Analytical Methods for Materials

Lesson 11
Crystallography and Crystal Structures, Part 3

Suggested Reading

- Chapter 6 in Waseda
- Chapter 1 in F.D. Bloss, Crystallography and Crystal Chemistry: An Introduction, (Holt, Rinehart and Winston, Inc., New York, 1971)

Point Groups

- Crystals possess symmetry in the arrangement of their external faces.

- Crystals also possess symmetry in the arrangement of lattice points and in the arrangement of objects placed on lattice points.

- When we put these two things together, we arrive at a new way to classify crystals in terms of symmetry.

Point Groups

► Relate internal symmetry to external symmetry of crystal.

- All symmetry elements intersect at a point. Symmetry operations are defined with respect to a point in space that does not move during the operation.
- There is no translational symmetry in a point group but there is always translational symmetry in a crystal.

Symmetry Operators

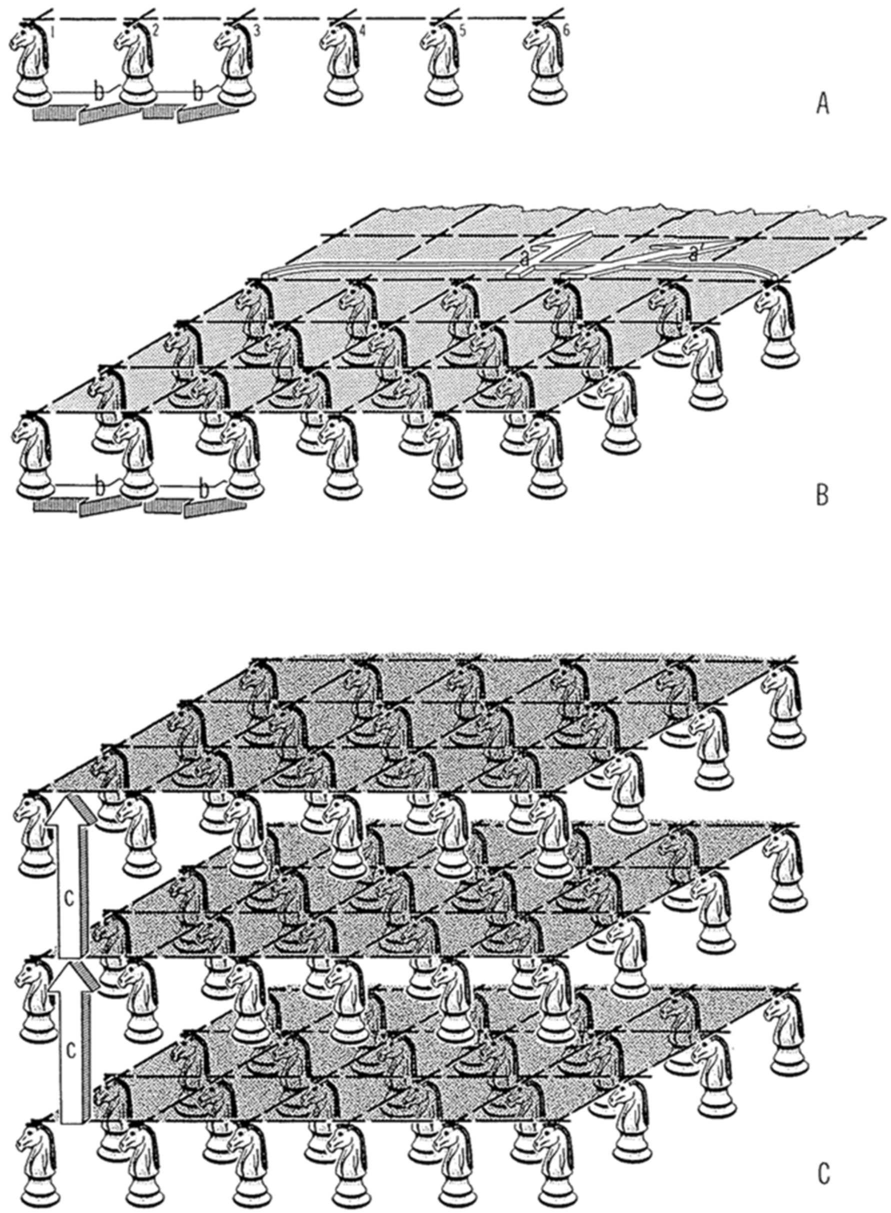
- All motions that allow a pattern to be transformed from an initial position to a final position such that the initial and final patterns are indistinguishable.

1. Translation
2. Reflection*
3. Rotation*
4. Inversion (center of symmetry)*
5. Roto-inversion (inversion axis)*
6. Roto-reflection*
7. Glide (translation + reflection)
8. Screw (rotation + translation)

***Point groups*:**

symmetry operations defined with respect to a point in space that remains stationary (i.e., does not move) during the operation.

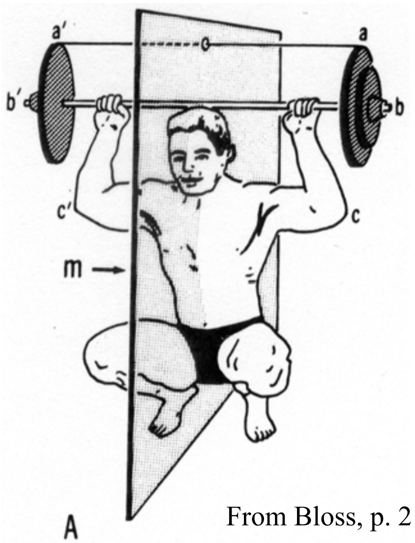
Applies to objects occupying lattice points.



From Bloss, p. 141

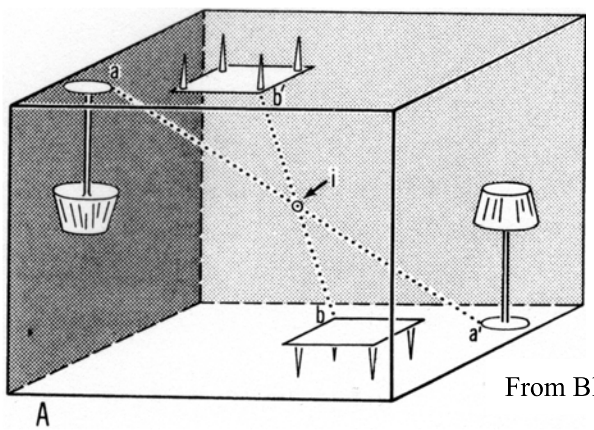
Inherent symmetry operation in crystals!

1. TRANSLATION



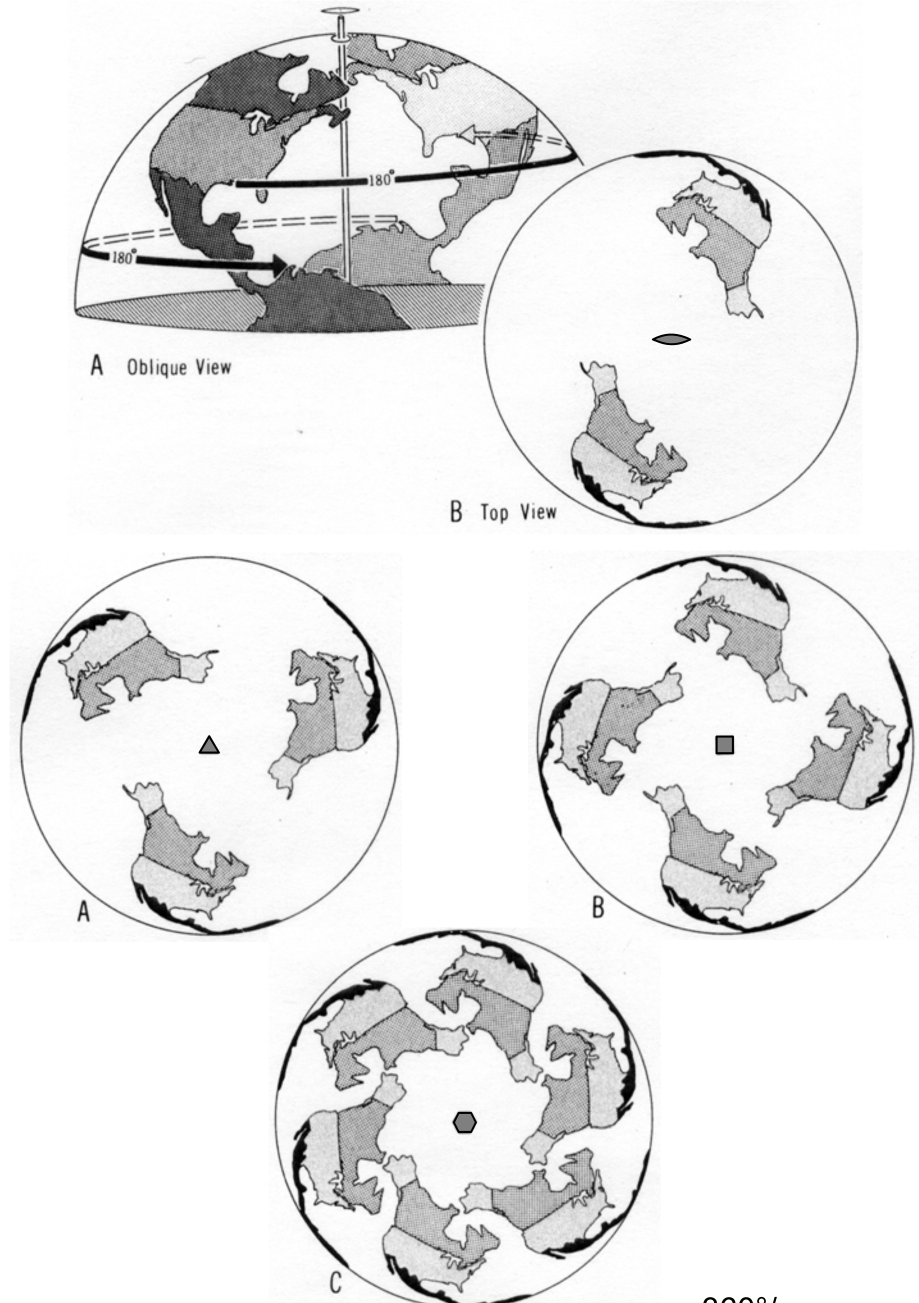
From Bloss, p. 2

2. REFLECTION = *m*



From Bloss, p. 6

4. INVERSION = *i*



From Bloss, pp. 4, 5

$\alpha = 360°/n$

n = fold of axis = 1,2,3,4 or 6

3. ROTATION

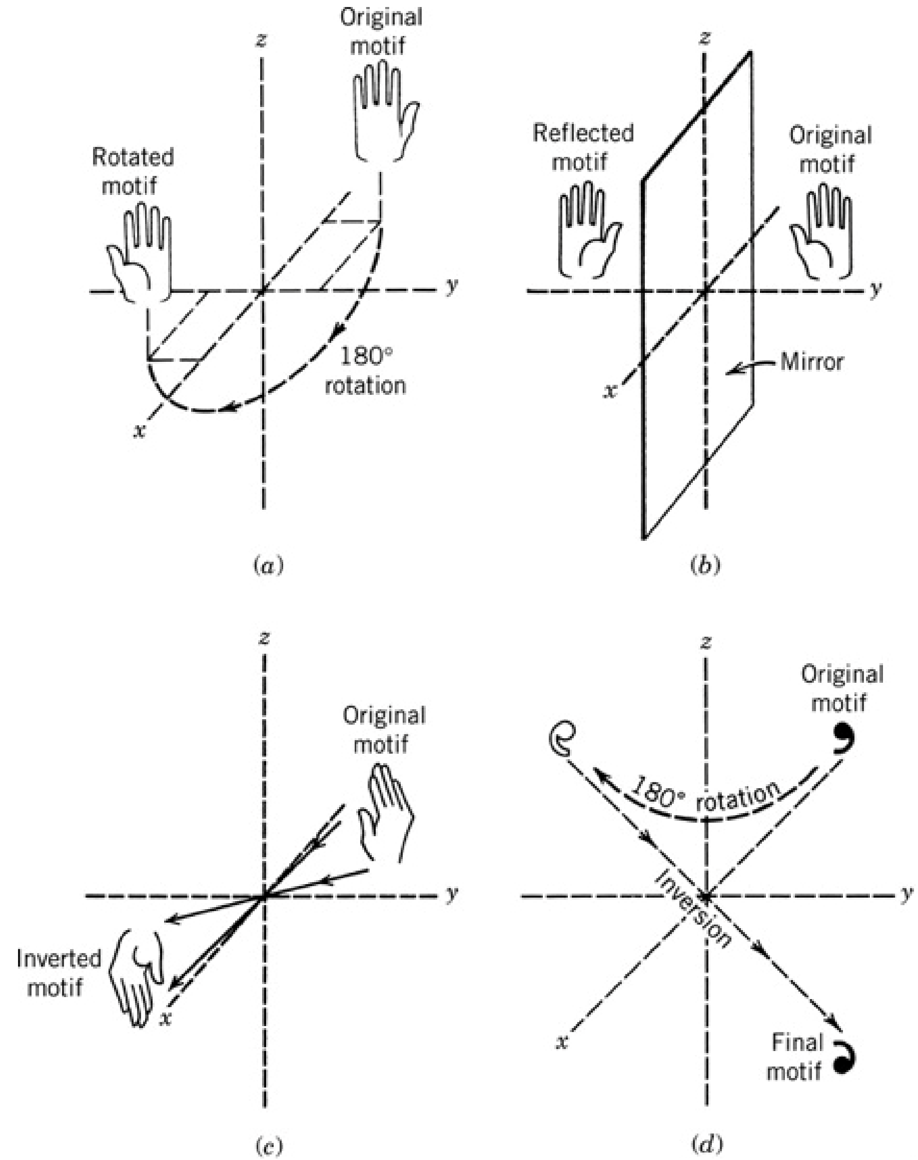


Fig. 6.9 Examples of symmetry operations. (a) Generation of a pattern by rotation of a motif through an angle of 180°. (b) Motifs as related by a mirror reflection. (c) Motifs related by inversion through a center. (d) Motifs related by 180° rotation an subsequent inversion; known as rotoinversion. From C. Klein and B. Dutrow, Manual of Mineral Science, 23rd Edition (John Wiley & Sons, 2007)

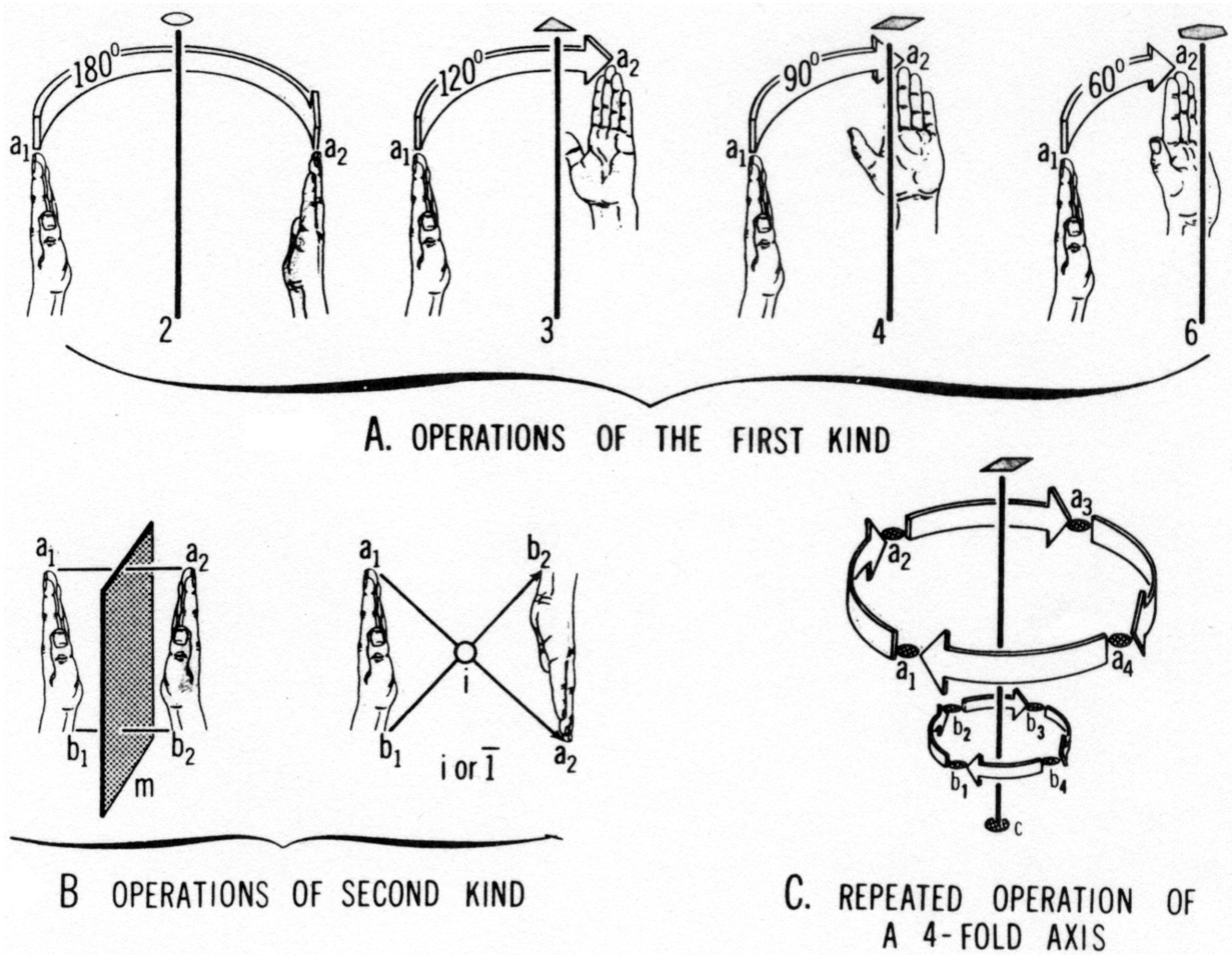
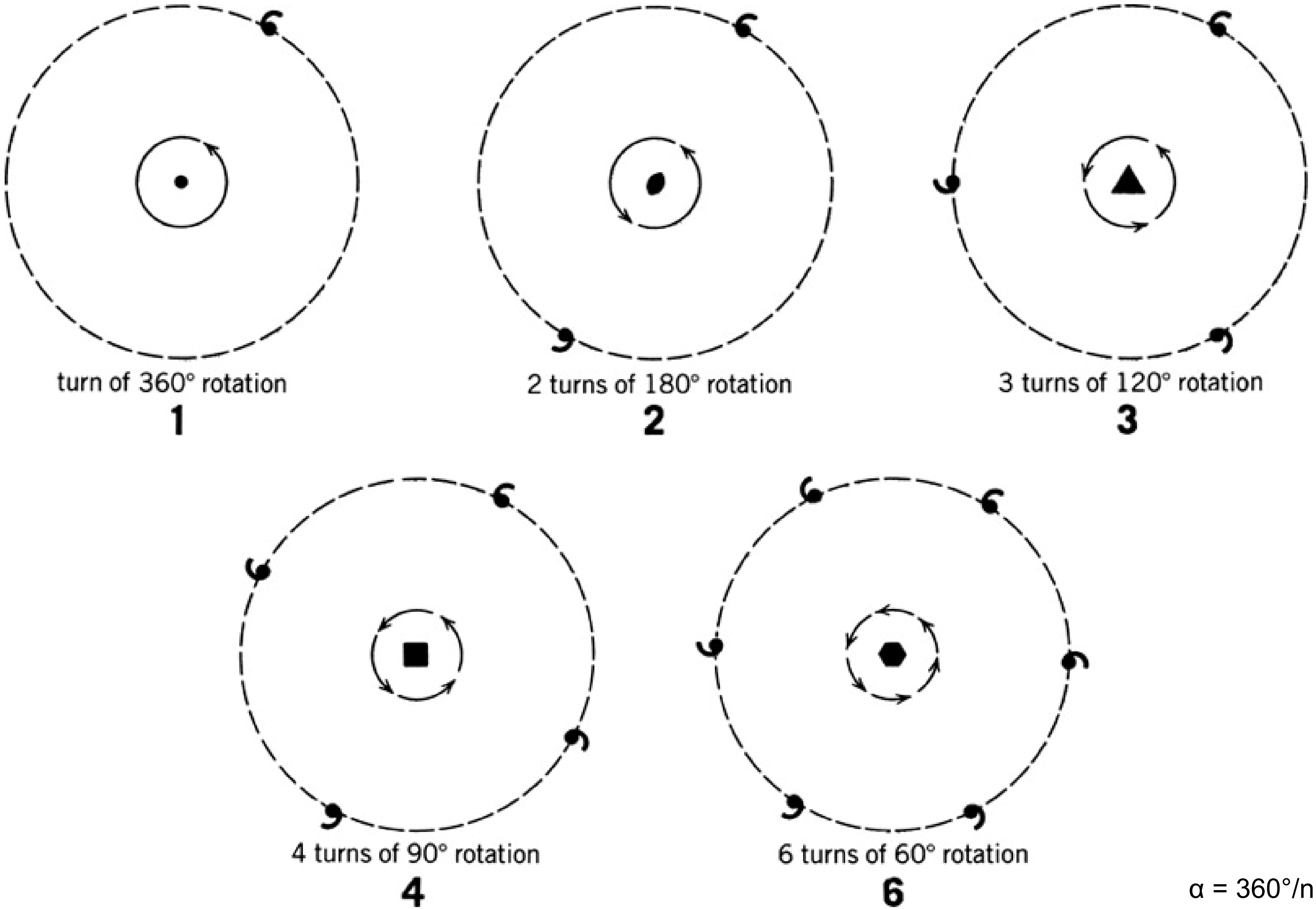


FIGURE 1–6

From Bloss, p. 7



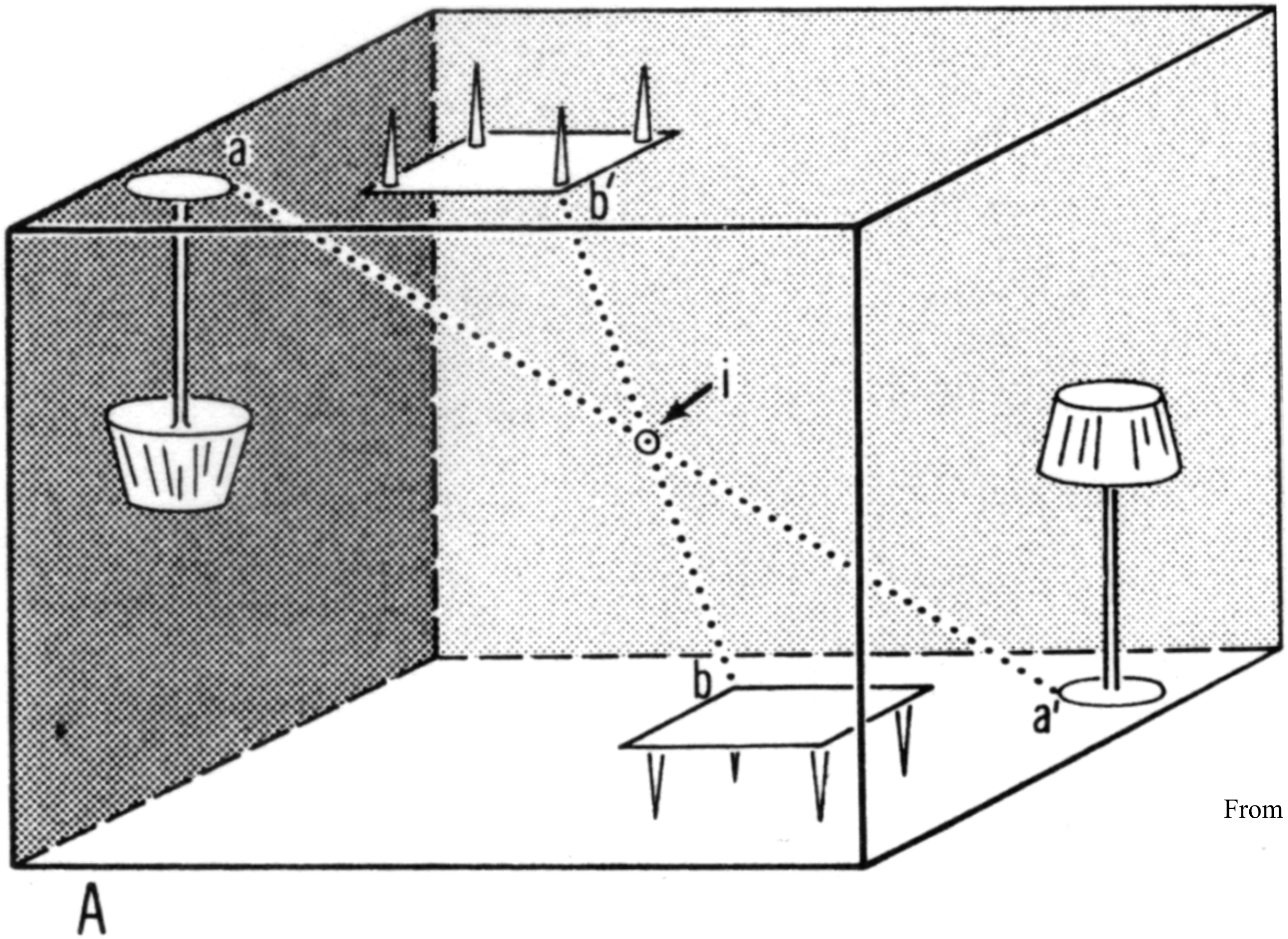
α = 360°/n
n = fold of axis = 1,2,3,4 or 6

Fig. 6.12 Illustration of rotations that allow the motif to coincide with an identical unit for one-, two-, three-, four-, or six-fold rotation axes. The diagram for **2** represents a projection onto the *xy* plane of Fig. 6.9a. From C. Klein and B. Dutrow, Manual of Mineral Science, 23rd Edition (John Wiley & Sons, 2007)

Rotation – Symbols and Notation

Name of rotation	Notation	Angle	Symbol
Diad	2-fold	180°	⬮
Triad	3-fold	120°	▲
Tetrad	4-fold	90°	■
Hexad	6-fold	60°	⬢

Inversion

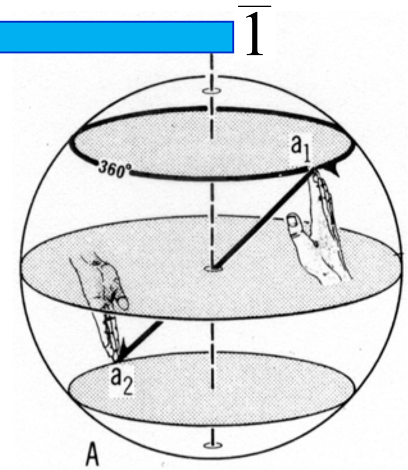


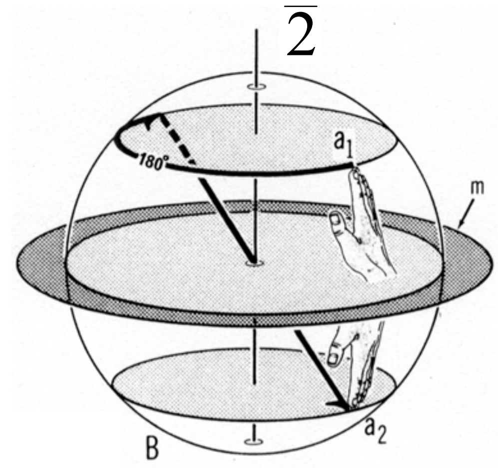
From Bloss, p. 6

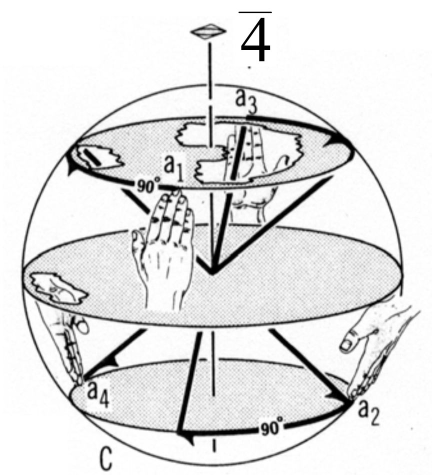
Inversion center = *i*

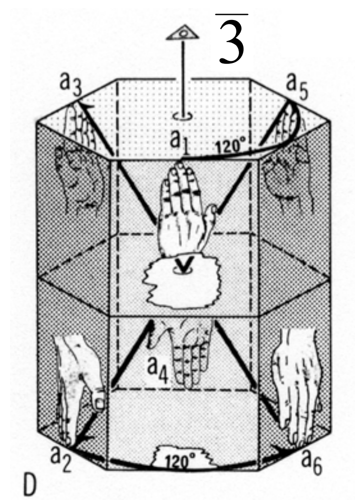
Roto-Inversion

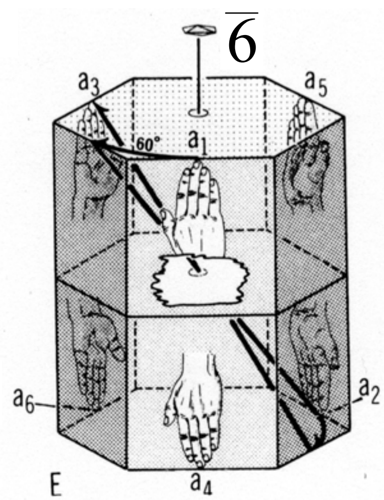
This one is the same is simple inversion (i)











$$\boxed{\bar{n}}$$

From Bloss, p. 8

$\alpha = 360°/n$

n = fold of axis = 1,2,3,4 or 6

Rotoinversion – Symbols and Notation

Name of rotation	Notation	Angle	Symbol
Diad	2-fold	180°	
Triad	3-fold	120°	
Tetrad	4-fold	90°	
Hexad	6-fold	60°	

Rotoinversion

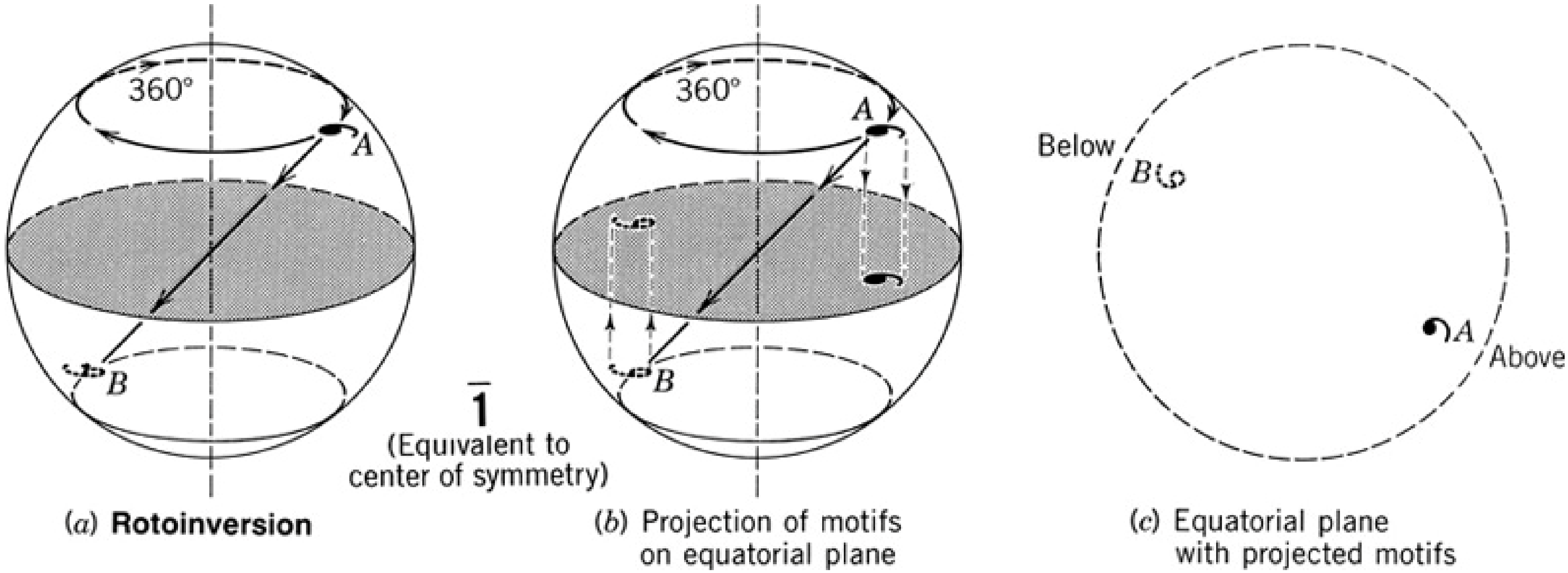


Fig. 6.14 (a) Illustration of an operation of rotoinversion, consisting of a 360° rotation and subsequent inversion through the center of the globe. (b) Projection of the two motif units (*A* and *B*) from the outer skin of the globe to the equatorial plane. (c) Location of the projected motifs on the equatorial plane. From C. Klein and B. Dutrow, Manual of Mineral Science, 23rd Edition (John Wiley & Sons, 2007)

Rotoinversion

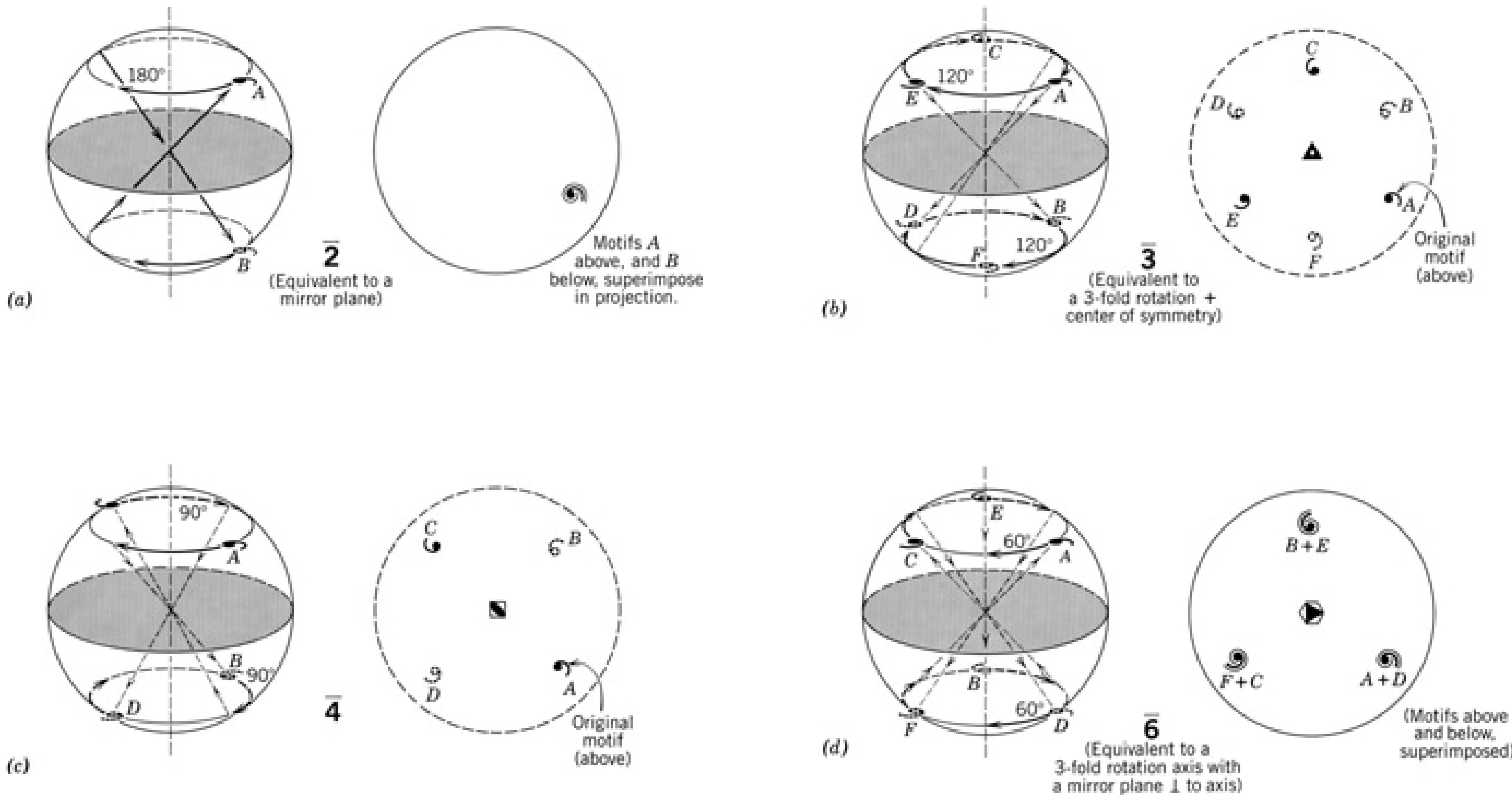


Fig. 6.15 Illustration of operations of rotoinversion on motif units for all possible rotoinversion axes. From C. Klein and B. Dutrow, Manual of Mineral Science, 23rd Edition (John Wiley & Sons, 2007)

Combinations of Rotations

- Axes of rotation can only be combined in symmetrically consistent ways such that an infinite set of axes is not generated.

- All symmetry axes must intersect at a point that remains unchanged by the operations.

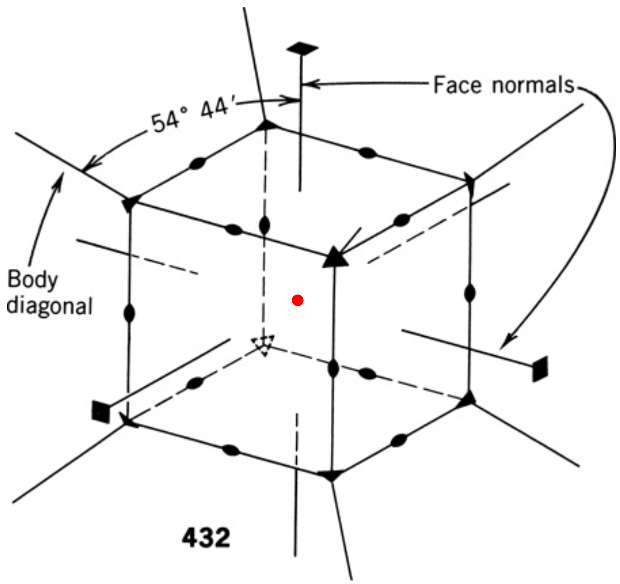


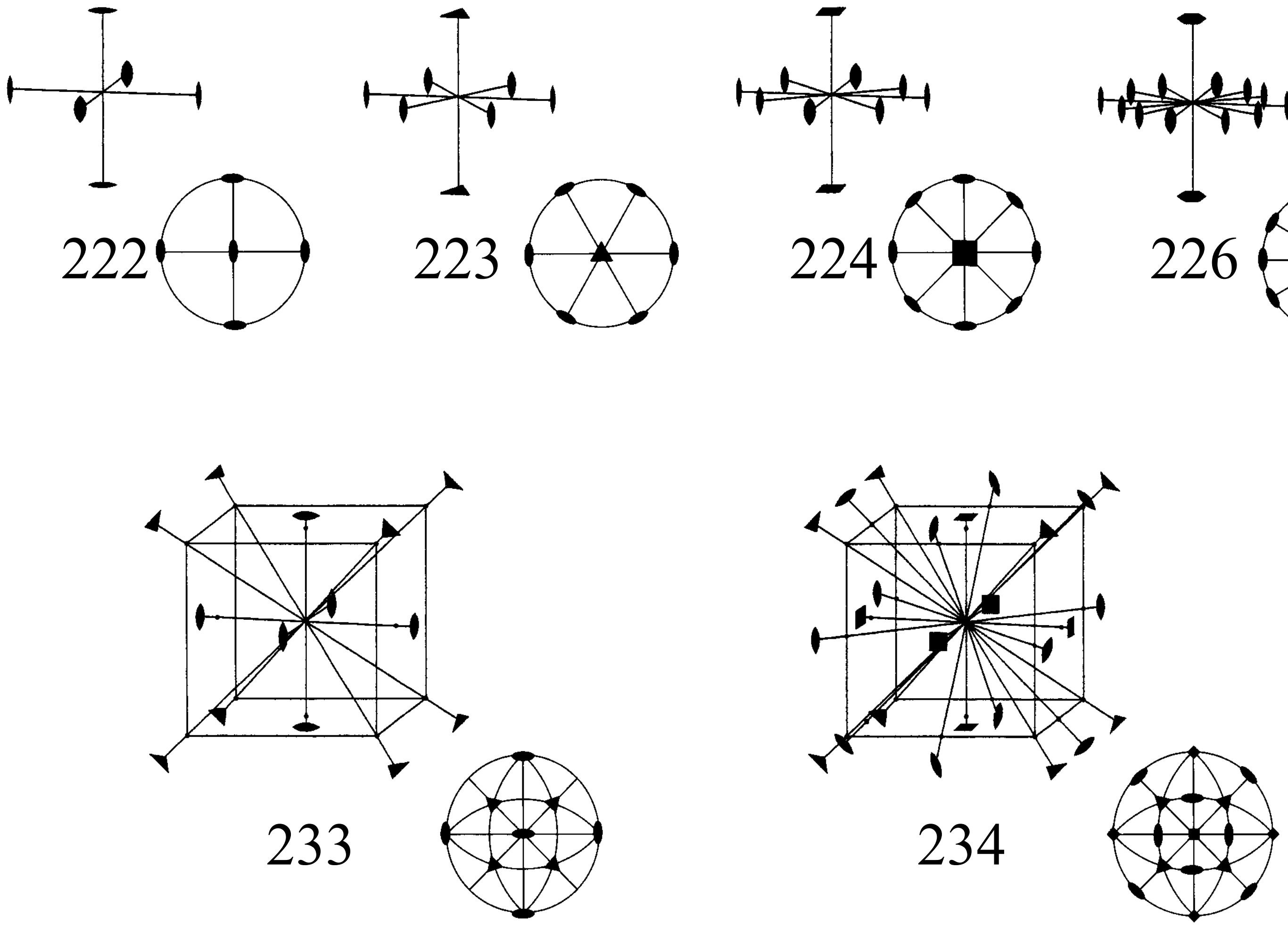
Fig. 6.18 The location of 4-, 3-, and 2-fold symmetry axes with respect to a cubic outline for 432. Note that the axes connect symbols on the opposite sides of the crystal and run through the center. Adapted from C. Klein and B. Dutrow, Manual of Mineral Science, 23rd Edition (John Wiley & Sons, 2007)

Permissible combinations of crystallographic rotation axes.

Axial Combination	α	β	γ	$w = \angle AB$	$u = \angle BC$	$v = \angle AC$
2 2 2	180°	180°	180°	90°	90°	90°
2 2 3	180°	180°	120°	60°	90°	90°
2 2 4	180°	180°	90°	45°	90°	90°
2 2 6	180°	180°	60°	30°	90°	90°
2 3 3	180°	120°	120°	54°44’	70°32’	54°44’
2 3 4	180°	120°	90°	35°16’	54°44’	45°

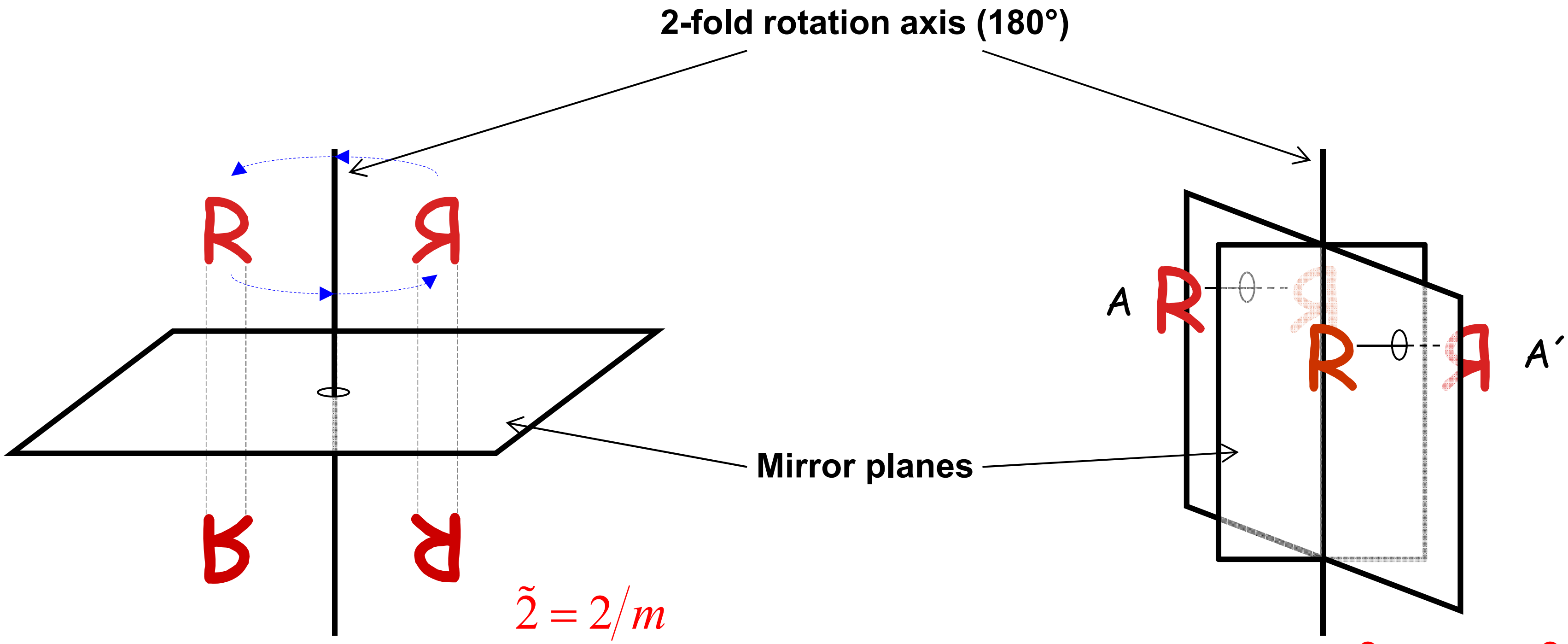
They’re pictured on next page

Spatial arrangements for the six permitted combinations of rotation symmetry axes in crystals.



Here's our friend symmetry again!
We'll address this again a little later!

ROTO-REFLECTION



$\tilde{2} = 2/m$

$2m = mm2 = 2mm$

$$\boxed{\tilde{n} = n/m}$$

α = 360°/n

n = fold of axis = 1,2,3,4 or 6

$$\boxed{nm}$$

α = 360°/n

n = fold of axis = 1,2,3,4 or 6

Only 3*m* is unique

Rotate through symmetry operations then reflect.

Mirrors can be parallel or perpendicular to rotation axis.

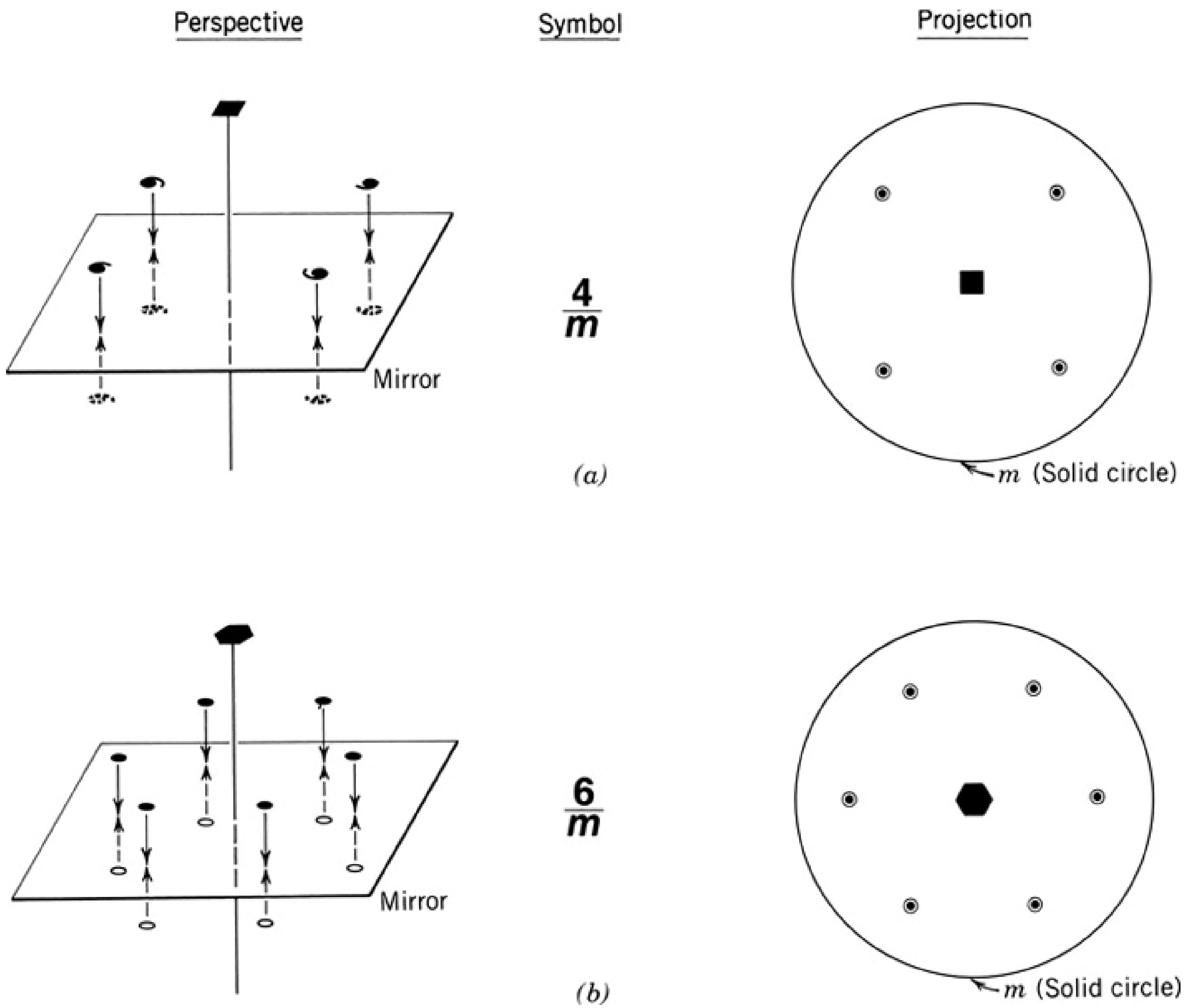


Fig. 6.19 (a) Combination of 4-fold symmetry axis with a perpendicular mirror plane. (b) 6-fold rotation axis with a perpendicular mirror plane. Motifs above and below the mirror can be represented by solid dots and small open circles. From C. Klein and B. Dutrow, Manual of Mineral Science, 23rd Edition (John Wiley & Sons, 2007)

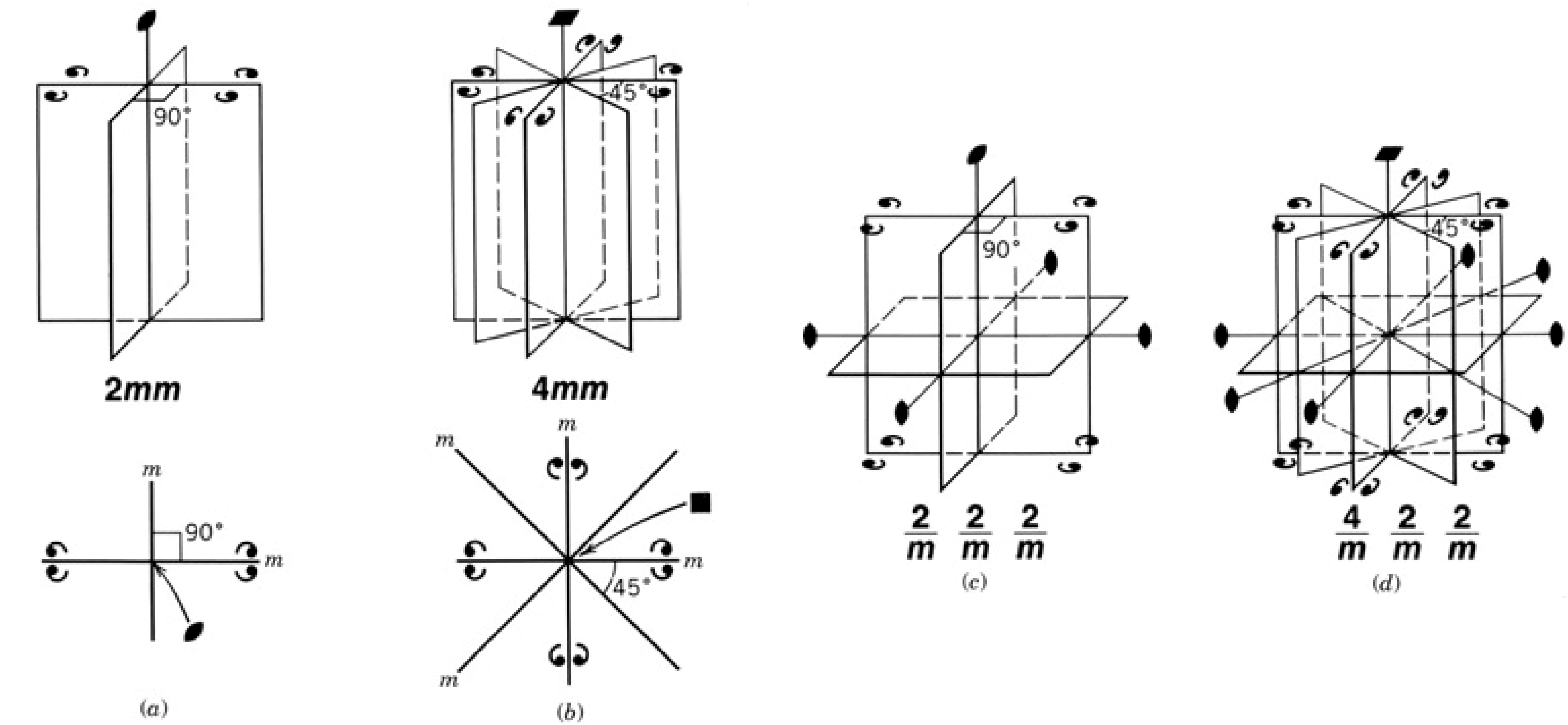


Fig. 6.21 Illustrations of intersecting parallel mirrors and the resultant lines of intersection, equivalent to rotation axes. (a) and (b) Perspective and plan views of 2*mm* and 4*mm*. In (c) and (d) horizontal mirrors are added. The horizontal intersection lines become 2-fold rotation axes in both figures. From C. Klein and B. Dutrow, Manual of Mineral Science, 23rd Edition (John Wiley & Sons, 2007)

$$\frac{4}{m}\,\bar{3}\,\frac{2}{m}$$

$\langle 100 \rangle \; \langle 111 \rangle \; \langle 110 \rangle$

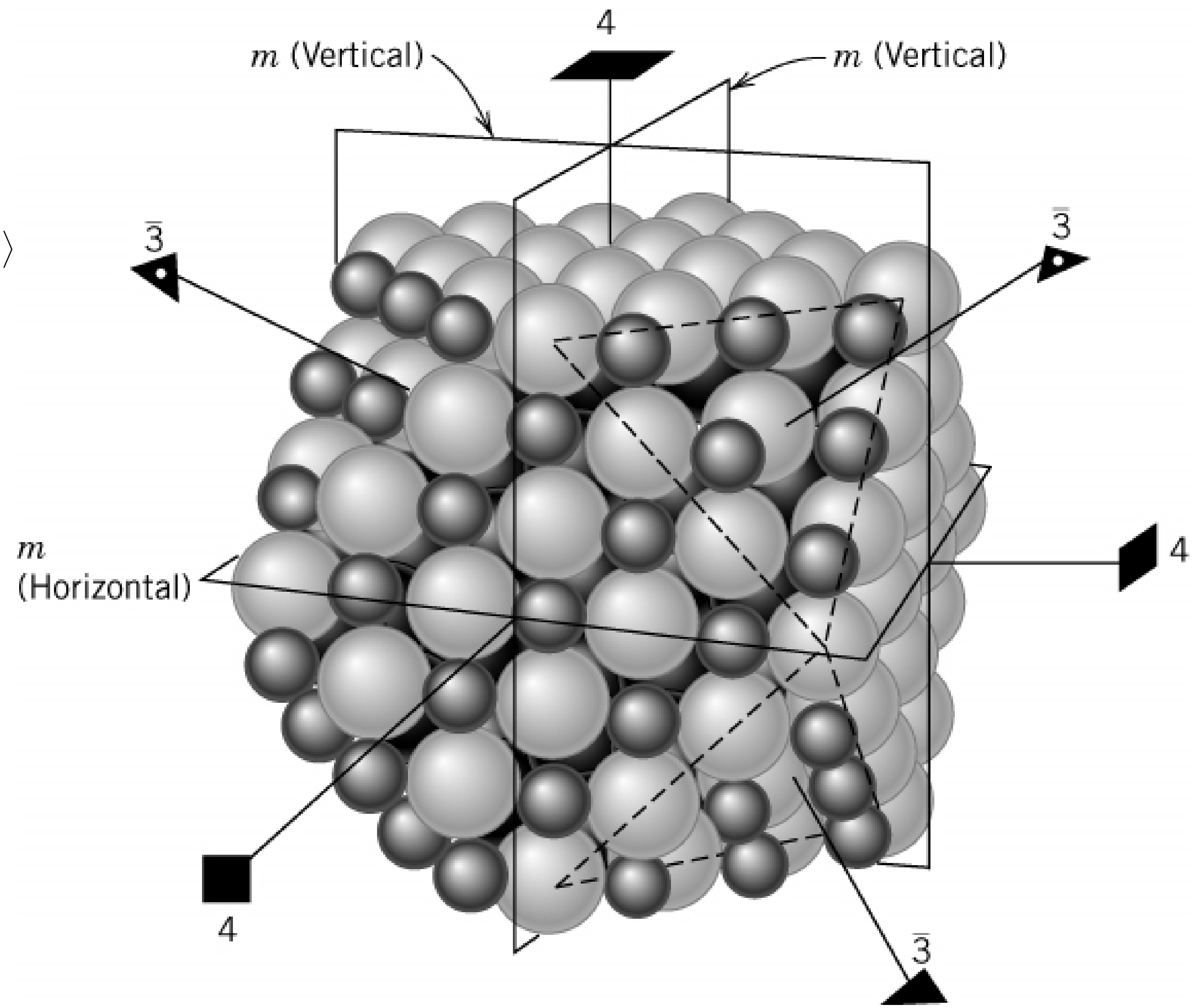


Fig. 6.22 Crystal structure of Halite (NaCl). This structure contains all symmetry elements that are present in a cube. From C. Klein and B. Dutrow, Manual of Mineral Science, 23rd Edition (John Wiley & Sons, 2007)

Some compound symmetry operators yield the same final results

► In crystallography rotoreflection and rotoinversion sometimes produce the same result.

When that happens, we **use rotoinversion** instead of rotoreflection.

Table 4.1 Correspondence of rotoreflection and rotoinversion axes.

Axis of rotoreflection	Axis of rotoinversion
$\tilde{1}$	$\bar{2}\,(m)$
$\tilde{2}$	$\bar{1}$
$\tilde{3}$	$\bar{6}$
$\tilde{4}$	$\bar{4}$
$\tilde{6}$	$\bar{3}$

R. Tilley, *Crystals and Crystal Structures*, John Wiley & Sons, Hoboken, NJ, 2006

Crystallographers use standard graphical symbols and stereograms to depict crystal symmetry.

32 Point groups – the way you'll see them in reference books

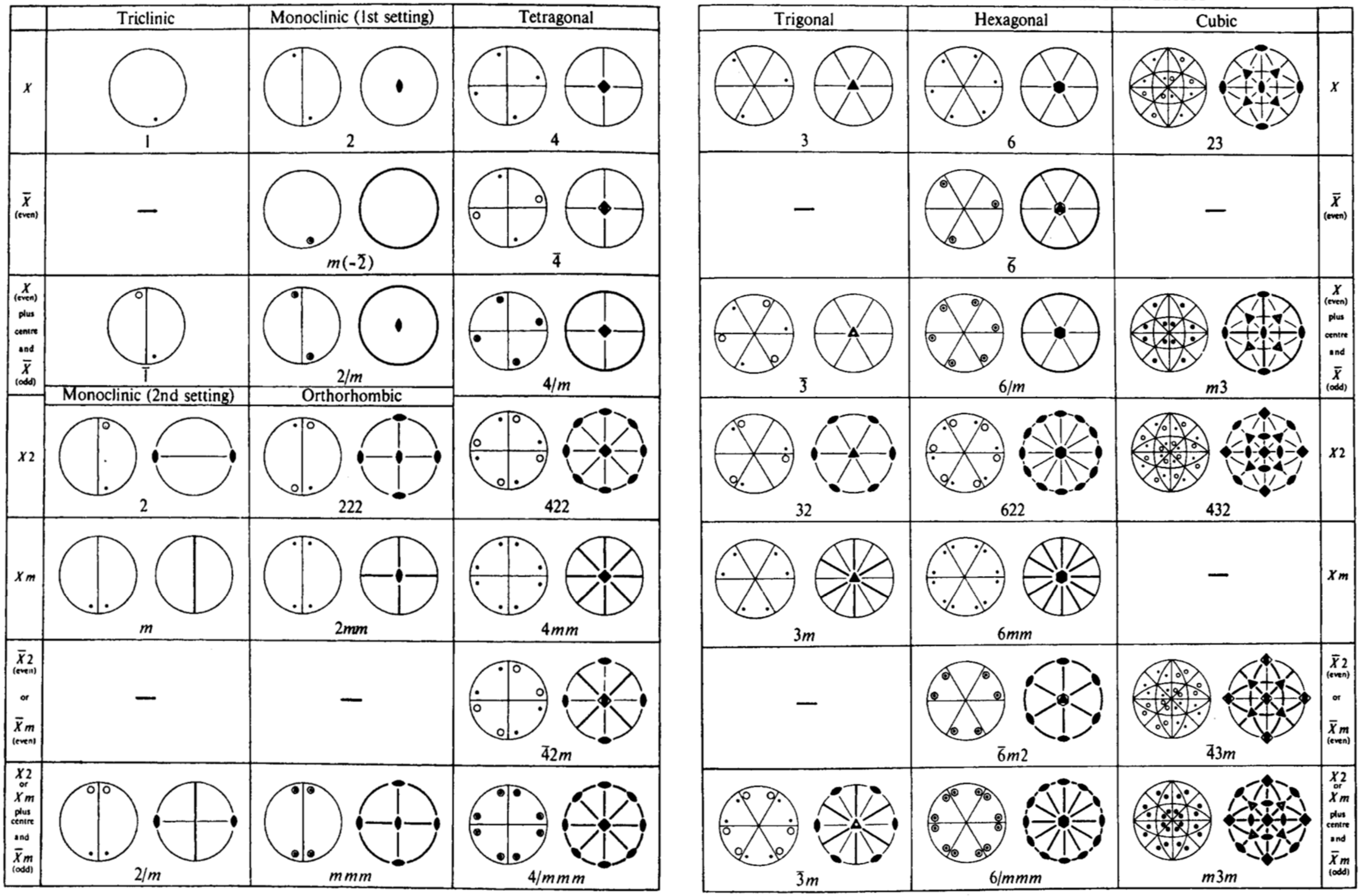


Figure 2.24 Stereograms of the poles of equivalent general directions and of the symmetry elements of each of the 32 point groups. The *z*-axis is normal to the paper. A. Kelly et al., Crystallography and crystal defects, Revised Edition (John Wiley & Sons, New York, NY, 2000) pp. 60, 61.

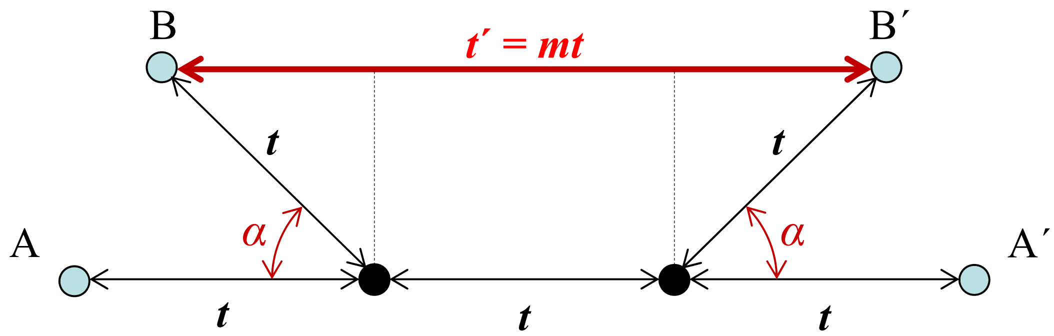
Why only 1-, 2-, 3-, 4-, and 6-fold rotation?

- Crystal structures are built by the regular stacking of unit cells that are translated.

- All symmetry operations must be self-consistent (internally and externally).

- This limits combinations of symmetry elements that are compatible in a unit cell.

Why only 1-, 2-, 3-, 4-, and 6-fold rotation?



- Rotation operators acting on points A and A′ produce points B and B′.
- For B and B′ to be valid lattice points, the distance between them, t', must be an integral number, m, of translation vectors

$$t' = mt$$

Allowed Rotation Angles

- From the diagram:

$$t' = mt$$
$$= t + 2t\cos\alpha$$

Therefore:

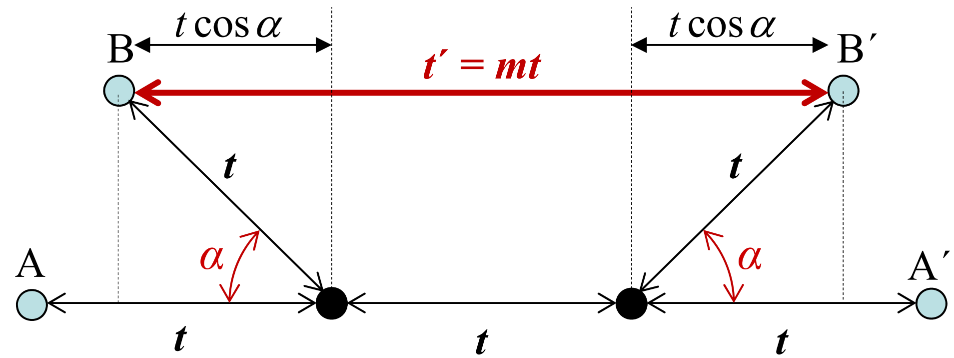
$$\cos\alpha = \frac{m-1}{2}$$

- If m is an integer, m-1 must be an integer.

- The angle α must lie between0 and 180° to obtain closure. Therefore:

$$|\cos\alpha| \le 1$$
$$\therefore$$
$$|m-1| \le 2$$

6



- **Thus: m-1 = -2, -1, 0, 1, or 2.**

- From this we find:

$$\alpha = 180°, 120°, 90°, 60°, \text{or } 0°$$

π	$2\pi/3$	$\pi/2$	$\pi/3$	0
2-fold	3-fold	4-fold	6-fold	1-fold

- Or, more succinctly:

$$\alpha = \pm\frac{2\pi}{n}$$

where n = order rotat. symmetry

Why only 1-, 2-, 3-, 4-, and 6-fold rotation?

Rotation Axes in Plane Space

n	$2\pi / n$	$2\cos(2\pi / n) = m$	Comments
1	360°	2	integer, ALLOWED
2	180°	–2	integer, ALLOWED
3	120°	–1	integer, ALLOWED
4	90°	0	integer, ALLOWED
5	72°	0.618	NOT ALLOWED
6	60°	1	integer, ALLOWED
7	51.43°	1.244	NOT ALLOWED

Symmetry Operators

- All motions that allow a pattern to be transformed from an initial position to a final position such that the initial and final patterns are indistinguishable.

1. Translation*
2. Reflection
3. Rotation
4. Inversion (center of symmetry)

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5. Roto-inversion (inversion axis)
6. Roto-reflection
7. Glide (translation + reflection)
8. Screw (rotation + translation)

These are compound symmetry operators (combinations of 1-4)

- All crystals exhibit translational symmetry.
- Any other symmetry elements must be consistent with translational symmetry of the lattice

We've considered 1-6

What about these?

Other Symmetry Operators

Translations "interact" with symmetry operators 1-6.

Results in the final two symmetry operators.

Screw Axis = Rotation Axis + Translation

2_1

3_1, 3_2

4_1, 4_2, 4_3

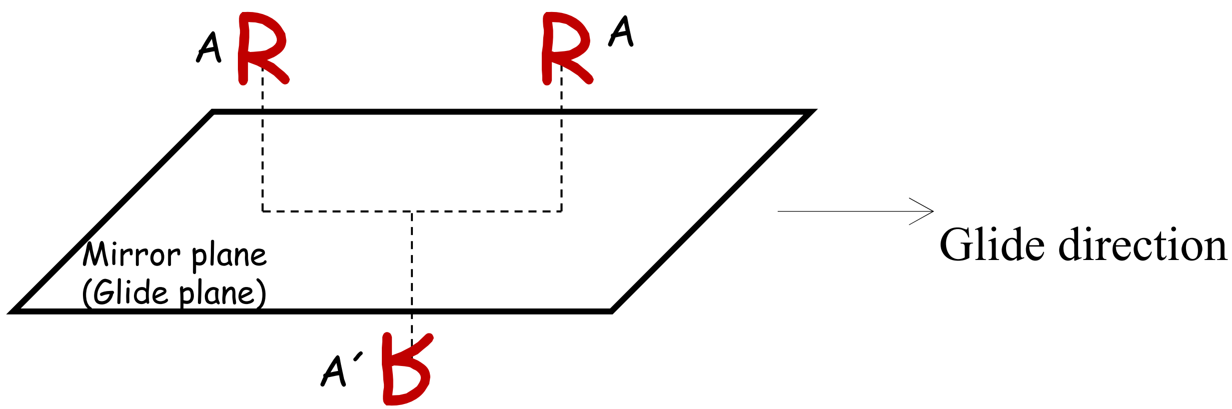
6_1, 6_2, 6_3, 6_4, 6_5

Glide Plane = Mirror Plane + Translation

a *b* *c* *n* *d*

7. Glide Planes

Combine reflection and translation



Nomenclature for glide planes

Glide Direction	Glide Magnitude	Designation
<100>	½ axis length	a, b, or c
<110>	½ face diagonal	n
<110>	¼ face diagonal	d

When going from a space group to the parent point group, all a's, b's, c's, n's, and d's are converted back into m's.

8. Screw Axes

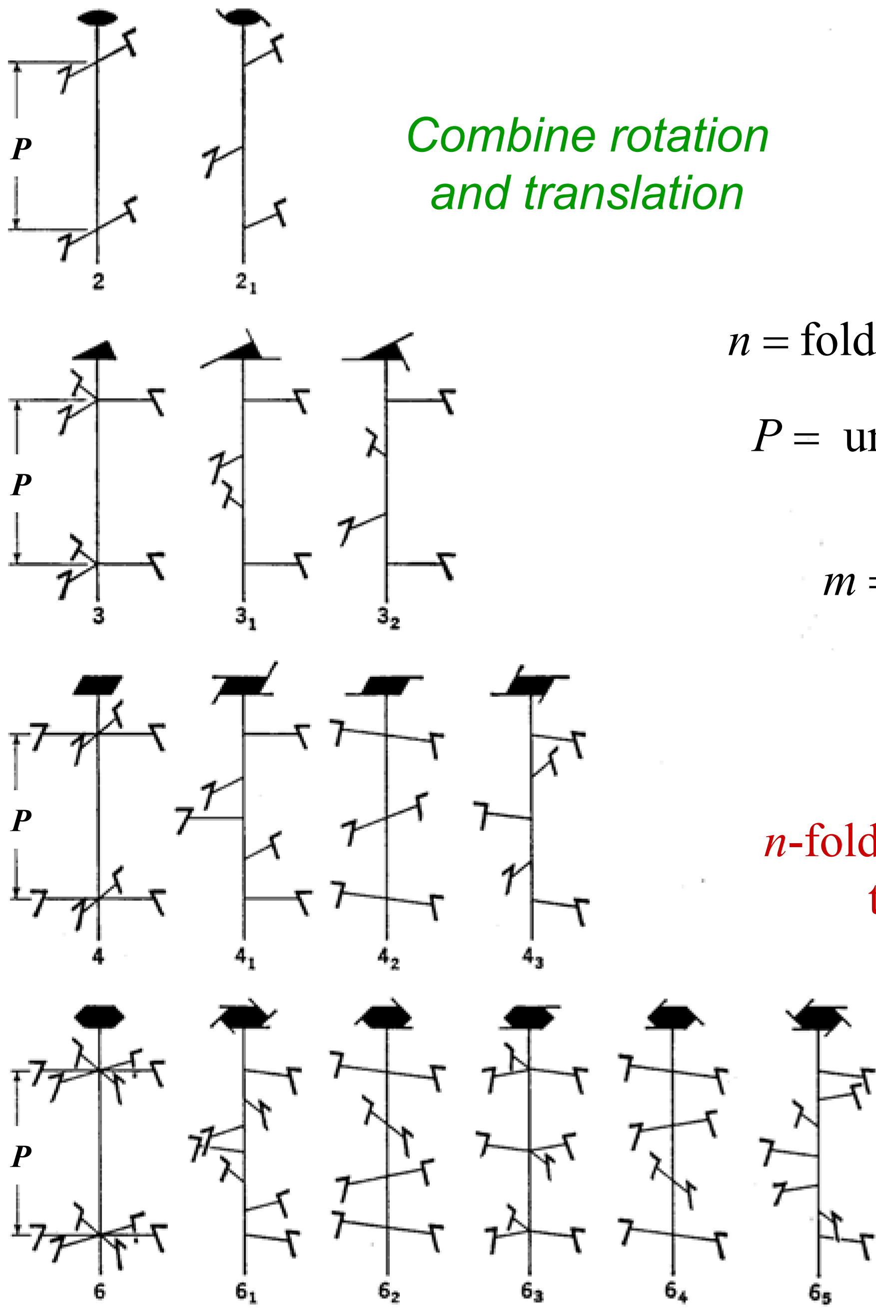


FIG. 24

Combine rotation and translation

$$\boxed{n_m}$$

$$nt = mP$$

$n =$ fold of rotation (2, 3, 4, or 6); each rotation $= 2\pi/n$

$P =$ unit translation (i.e., the shortest lattice vector) parallel to screw axis

$m =$ # of cells/steps back to starting position

$t =$ pitch of screw axis $\left[t = (m/n)P\right]$

n-fold rotation followed by a translation parallel to the rotation axis *P* by a vector $t = mP/n$.

Adapted from L.V. Azaroff, *Introduction to Solids*, McGraw-Hill, New York, 1960, p. 22.

These can be difficult to visualize.

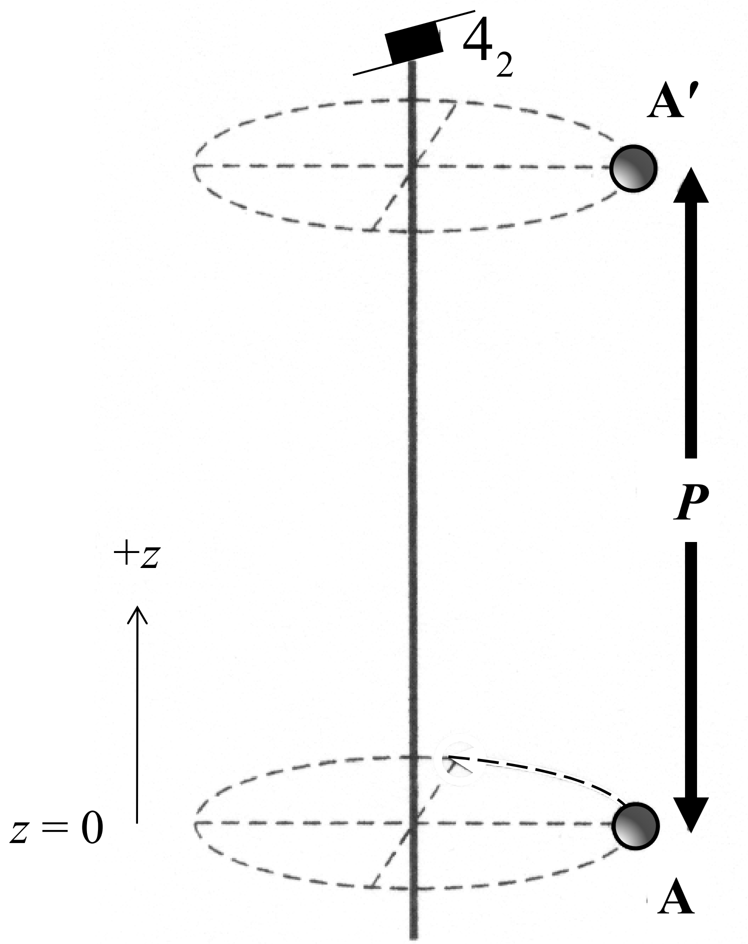
Let's step through one:

4_2 screw axis

$\boxed{n_m} = \boxed{4_2}$

$$t = \left(m/n\right)P = \left(2/4\right)P$$

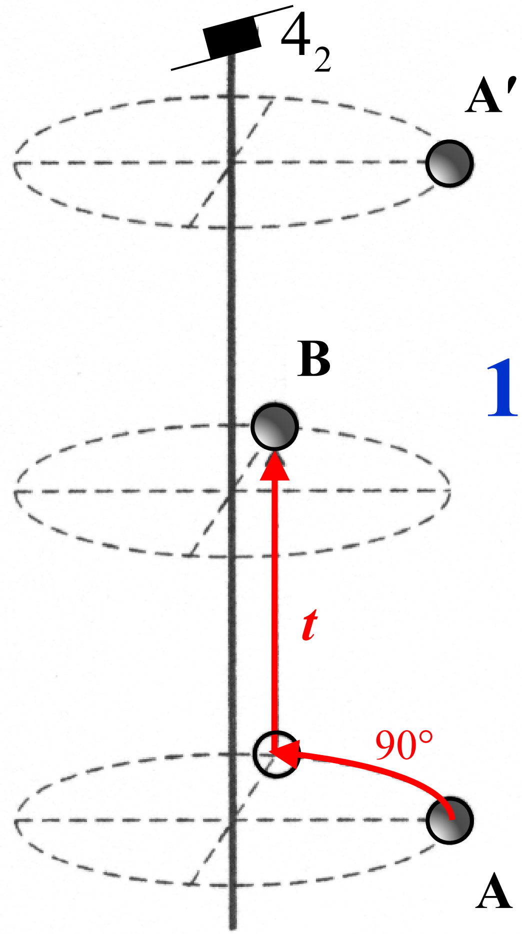
The objective is to repeat object A at position A′.



Object A at $z = 0$ is rotated counter clockwise by 90°

$\boxed{n_m} = \boxed{4_2}$

$t = \left({}^{m}\!/_{n}\right)P = \left({}^{2}\!/_{4}\right)P$

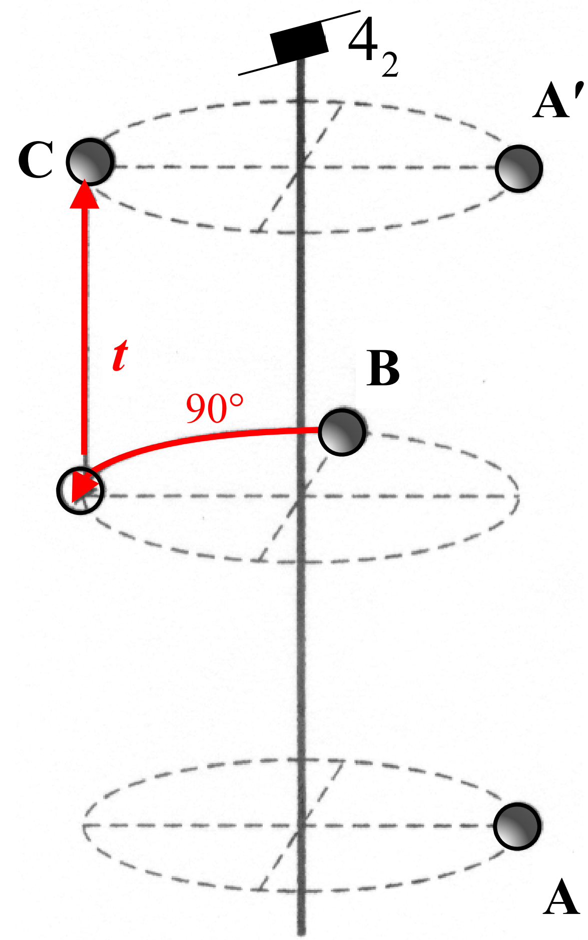


Object A at $z = 0$ is rotated counter clockwise by 90° followed by translation parallel to z by a distance of $t = 2P/4$, i.e. $P/2$, to create object B

$\boxed{n_m} = \boxed{4_2}$

$t = \left(\frac{m}{n}\right)P = \left(\frac{2}{4}\right)P$

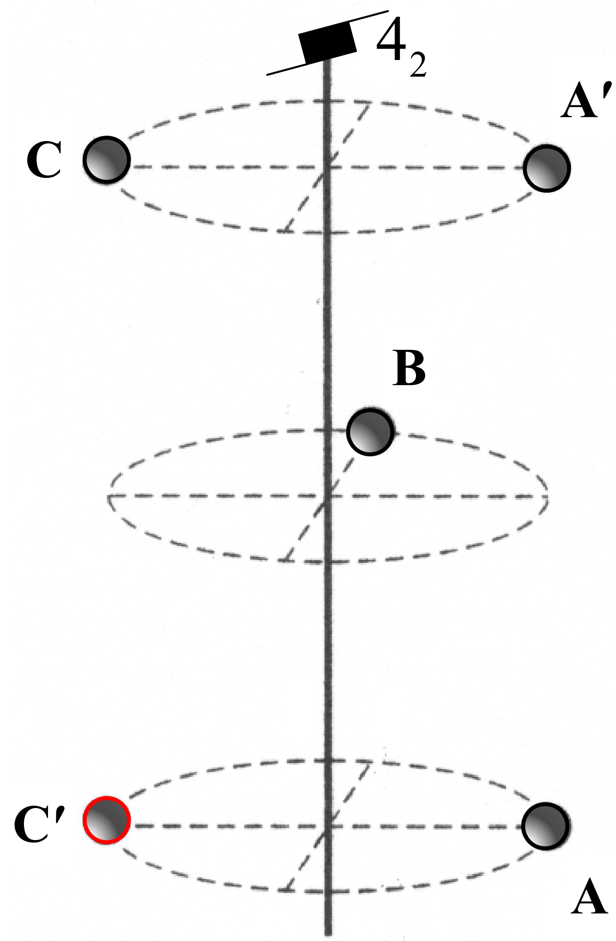
2



Object B is rotated counter clockwise by 90° and translated parallel to *z* by a distance of $t = P/2$, producing object C

$\boxed{n_m} = \boxed{4_2}$

$$t = \left({}^{m}\!/_{n}\right)P = \left({}^{2}\!/_{4}\right)P$$

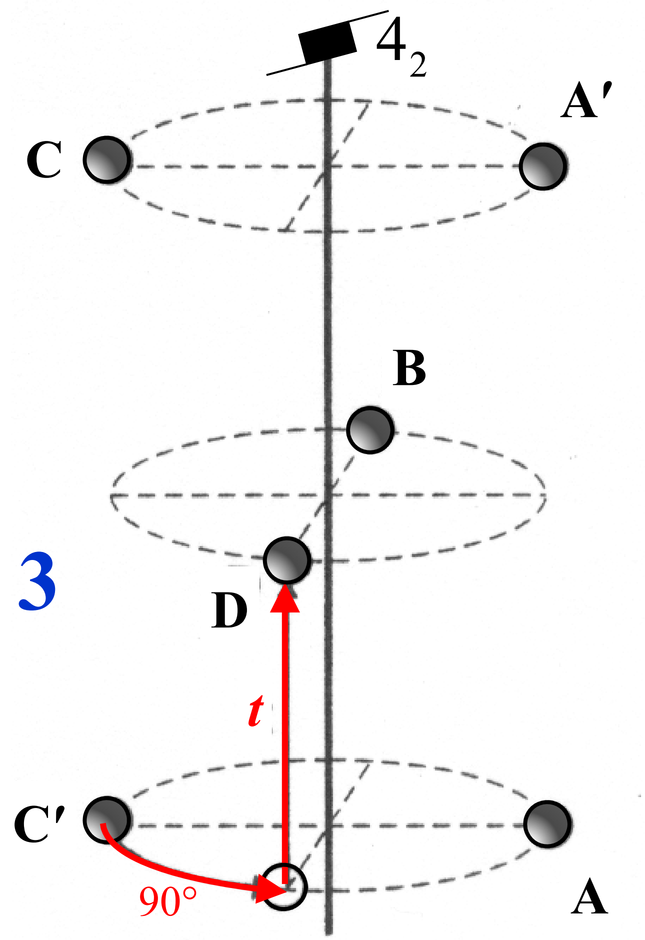


2… cont'd

Object C is at now at $z = P$, the lattice repeat distance; thus we repeat it at z =0 (i.e., position C′)

$$\boxed{n_m} = \boxed{4_2}$$

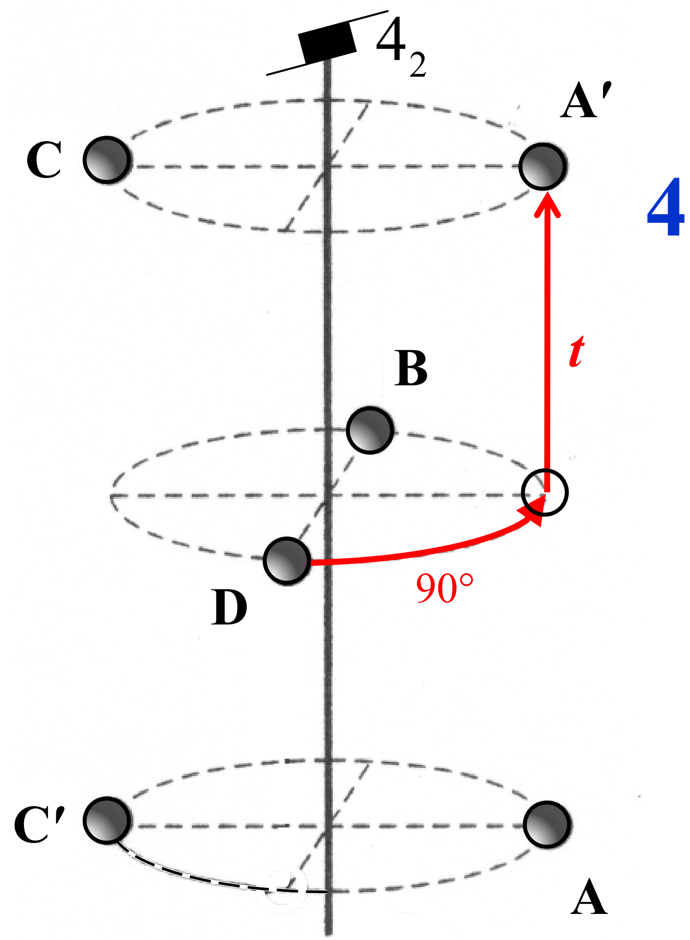
$$t = \left({}^{m}\!/_{n} \right) P = \left({}^{2}\!/_{4} \right) P$$



Repeat of the symmetry operation produces object D at $z = P/2$.

$\boxed{n_m} = \boxed{4_2}$

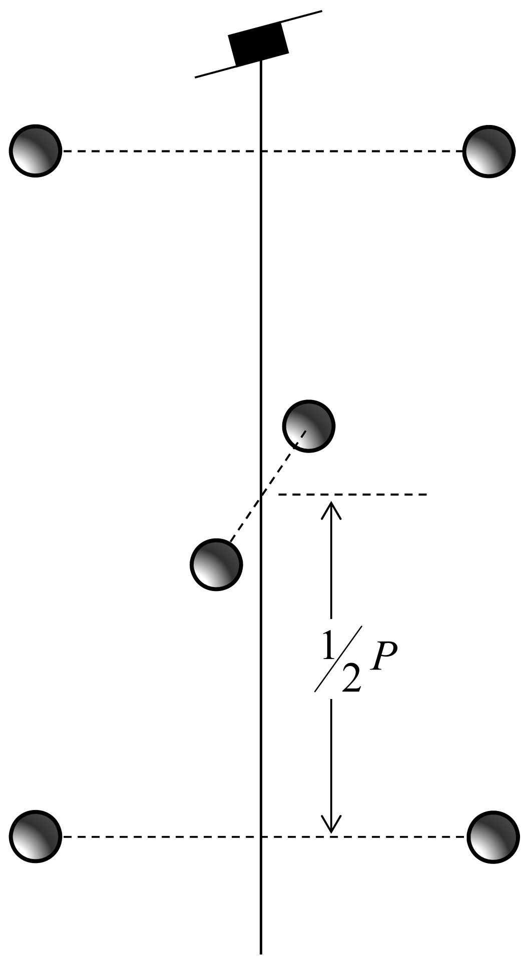
$$t = \left(\frac{m}{n}\right)P = \left(\frac{2}{4}\right)P$$

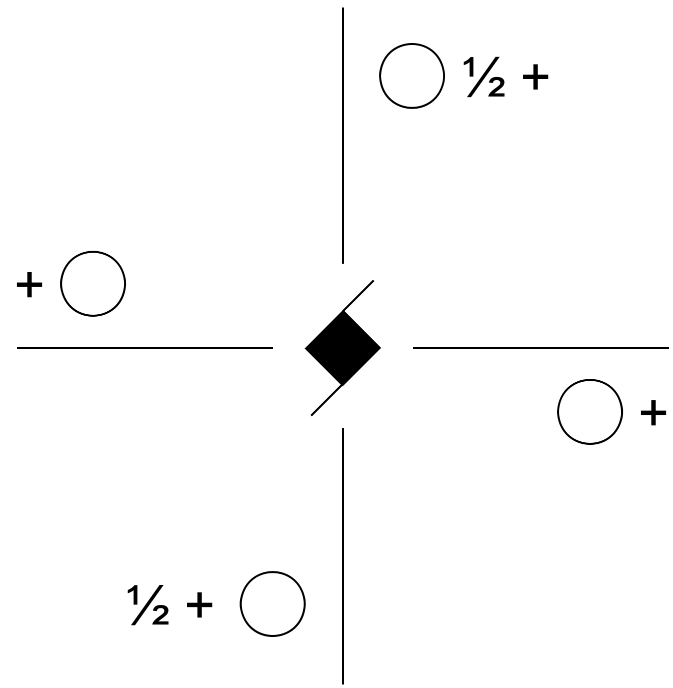


Repeat of the symmetry operation on object D brings everything back into coincidence

$$\boxed{n_m} = \boxed{4_2}$$

$$t = \left({}^{m}\!/\!{}_{n} \right) P = \left({}^{2}\!/\!{}_{4} \right) P$$

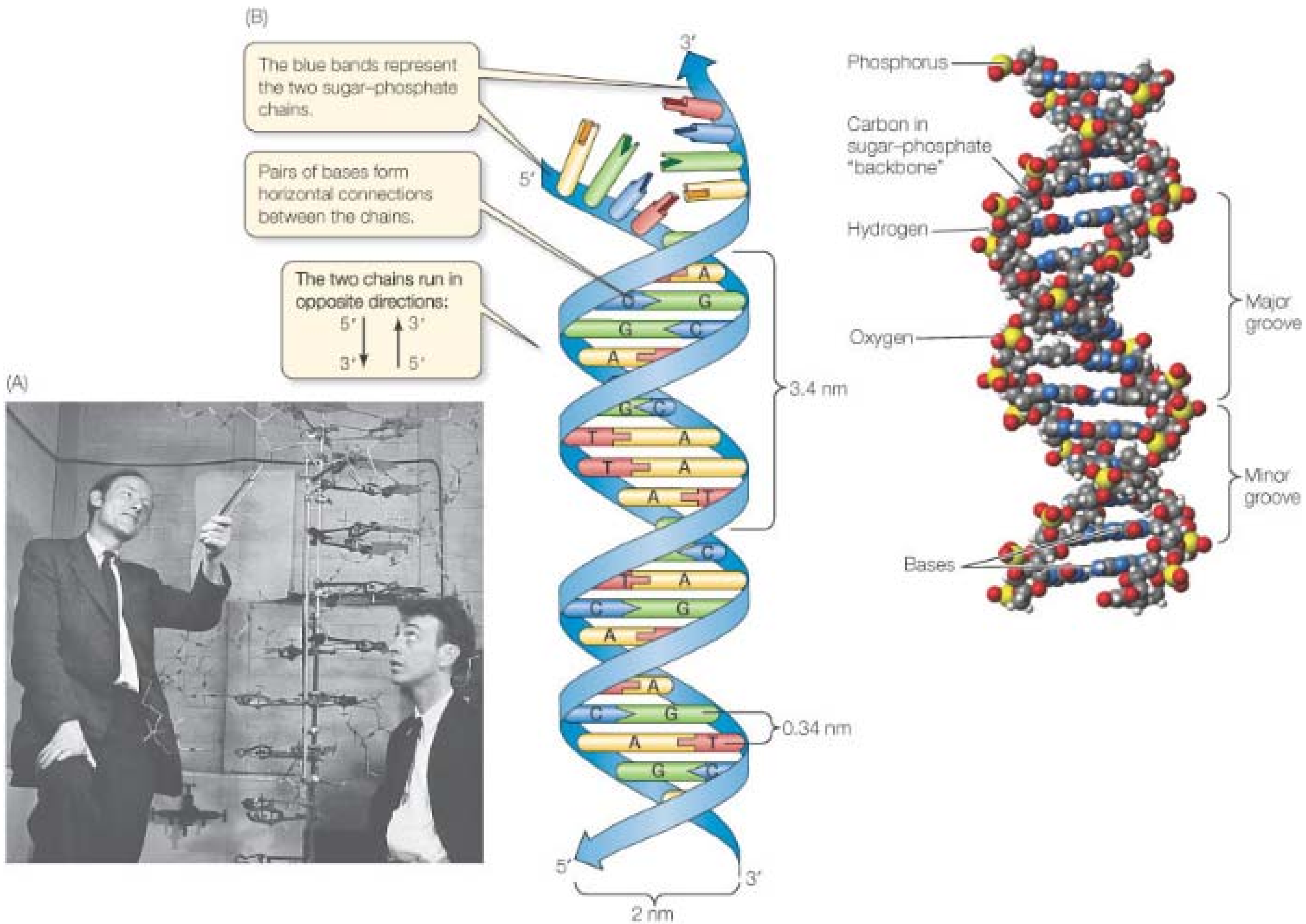




Standard crystallographic representation of a 4_2 screw axis viewed normal to the axis

Do you see things like this in real materials?

DNA double helix consisting of 2 anti-parallel screws



http://www.nature.com/scitable/nated/content/24263/sadava_11_8_large_2.jpg

Atomic structure around a screw dislocation

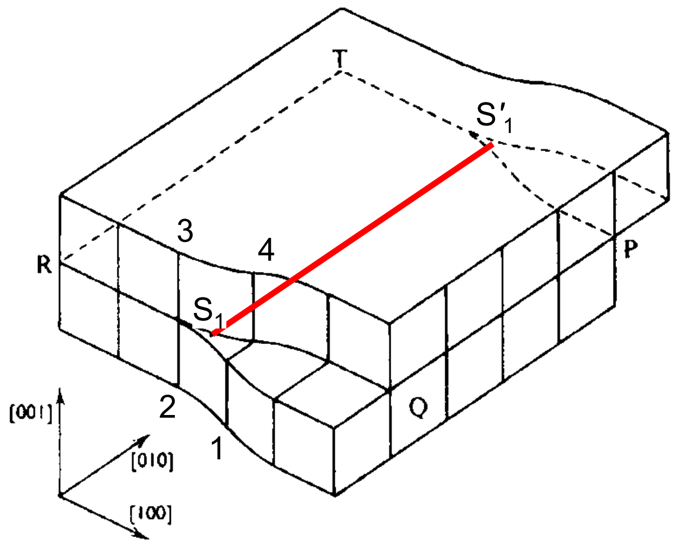


Figure 7.1 A screw dislocation in a primitive cubic lattice

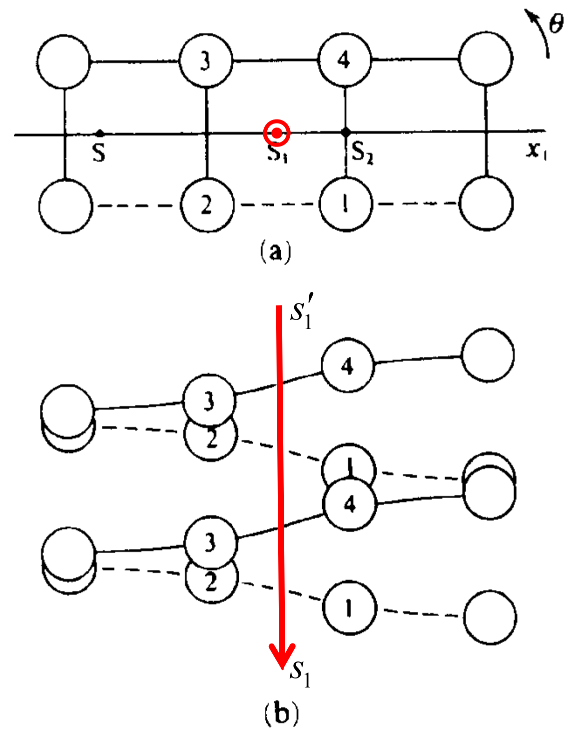
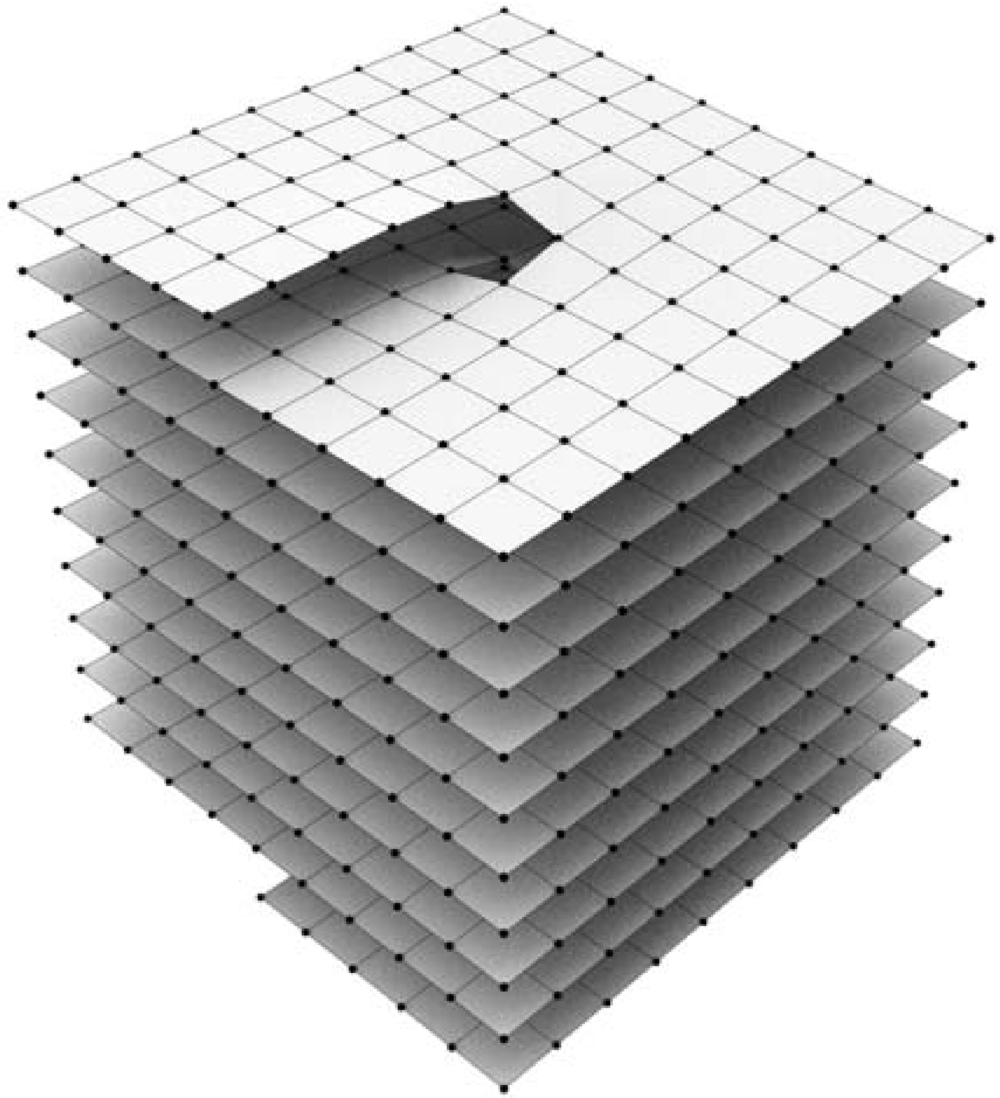
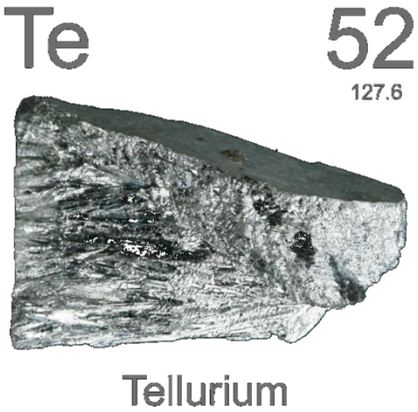


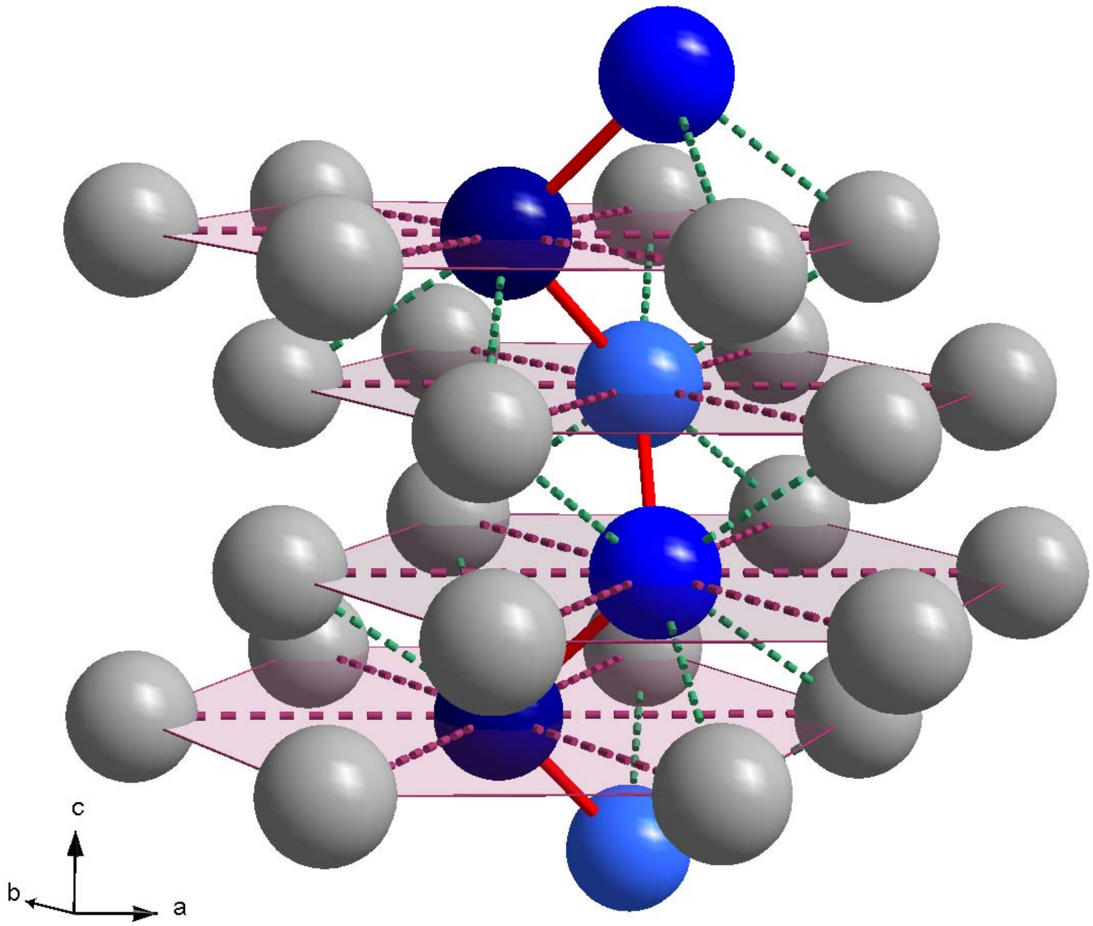
Figure 7.6 Screw dislocation in a simple cubic crystal (a) looking along the dislocation and (b) looking normal to the dislocation which lies along $S_1S'_1$.

Adapted from Kelly, Groves and Kidd, *Crystallography and Crystal Defects, Revised Edition*, John Wiley & Sons, 2000



http://www.flickr.com/photos/l2xy2/4644933597/sizes/o/in/photostream/





The chains in the crystal structure of tellurium along the 3_1-screw axis. The chain is highlighted in blue colors where the dark blue atom is situated on c = 1/3, middle blue on c = 2/3 and light blue on c = 0. Thick red bonds represent covalent bonds between atoms in the chain (d = 284 pm), dashed green bonds secondary contacts between chains (d = 349 pm) and dashed purple bonds represent the hexagonal surrounding within a "layer" of tellurium (d = 446 pm).

http://www.periodictable.com/Elements/052/index.html

http://en.wikipedia.org/wiki/File:Te_chains.png