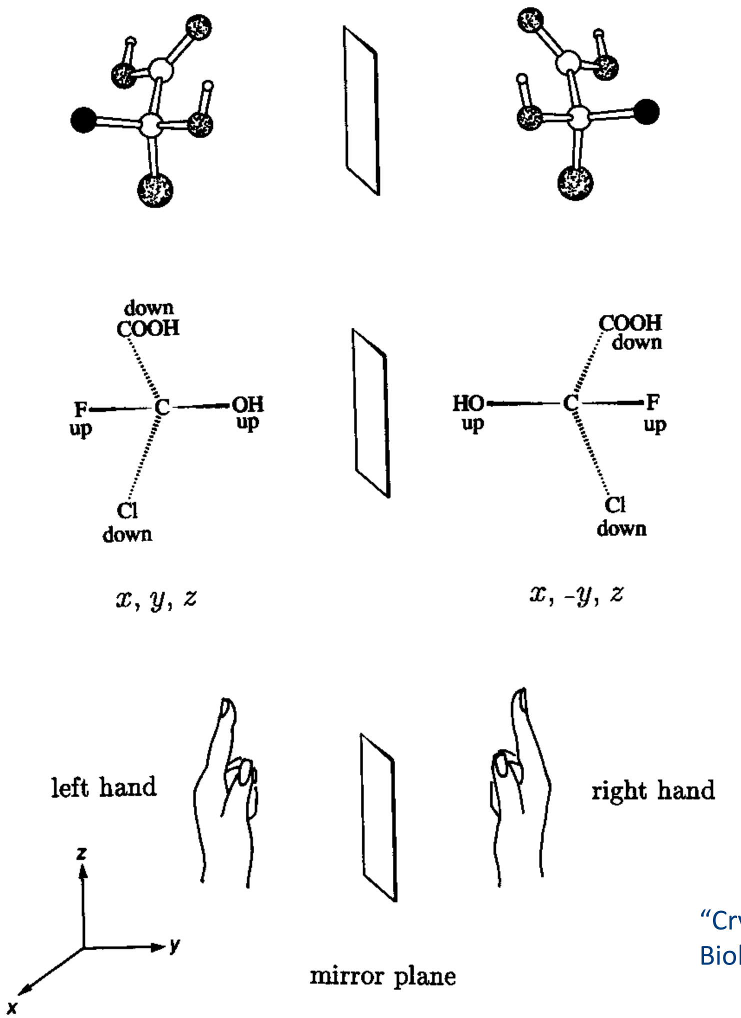
Mirror planes

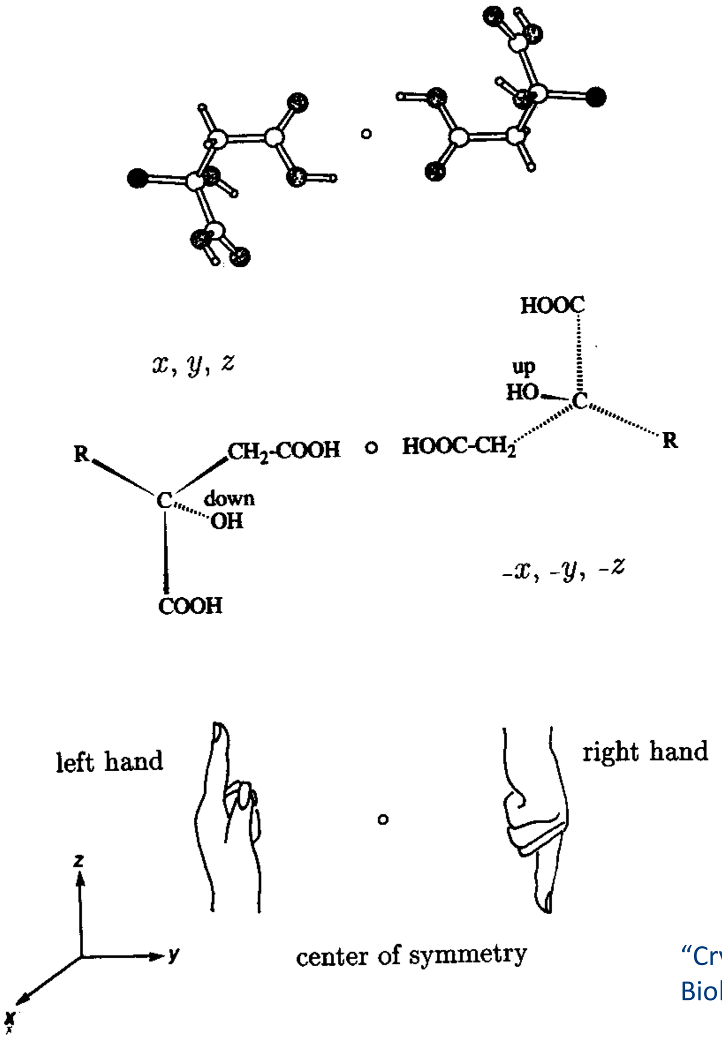


- **A mirror plane changes the handedness of the object it is operating on**
  - cannot exist in crystals of an enantiomerically pure substance
  - referred to as “improper symmetry operation”
- **Symbol: m**

“Crystal Structure Analysis for Chemists and Biologists”, Glusker, Lewis and Rossi, VCH, 1994.

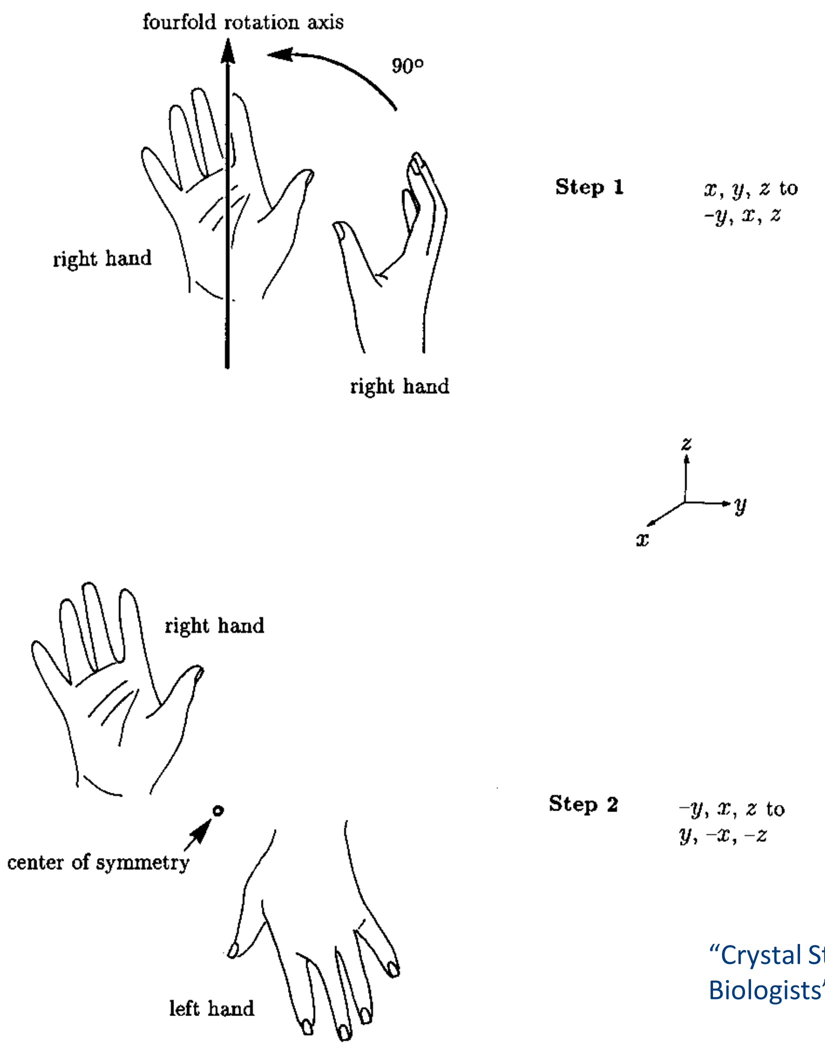
Inversion centers

- **"Turning an object inside out"**
- **Equivalent to a "point reflection" through the inversion center**
    - similar to focal point of a lense
    - changes handedness
- **Symbol: i**



"Crystal Structure Analysis for Chemists and Biologists", Glusker, Lewis and Rossi, VCH, 1994.

Rotation-inversion centers



- Rotation followed by inversion
- An inversion center can be regarded as a "one-fold rotation" followed by an inversion
- Symbol: -*n* or $\bar{n}$

"Crystal Structure Analysis for Chemists and Biologists", Glusker, Lewis and Rossi, VCH, 1994.

Watch out…

- **Crystallographers work with rotation-inversion axes**
- **If you take a class in Group Theory or another subject involving symmetry operations, your teacher may not consider rotation-inversion axes a symmetry operation**
  - they use rotation-reflection axes (symbol: S_n)
  - rotation-inversion and rotation-reflection axes are NOT the same!
    - an inversion center corresponds to a "–1 axis", but to an S_2 axis!
  - however, any compound that has a –4 axis will also possess an S_4 axis

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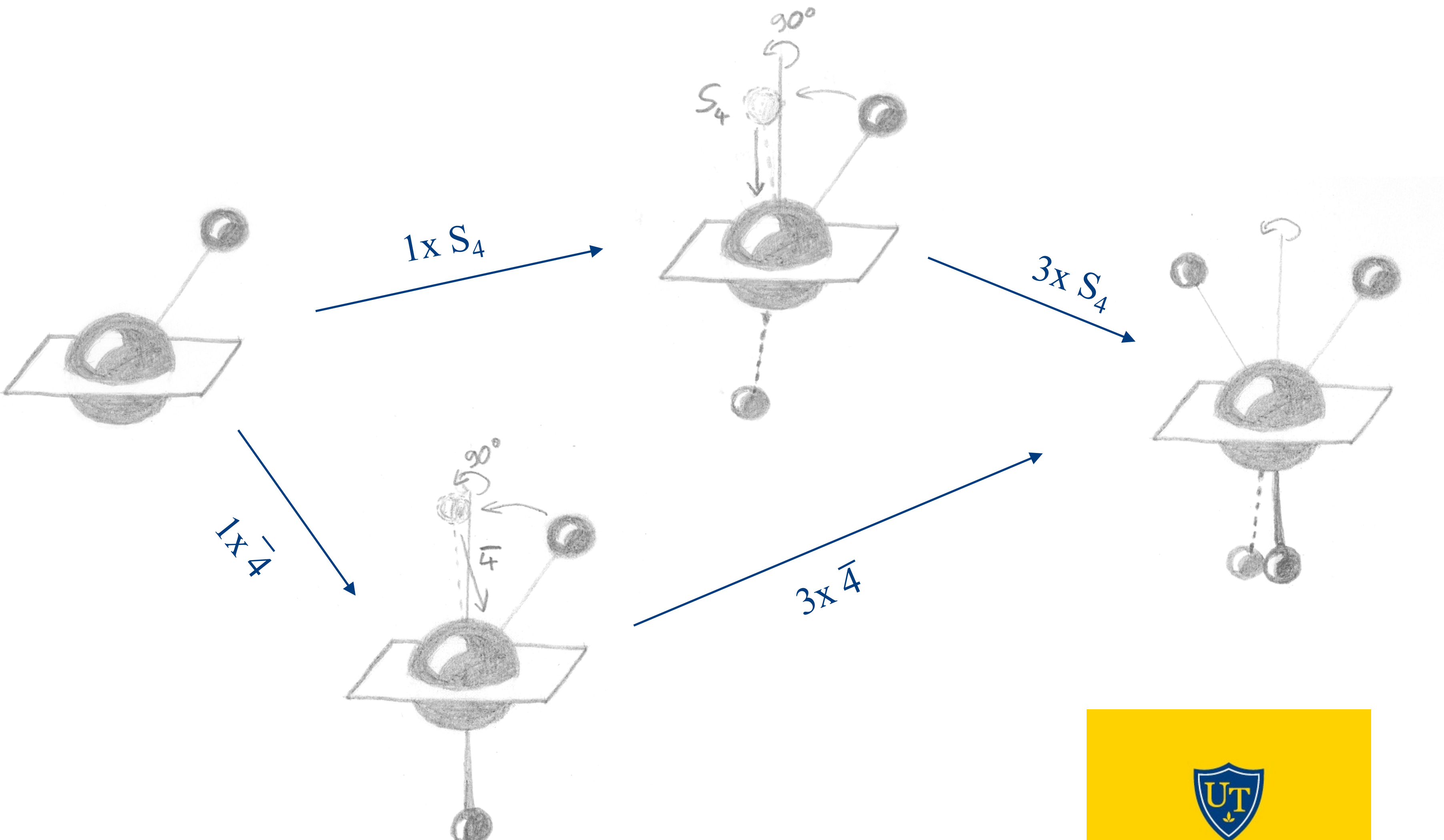
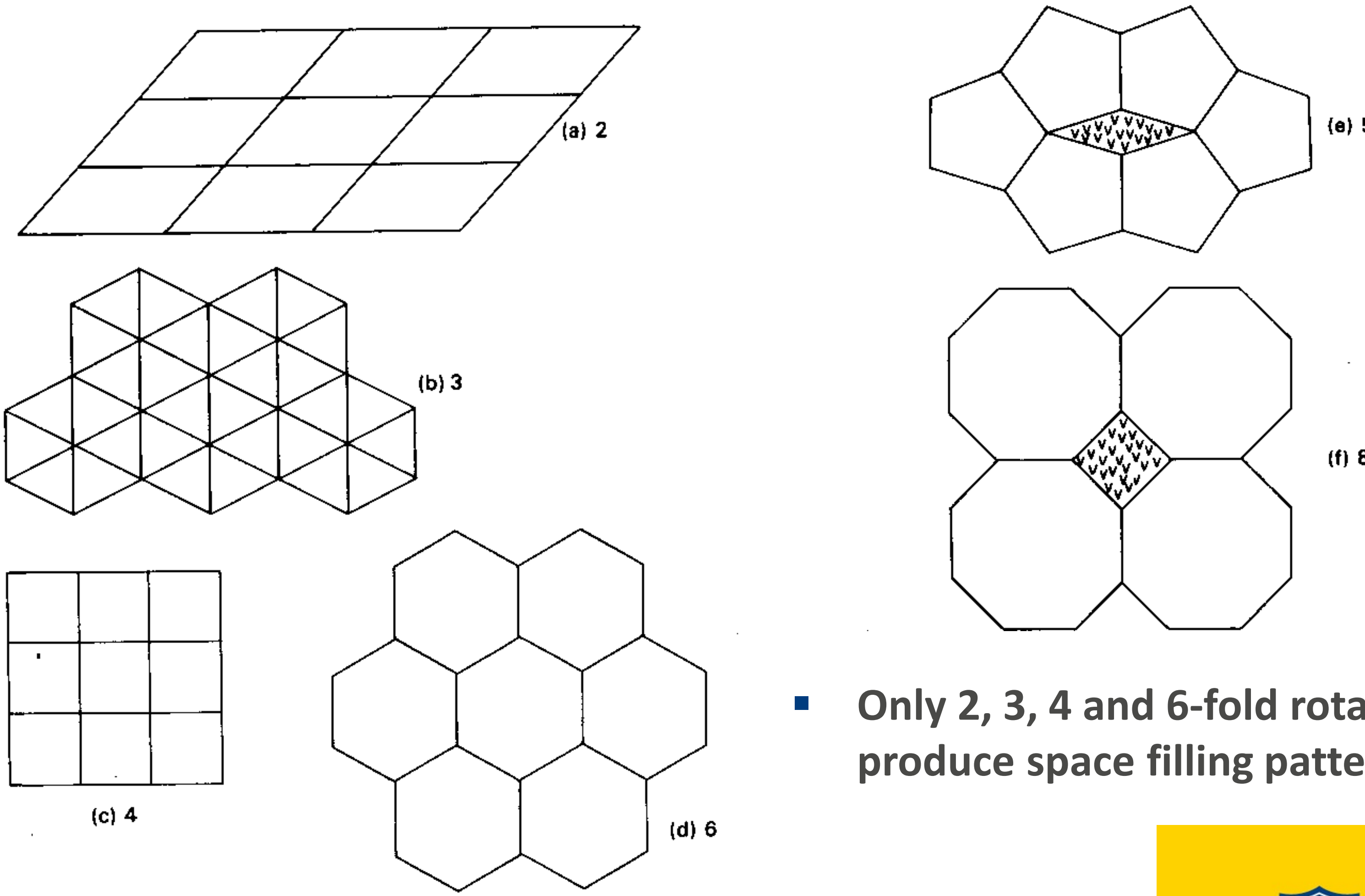
S_4 versus -4



Combining symmetry operations

- **An object can possess several symmetry elements**
- **Not all symmetry elements can be combined arbitrarily**
  - for example, two perpendicular two-fold axes imply the existence of a third perpendicular two-fold
- **Translational symmetry in 3D imposes limitations**
  - only 2, 3, 4 and 6-fold rotation axes allow for space filling translational symmetry
- **The allowed combinations of symmetry elements are called point groups**
  - there are 32-point groups that give rise to periodicity in 3D

Space Filling Repeat Patterns



- **Only 2, 3, 4 and 6-fold rotations can produce space filling patterns**

"Structure Determination by X-ray Crystallography", Ladd and Palmer, Plenum, 1994.

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Point groups

- Show 3D repeat pattern
- Contain symmetry elements
- 32-point groups exist

System	Point groups	Symbol meaning, appropriate to position occupied: First position	Second position	Third position
Triclinic	1, $\bar{1}$	One symbol position only, denoting all directions in the crystal		
Monoclinic[a,b]	2, m, $2/m$	One symbol position only: 2 or $\bar{2}$ along y		
Orthorhombic	222, $mm2$, mmm	2 and/or $\bar{2}$ along x	2 and/or $\bar{2}$ along y	2 and/or $\bar{2}$ along z
Tetragonal	4, $\bar{4}$, $4/m$	4 and/or $\bar{4}$ along z	—	—
	422, $4mm$, $\bar{4}2m$, $\frac{4}{m}mm$	4 and/or $\bar{4}$ along z	2 and/or $\bar{2}$ along x, y	2 and/or $\bar{2}$ at 45° xy plane
Trigonal[c]	3, $\bar{3}$	3 or $\bar{3}$ along z	—	—
	32, $3m$, $\bar{3}m$	3 or $\bar{3}$ along z	2 and/or $\bar{2}$ along x, y, u	—
Hexagonal	6, $\bar{6}$, $6/m$	6 and/or $\bar{6}$ along z	—	—
	622, $6mm$, $\bar{6}m2$, $\frac{6}{m}mm$	6 and/or $\bar{6}$ along z	2 and/or $\bar{2}$ along x, y, u	2 and/or $\bar{2}$ at 30° to x, y, u in the xyu plane
Cubic	23, $m3$	2 and/or $\bar{2}$ along x, y, z	3 or $\bar{3}$ at 54.74°[d] to x, y, z	—
	432, $\bar{4}3m$, $m3m$	4 and/or $\bar{4}$ along x, y, z	3 or $\bar{3}$ at 54.74°[d] to x, y, z	2 and/or $\bar{2}$ at 45° to x, y, z in xy, yz, and zx planes

[a] In the monoclinic system, the y axis is taken as the unique 2 or $\bar{2}$ axis. Since $\bar{2} \equiv m$, then if $\bar{2}$ is along y, the m plane represented by the same position in the point-group symbol is perpendicular to y. The latter comment applies *mutatis mutandis* in other crystal systems. (It is best to specify the orientation of a plane by that of its normal.)

[b] R/m occupies a single position in a point-group symbol.

[c] For convenience, the trigonal system is referred to hexagonal axes.

[d] Actually $\cos^{-1}(1/\sqrt{3})$.

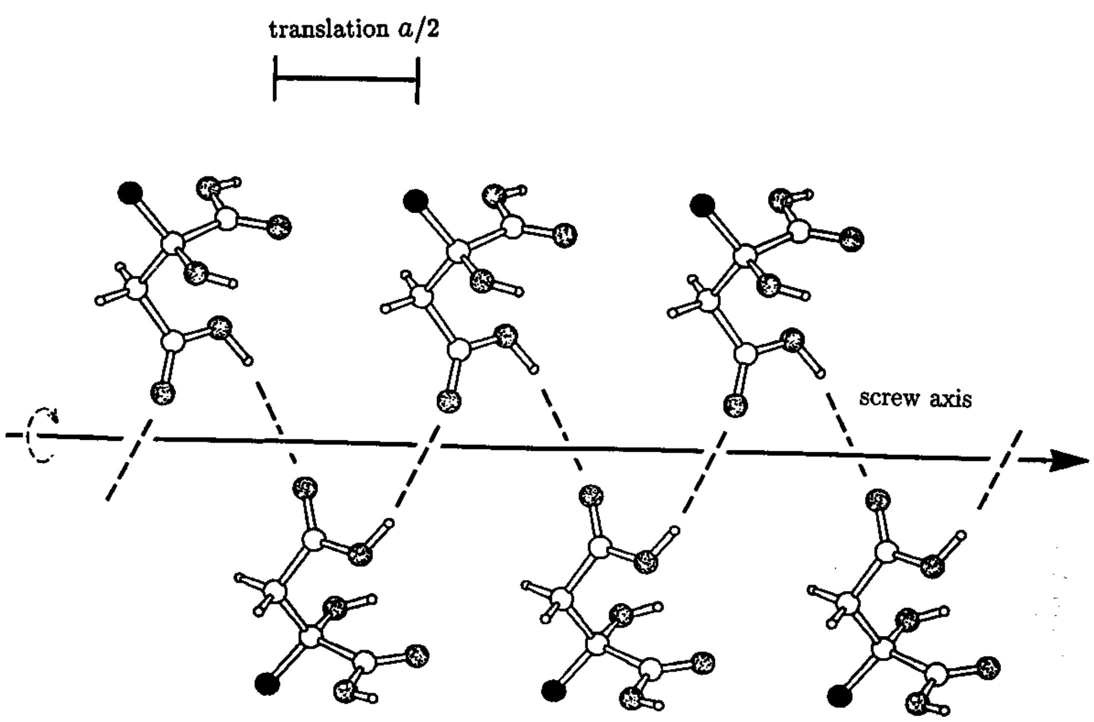
"Structure Determination by X-ray Crystallography", Ladd and Palmer, Plenum, 1994.

Space groups

- **When talking about crystal structures, people will usually report the *space group* of a crystal**
- **Space groups are made up from**
  - lattice symmetry (translational)
  - point symmetry (not translational)
  - glide and/or screw axes (some translational component)
- **There are 230 space groups**

7 crystal systems → 14 Bravais lattices → 32-point groups → 230 space groups

Screw axes



- **A 2_1 screw axis translates an object by half a unit cell in the direction of the screw axis, followed by a 180° rotation**

"Crystal Structure Analysis for Chemists and Biologists",
Glusker, Lewis and Rossi, VCH, 1994.

Higher order screws

“Structure Determination by X-ray Crystallography”, Ladd and Palmer, Plenum, 1994.

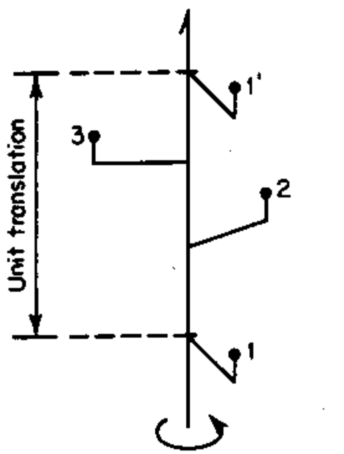


Figure 3.20. Screw axis 3_1.

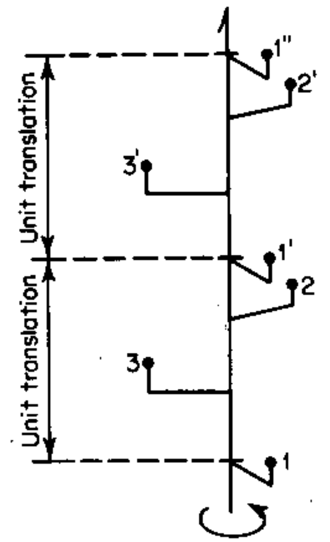


Figure 3.21. Screw axis 3_2.

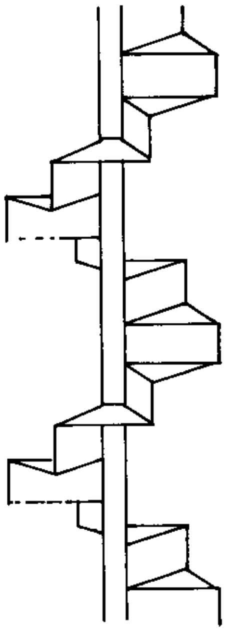


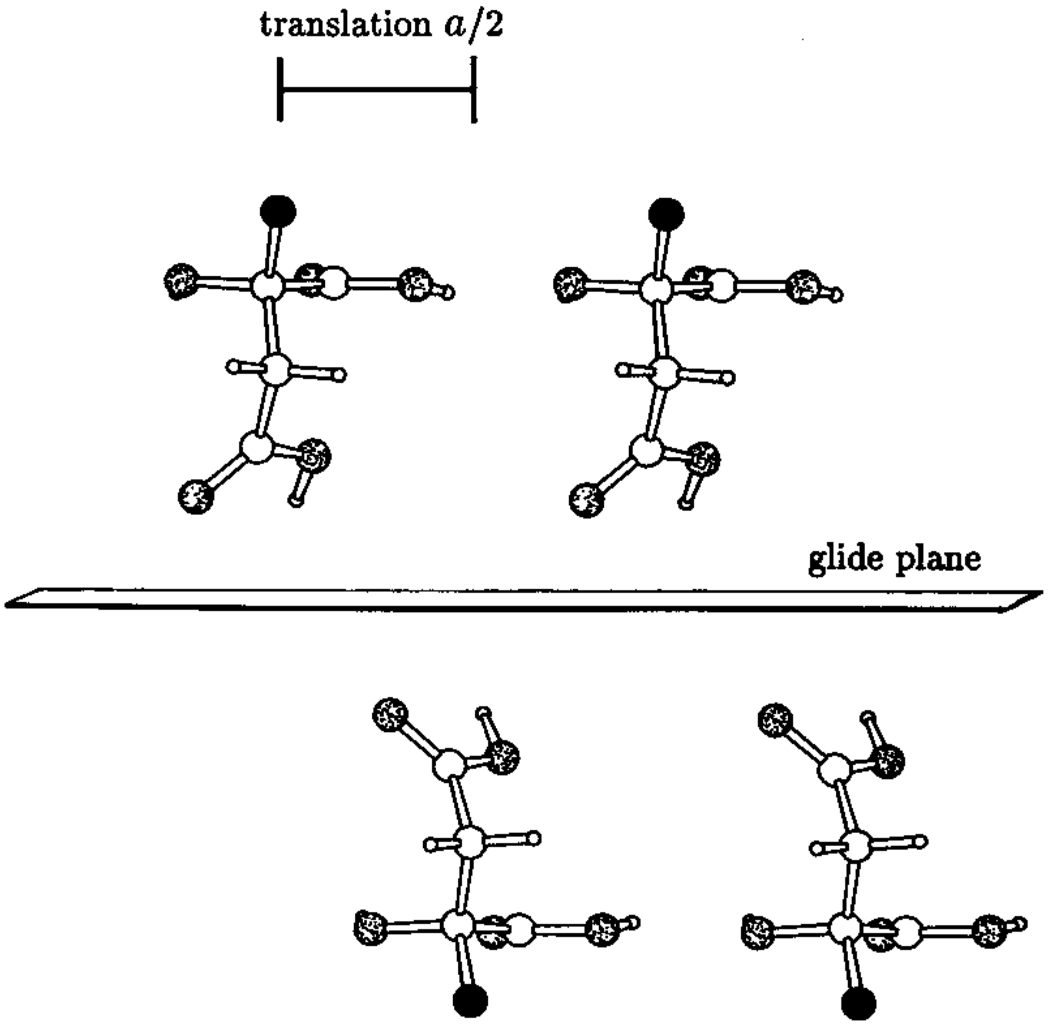
FIGURE 2.30. Spiral staircase: illustration of 6_1 screw axis symmetry.

- **A C_n screw axis translates an object by the unit cell dimension multiplied by n/C along the direction of the screw axis, followed by a C-fold rotation**

Glide planes

- **A glide plane corresponds to a reflection-translation operation**
  - reflection through the glide plane
  - translation within/parallel to the glide plane
  - exact translation depends on type of glide
- **There are a, b, c, n and d glide planes**
  - a, b and c glides correspond to translations of ½ a, ½ b and ½ c respectively
    - called "axial glide planes"
  - n glide corresponds to a translation of ½ a + ½ b, ½ a + ½ c, or ½ b + ½ c
    - called "diagonal glide plane"
  - d glide corresponds to a translation of ¼ a + ¼ b, ¼ a + ¼ c, or ¼ b + ¼ c
    - called "diamond glide plane"

Example of an “a” glide plane



“Crystal Structure Analysis for Chemists and Biologists”, Glusker, Lewis and Rossi, VCH, 1994.

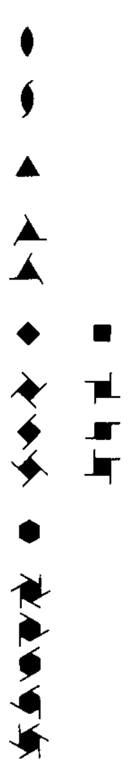
Limitations on combination of symmetry elements

- **As for point groups, not all symmetry elements can be combined arbitrarily**
- **For three dimensional lattices**
  - 14 Bravais lattices
  - 32-point groups
  - but only 230 space groups
- **For two dimensional lattices**
  - 5 lattices
  - 10-point groups
  - but only 17 plane groups

Graphical symbols used for symmetry operations

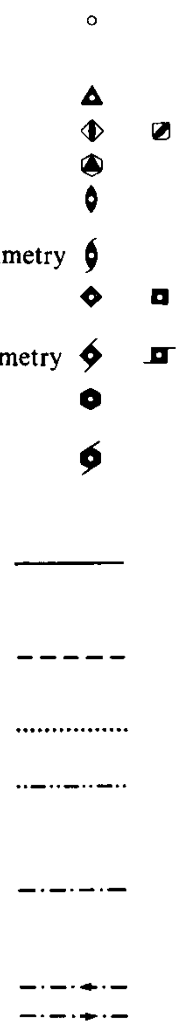
(d) Symmetry axes normal to the plane of projection (three dimensions) and symmetry points in the plane of the figure (two dimensions)

Symmetry axis or symmetry point	Graphical symbol†	Screw vector of a right-handed screw rotation in units of the shortest lattice translation vector parallel to the axis	Printed symbol (partial elements in parentheses)
Identity	None	None	1
Twofold rotation axis Twofold rotation point (two dimensions)		None	2
Twofold screw axis: '2 sub 1'		$\frac{1}{2}$	2_1
Threefold rotation axis Threefold rotation point (two dimensions)		None	3
Threefold screw axis: '3 sub 1'		$\frac{1}{3}$	3_1
Threefold screw axis: '3 sub 2'		$\frac{2}{3}$	3_2
Fourfold rotation axis Fourfold rotation point (two dimensions)		None	4 (2)
Fourfold screw axis: '4 sub 1'		$\frac{1}{4}$	4_1 (2_1)
Fourfold screw axis: '4 sub 2'		$\frac{1}{2}$	4_2 (2)
Fourfold screw axis: '4 sub 3'		$\frac{3}{4}$	4_3 (2_1)
Sixfold rotation axis Sixfold rotation point (two dimensions)		None	6 (3,2)
Sixfold screw axis: '6 sub 1'		$\frac{1}{6}$	6_1 $(3_1,2_1)$
Sixfold screw axis: '6 sub 2'		$\frac{1}{3}$	6_2 $(3_2,2)$
Sixfold screw axis: '6 sub 3'		$\frac{1}{2}$	6_3 $(3,2_1)$
Sixfold screw axis: '6 sub 4'		$\frac{2}{3}$	6_4 $(3_1,2)$
Sixfold screw axis: '6 sub 5'		$\frac{5}{6}$	6_5 $(3_2,2_1)$



"International Tables for Crystallography, Vol. A", Kluwer, 1993.

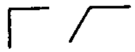
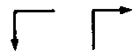
Graphical symbols (2)

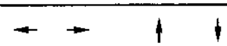
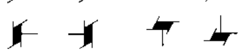


Centre of symmetry, inversion centre: '1 bar'; Reflection point, mirror point (one dimension)	None	$\bar{1}$
Inversion axis: '3 bar'	None	$\bar{3}$ (3,$\bar{1}$)
Inversion axis: '4 bar'	None	$\bar{4}$ (2)
Inversion axis: '6 bar'	None	$\bar{6} \equiv 3/m$
Twofold rotation axis with centre of symmetry	None	$2/m$ ($\bar{1}$)
Twofold screw axis with centre of symmetry	$\frac{1}{2}$	$2_1/m$ ($\bar{1}$)
Fourfold rotation axis with centre of symmetry	None	$4/m$ ($\bar{4}$,2,$\bar{1}$)
'4 sub 2' screw axis with centre of symmetry	$\frac{1}{2}$	$4_2/m$ ($\bar{4}$,2,$\bar{1}$)
Sixfold rotation axis with centre of symmetry	None	$6/m$ ($\bar{6}$,$\bar{3}$,3,2,$\bar{1}$)
'6 sub 3' screw axis with centre of symmetry	$\frac{1}{2}$	$6_3/m$ ($\bar{6}$,$\bar{3}$,3,2_1,$\bar{1}$)
Reflection plane, mirror plane; Reflection line, mirror line (two dimensions)	None	*m*
'Axial' glide plane; Glide line (two dimensions)	$\frac{1}{2}$ lattice vector along line in projection plane; $\frac{1}{2}$ lattice vector along line in plane	*a*, *b*, or *c*; *g*
'Axial' glide plane	$\frac{1}{2}$ normal to projection plane	*a*, *b*, or *c*
'Double' glide plane# (in centred cells only)	*Two* glide vectors: $\frac{1}{2}$ along line parallel to projection plane, $\frac{1}{2}$ normal to projection plane	*e*
'Diagonal' glide plane	*One* glide vector with *two* components: $\frac{1}{2}$ along line parallel to projection plane, $\frac{1}{2}$ normal to projection plane	*n*
'Diamond' glide plane§ (pair of planes; in centred cells only)	$\frac{1}{4}$ along line parallel to projection plane, combined with $\frac{1}{4}$ normal to projection plane (arrow indicates direction parallel to the projection plane for which the normal component is positive)	*d*

"International Tables for Crystallography, Vol. A", Kluwer, 1993.

Symmetry elements parallel to the plane of projection

Symmetry plane	Graphical symbol†	Glide vector in units of lattice translation vectors parallel to the projection plane	Printed symbol
Reflection plane, mirror plane		None	*m*
'Axial' glide plane		½ lattice vector in the direction of the arrow	*a*, *b*, or *c*
'Double' glide plane# (in centred cells only)		*Two* glide vectors: ½ in either of the directions of the two arrows	*e*
'Diagonal' glide plane		*One* glide vector: ½ in the direction of the arrow	*n*
'Diamond' glide plane§ (pair of planes; in centred cells only)		½ in the direction of the arrow; the glide vector is always half of a centring vector, *i.e.* one quarter of a diagonal of the conventional face-centred cell	*d*

Symmetry axis	Graphical symbol†	Screw vector of a right-handed screw rotation in units of the shortest lattice translation vector parallel to the axis	Printed symbol (partial elements in parentheses)
Twofold rotation axis		None	2
Twofold screw axis: '2 sub 1'		½	2_1
Fourfold rotation axis		None	4 (2)
Fourfold screw axis: '4 sub 1'		¼	4_1 (2_1)
Fourfold screw axis: '4 sub 2'		½	4_2 (2)
Fourfold screw axis: '4 sub 3'		¾	4_3 (2_1)
Inversion axis: '4 bar'		None	$\bar{4}$ (2)
Inversion point on '4 bar'-axis			$\bar{4}$-point

in cubic space groups only

"International Tables for Crystallography, Vol. A", Kluwer, 1993.

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Symmetry elements inclined to the plane of projection

(c) Symmetry planes inclined to the plane of projection (in cubic space groups of classes $\bar{4}3m$ and $m\bar{3}m$ only

Symmetry plane	Graphical symbol* for planes normal to [011] and [01$\bar{1}$]	Graphical symbol* for planes normal to [101] and [10$\bar{1}$]	Glide vector in units of lattice translation vectors for planes normal to [011] and [01$\bar{1}$]	Glide vector in units of lattice translation vectors for planes normal to [101] and [10$\bar{1}$]	Printed symbol
Reflection plane, mirror plane			None	None	*m*
'Axial' glide plane			½ lattice vector along [100]	½ lattice vector along [010]	*a* or *b*
'Axial' glide plane			½ along [01$\bar{1}$] or along [011]	½ along [10$\bar{1}$] or along [101]	
'Double' glide plane* (in space groups $I\bar{4}3m$ (217) and $Im\bar{3}m$ (229) only)			*Two* glide vectors: ½ along [100] *and* ½ along [01$\bar{1}$] or ½ along [011]	*Two* glide vectors: ½ along [010] *and* ½ along [10$\bar{1}$] or ½ along [101]	*e*
'Diagonal' glide plane			*One* glide vector: ½ along [11$\bar{1}$] or along [111]†	*One* glide vector: ½ along [11$\bar{1}$] or along [111]†	*n*
'Diamond' glide plane§ (pair of planes; in centred cells only)			½ along [1$\bar{1}$1] or along [111]‡	½ along [$\bar{1}$11] or along [111]‡	*d*
			½ along [$\bar{1}\bar{1}$1] or along [$\bar{1}$11]‡	½ along [$\bar{1}\bar{1}$1] or along [1$\bar{1}$1]‡	

(f) Symmetry axes inclined to the plane of projection (in cubic space groups only)

Symmetry axis	Graphical symbol†			Screw vector of a right-handed screw rotation in units of the shortest lattice translation vector parallel to the axis	Printed symbol
Twofold rotation axis			parallel to a face diagonal of the cube	None	2
Twofold screw axis: '2 sub 1'				½	2_1
Threefold rotation axis			parallel to a body diagonal of the cube	None	3
Threefold screw axis: '3 sub 1'				⅓	3_1
Threefold screw axis: '3 sub 2'				⅔	3_2
Inversion axis: '3 bar'				None	$\bar{3}$

"International Tables for Crystallography, Vol. A", Kluwer, 1993.

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