Analytical Methods for Materials

Lesson 12
Crystallography and Crystal Structures – continued

Suggested Reading

- Ch. 6 in Waseda
- Ch. 1 – C. Kittel, Introduction to Solid State Physics, 3rd Edition, Wiley (1956).
- Excerpt from ASM Metals Handbook.
- Chs. 1 and 3 – M. DeGraef and M.E. McHenry, Structure of Materials, Cambridge (2007).
- Chs. 1 and 3 – S.M. Allen and E.L. Thomas, The Structure of Materials, Wiley (1999).
- Chs. 3 and 4 – R. Tilley, Crystals and Crystal Structures, Wiley (2006).

Recall

- All crystal structures can be classified into 7 crystal systems!
- The distribution of atoms in crystals is characterized by periodicity in a 3-D lattice.
- We classify atomic arrangements into 32 point groups using 8 symmetry operators.

Space Groups

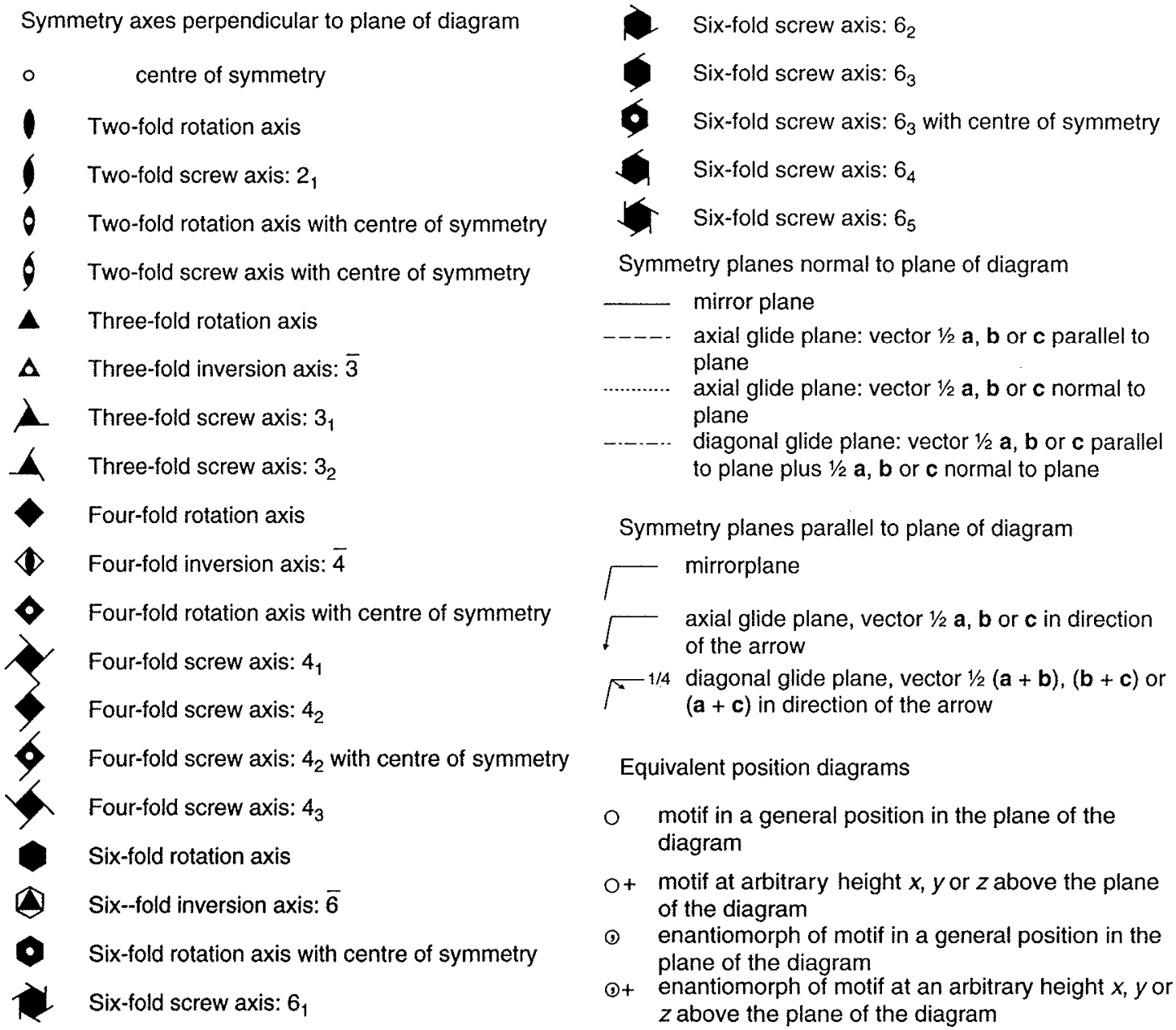
- Combine all geometrical symmetry operations that take a 3-dimensional periodic object into itself.

- Describes the entire symmetry of the crystal (internal and external).

- "Describe how all symmetry elements are distributed in space."

  - There are 17 space groups in 2D

  - There are 230 space groups in 3D



Graphical symbols used in space group diagrams. Figure from R. Tilley, *Crystals and Crystal Structures*, (John Wiley & Sons, Hoboken, NJ, 2006), p. 99

2-D example

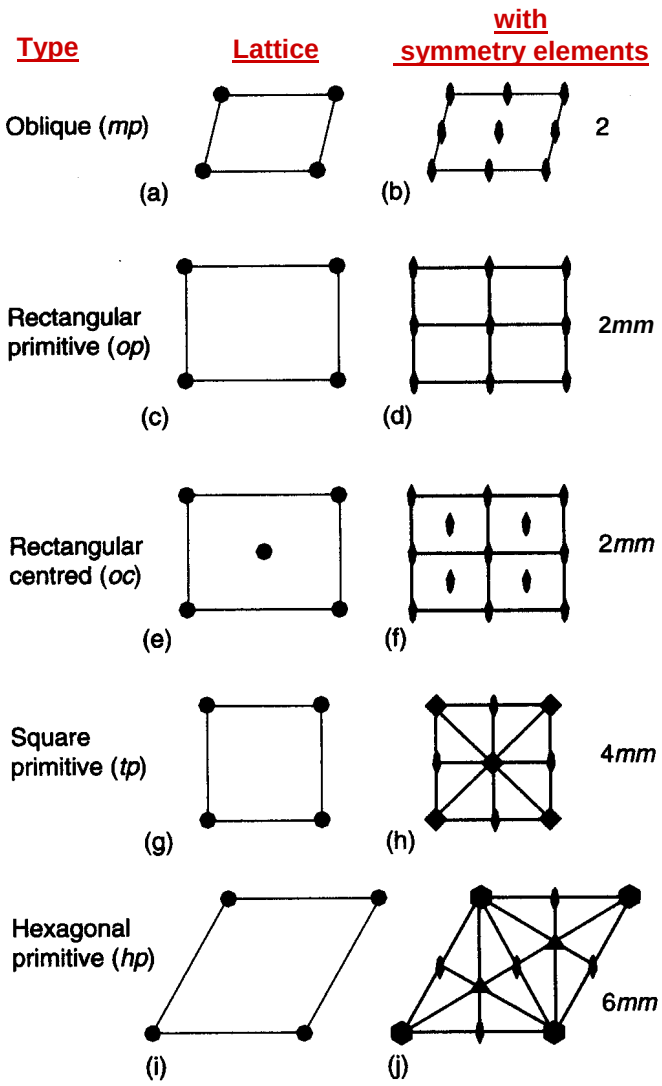
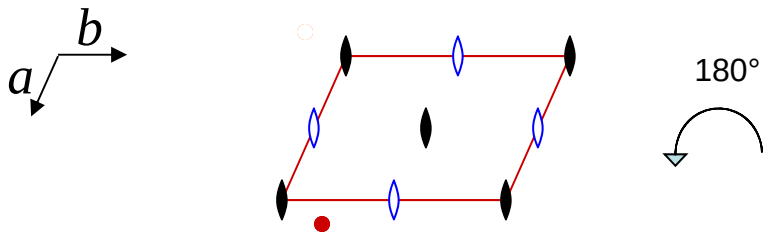


Figure 3.5 Symmetry of the plane lattices: (a, b) oblique primitive, *mp*, 2; (c, d) rectangular primitive, *op*, 2*mm*; (e, f) rectangular centred, *oc*, 2*mm*; (g, h) square, *tp*, 4*mm*; (i, j) hexagonal primitive, *hp*, 6*mm*

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

- Symmetry operators must leave every lattice point unchanged (identical).
- Form for symmetry symbols
  - Primary · Secondary · Tertiary
    e.g., 2*mm*, 6*mm*, etc.
- Consider the oblique lattice



- Symmetry requires a 2-fold rotation axis (i.e., diad) at the center of the cell.
- Therefore, diads must be present on each lattice point.
- There will be implied diads centered on cell sides.

2-D Symmetry

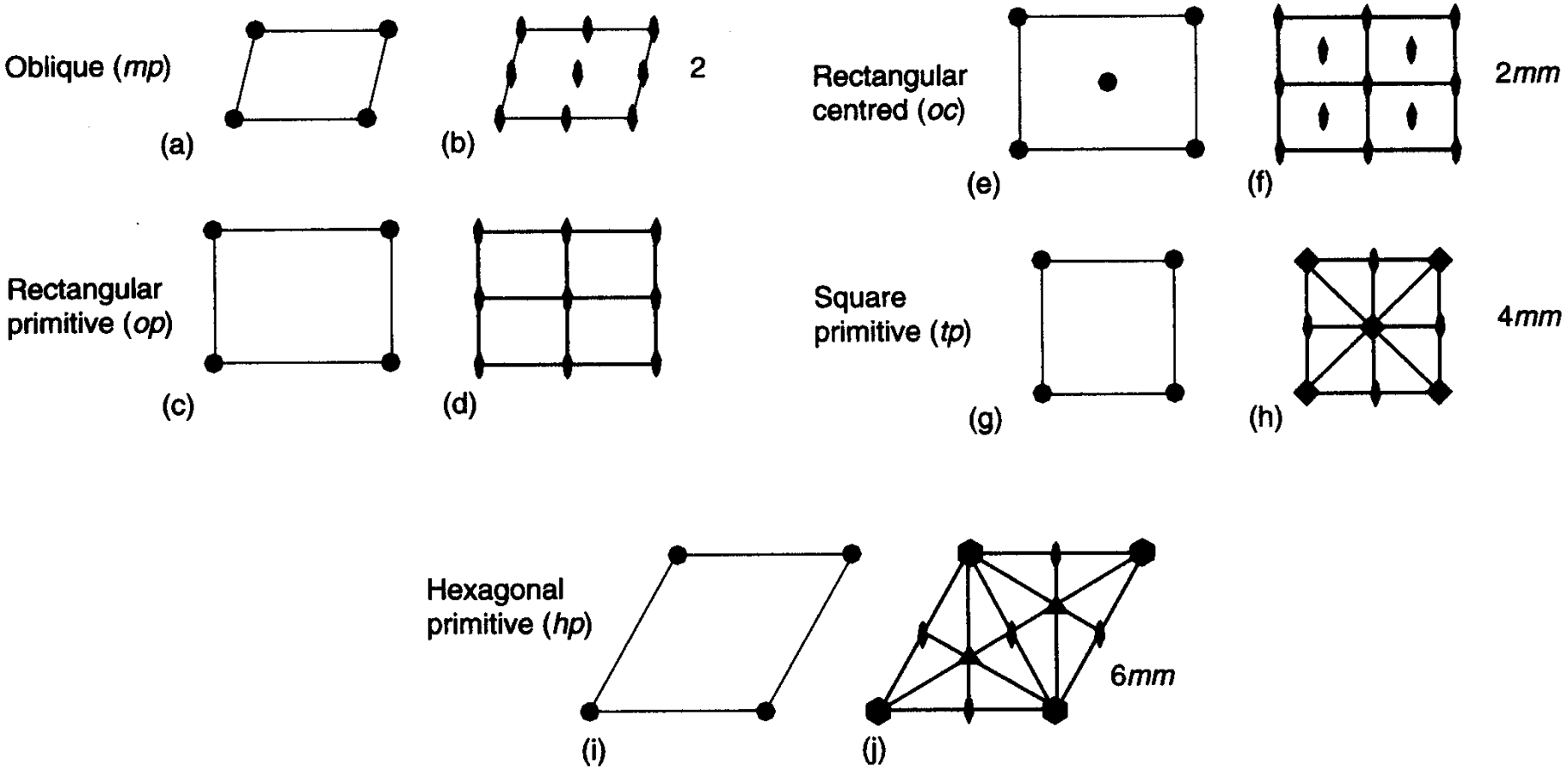
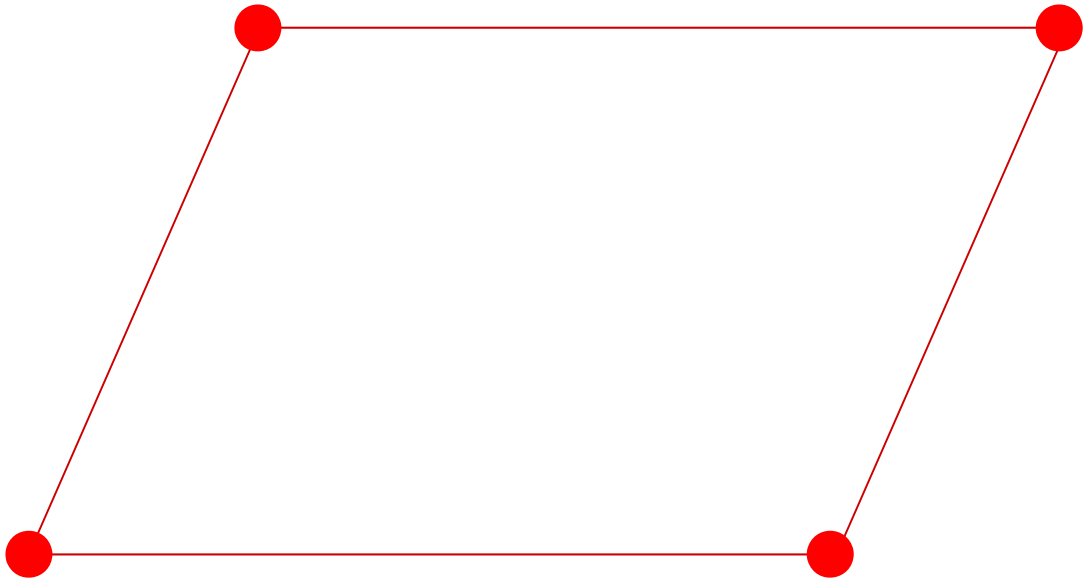


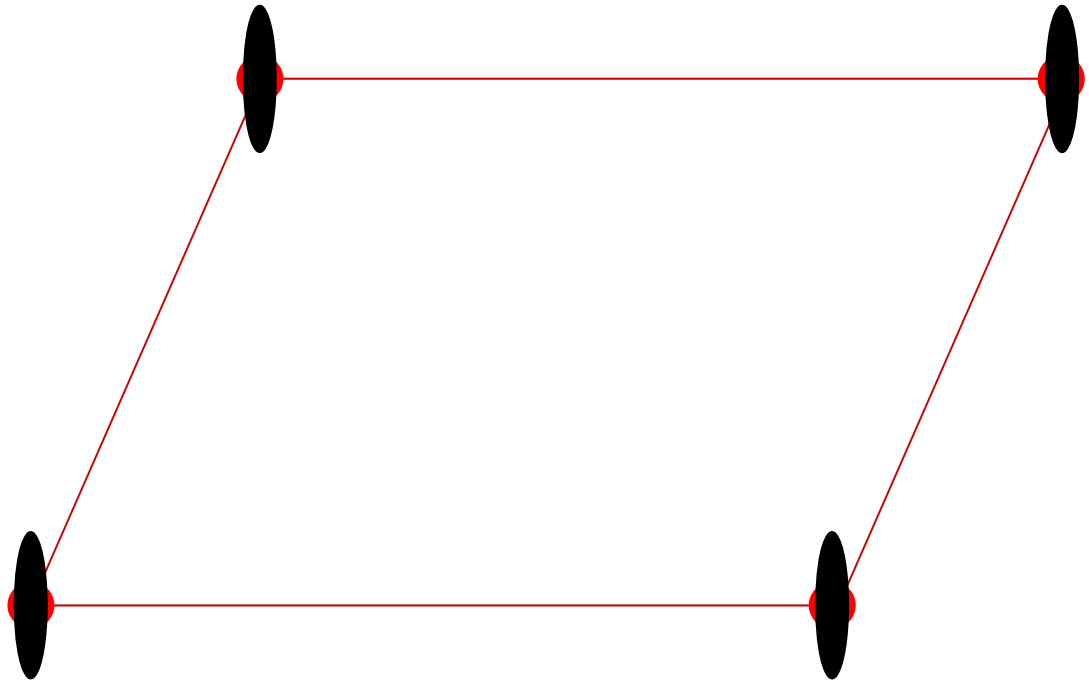
Figure 3.5 Symmetry of the plane lattices: (a,b) oblique primitive, mp, 2; (c,d) rectangular primitive, op, 2mm; (e,f) rectangular centered, oc, 2mm; (g,h) square, tp, 4mm; (I,j) hexagonal primitive, hp, 6mm. From R. Tilley, *Crystals and Crystal Structures*, John Wiley & Sons, Hoboken, NJ, 2006

Primitive Oblique Lattice (*mp*)



This 2-D lattice exhibits 2-fold rotational symmetry about it’s center.

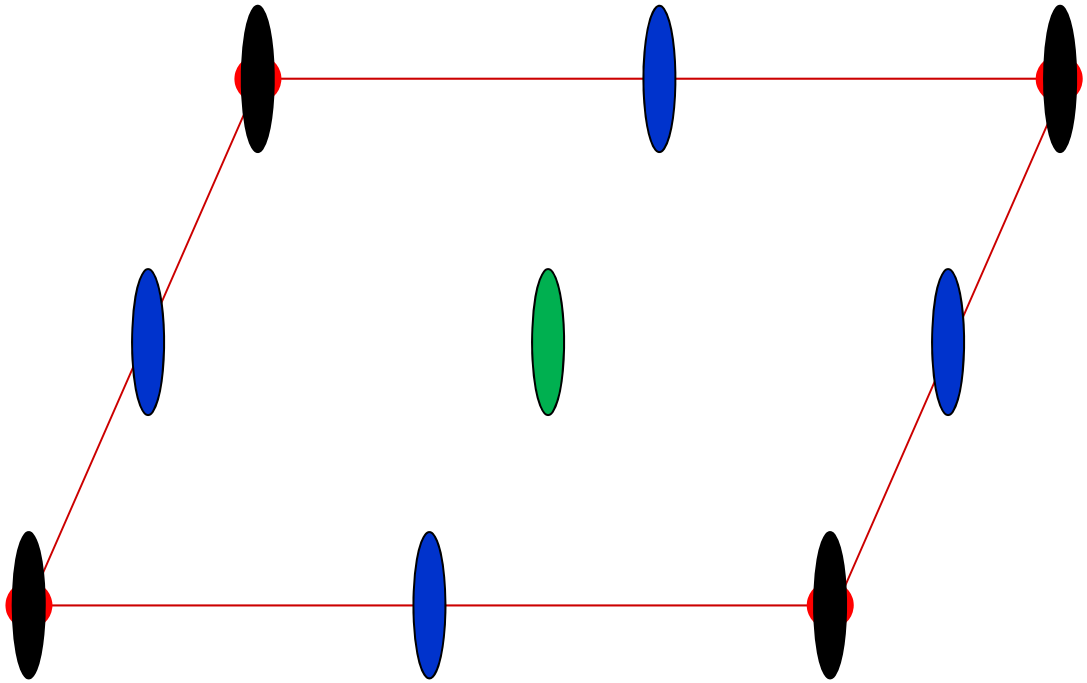
Primitive Oblique Lattice (*mp*)



The symmetry of the unit cell can be conveniently placed at the origin without losing generality.

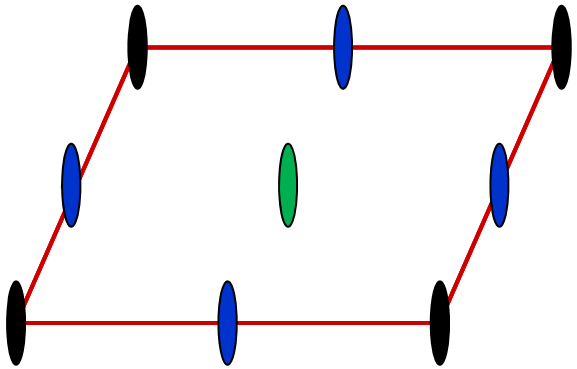
THUS, there must be 2-fold symmetry axes on all lattice points.

Primitive Oblique Lattice (*mp*)

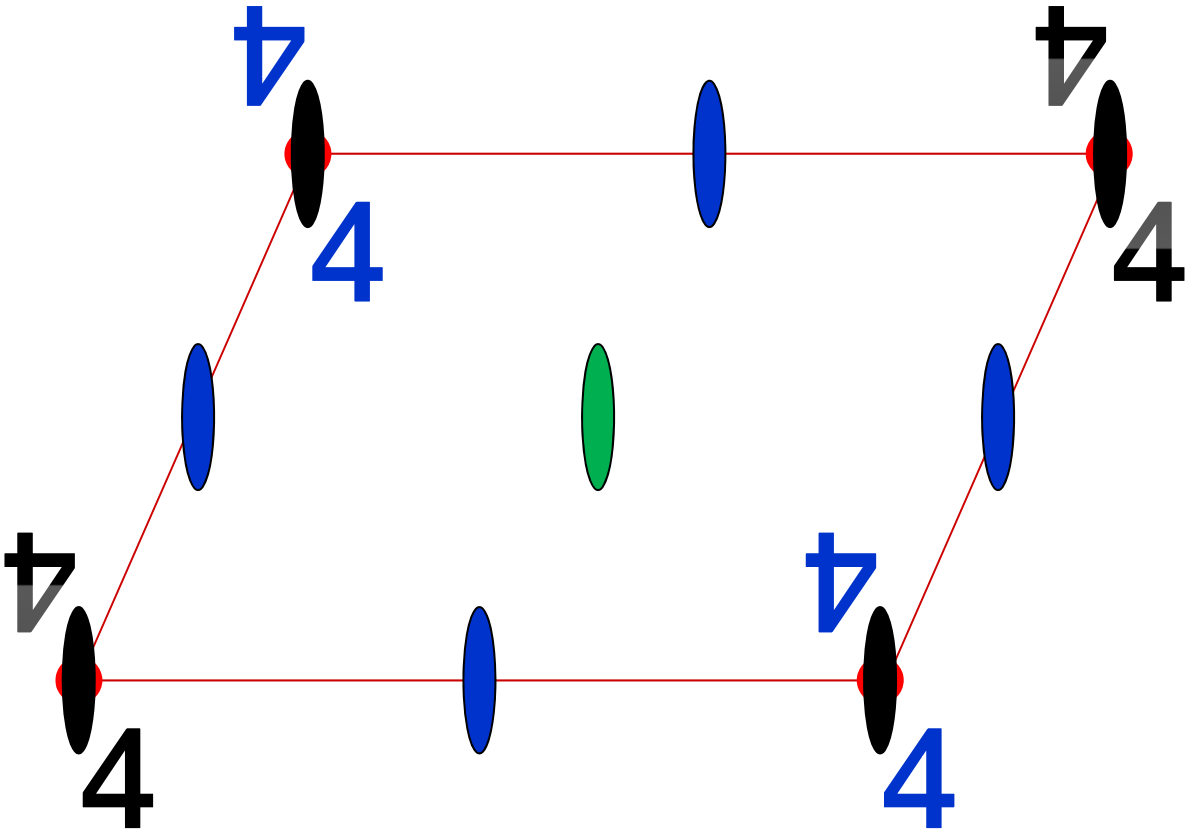


The presence of these 2-fold axes forces diads to be placed at the center of each of the cell sides and in the cell center. I've drawn them in blue and green. They are 'implied' symmetries.

Animated illustration of implied symmetries in the oblique lattice

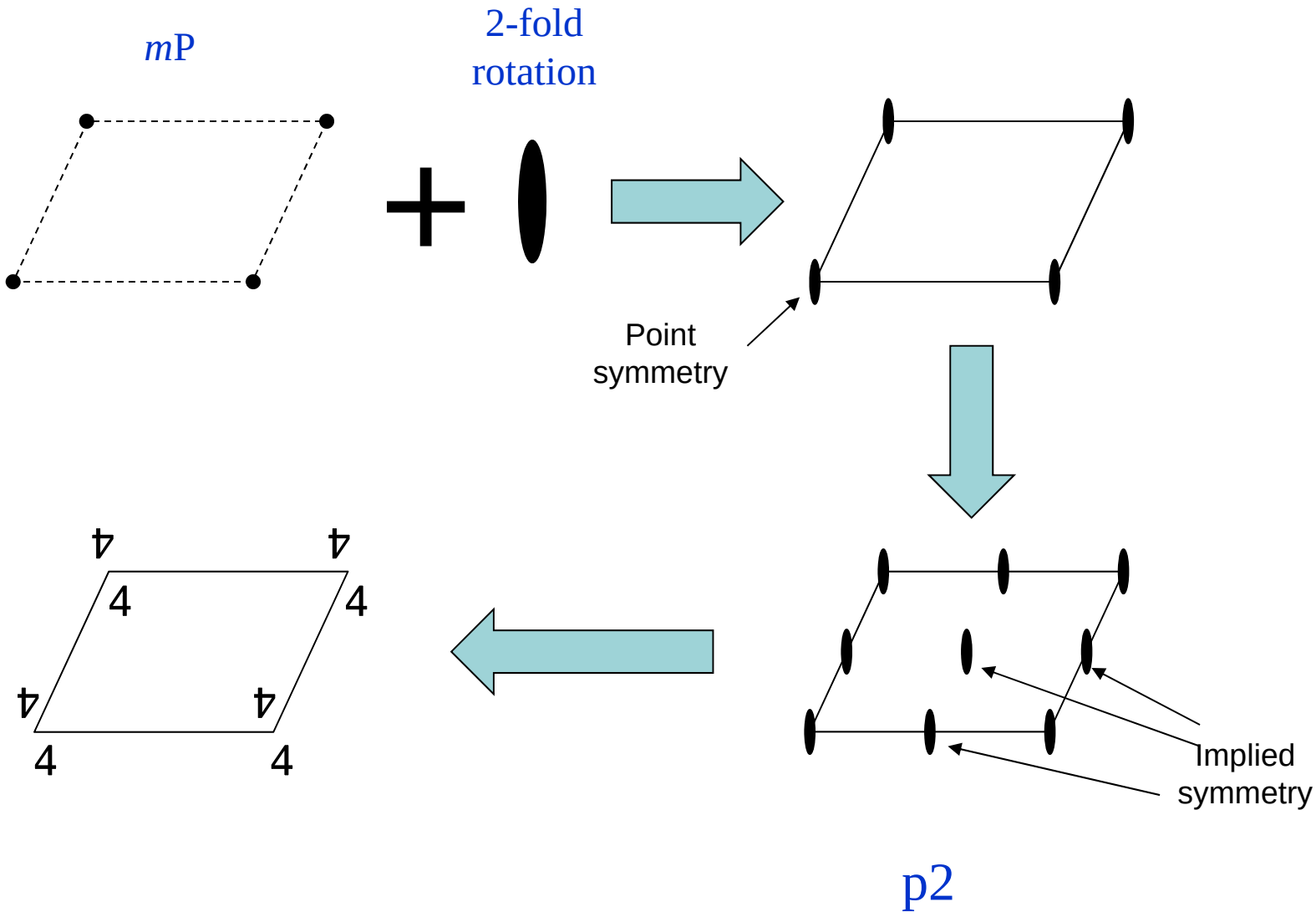


Primitive Oblique Lattice (*mp*)

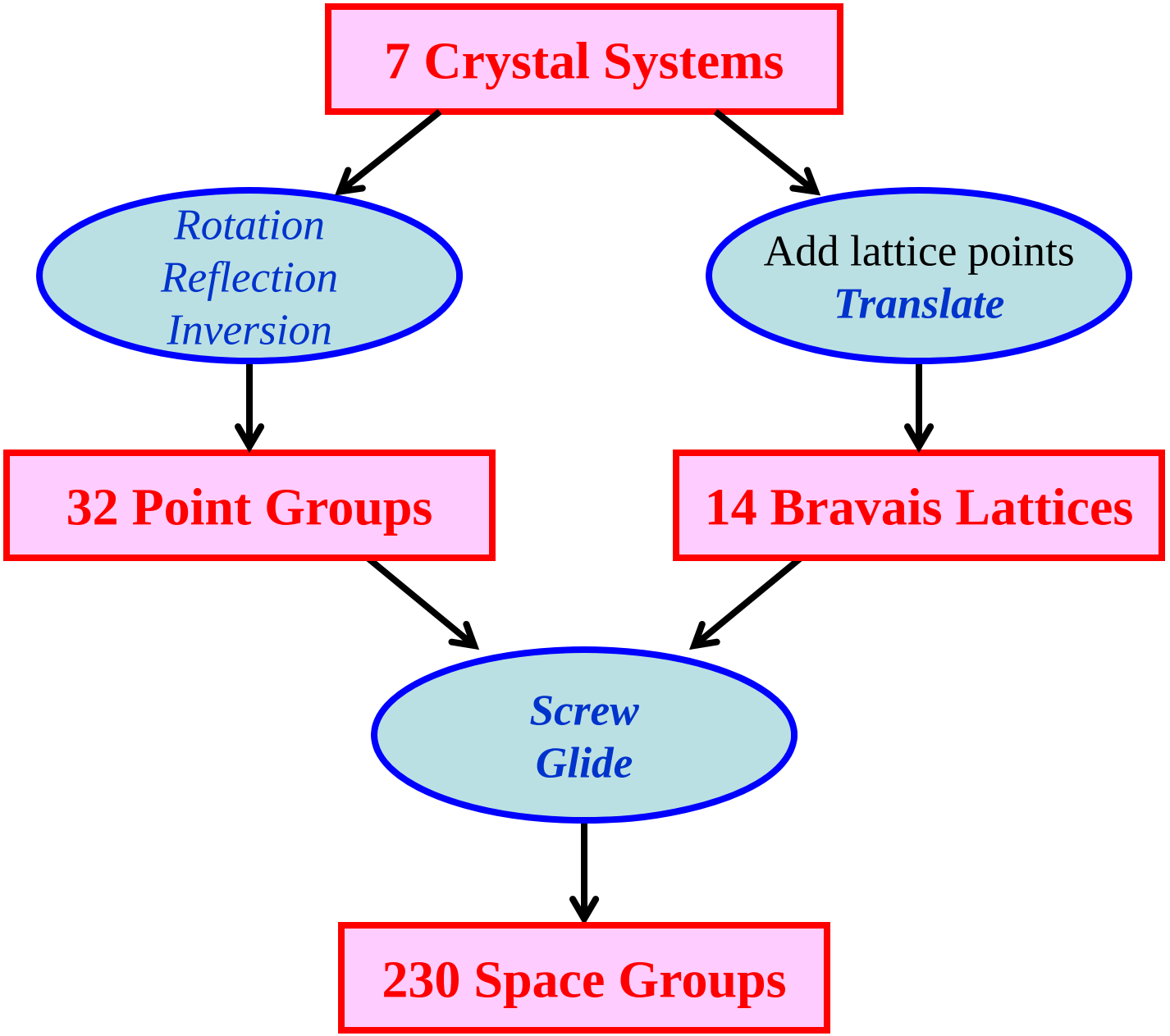


Start w/ an asymmetric unit
2-fold symmetry of shape and lattice points reproduces 3 more (black)
Implied symmetry produces other two (blue)

Synopsis of Symmetry in an Oblique Lattice



Synopsis of relationships between crystal systems, Bravais lattices, point groups, and space groups



The previous viewgraph in words – 1

- The 7 crystal systems are a set of unit cell shapes that characterize all types of crystal lattices in space.

- The 14 Bravais lattices represent all three-dimensional periodic arrays of points in space.

- Any three-dimensional periodic structure can be classified into one of these cell types (thus into one of the 7 crystal systems).

The previous viewgraph in words - 2

- The 32 point groups represent the 32 unique combinations of symmetry operations about a point in space. They can be grouped according to crystal systems.
- Crystal systems are defined in terms of the minimum point group symmetry required to be compatible with such cells.
- They are grouped according to the highest ranking rotation axis compatible with the system and the number of such axes that are present.

Synopsis of the 230 Space Groups

- Describe complete symmetry of a crystal (internal and external).
- 230 possible combinations. This means that there are only 230 possible crystal structures!
- All possibilities can be found in the International Tables for Crystallography.

Table 7.4 The 230 Space Groups, and the Isogonal 32 Crystal Classes (Point Groups). The Space Group Symbols Are, in general, Unabbreviated*

Crystal Class	Space Group
$\underline{1}$	$P\underline{1}$
$\bar{1}$	$P\bar{1}$
2	$P2$, $P2_1$, $C2$
m	Pm, Pc, Cm, Cc
$2/m$	$P2/m$, $P2_1/m$, $C2/m$, $P2/c$, $P2_1/c$, $C2/c$
222	$P222$, $P222_1$, $P2_12_12$, $P2_12_12_1$, $C222_1$, $C222$, $F222$, $I222$, $I2_12_12_1$
$mm2$	$Pmm2$, $Pmc2_1$, $Pcc2$, $Pma2$, $Pca2_1$, $Pnc2$, $Pmn2_1$, $Pba2$, $Pna2_1$, $Pnn2$, $Cmm2$, $Cmc2_1$, $Ccc2$, $Amm2$, $Abm2$, $Ama2$, $Aba2$, $Fmmc$, $Fdd2$, $Imm2$, $Iba2$, $Ima2$
$2/m2/m2/m$	$P2/m2/m2/m$, $P2/n2/n2/n$, $P2/c2/c2/m$, $P2/b2/a2/n$, $P2_1/m2/m2/a$, $P2/n2_1/n2/a$, $P2/m2/n2_1/a$, $P2_1/c2/c2/a$, $P2_1/b2_1/a2/m$, $P2_1/c2_1/c2/n$, $P2/b2_1/c2_1/m$, $P2_1/n2_1/n2/m$, $P2_1/m2_1/m2/n$, $P2_1/b2/c2_1/n$, $P2_1/b2_1/c2_1/a$, $P2_1/n2_1/m2_1/a$, $C2/m2/c2/m$, $C2/m2/c2_1/a$, $C2/m2/m2/m$, $C2/c2/c2/m$, $C2/m2/m2/a$, $C2/c2/c2/a$, $F2/m2/m2/m$, $F2/d2/d2/d$, $I2/m2/m2/m$, $I2/b2/a2/m$, $12/b2/c2/a$, $I2/m2/m2/a$
$\underline{4}$	$P4$, $P4_1$, $P4_2$, $P4_3$, $I4$, $I4_1$
$\bar{4}$	$P\bar{4}$, $I\bar{4}$
$4/m$	$P4/m$, $P4_2/m$, $P4/n$, $P4_2/n$, $I4/m$, $I4_1/a$
422	$P422$, $P42_12$, $P4_122$, $P4_12_12$, $P4_222$, $P4_22_12$, $P4_322$, $P4_32_12$, $I422$, $I4_122$
$4/mm$	$P4/mm$, $P4bm$, $P4_2cm$, $P4_2nm$, $P4cc$, $P4nc$, $P4_2mc$, $P4_2bc$, $I4mm$, $I4cm$, $I4_1md$, $I4_1cd$
$\bar{4}2m$	$P\bar{4}2m$, $P\bar{4}2c$, $P\bar{4}2_1m$, $P\bar{4}2_1c$, $P\bar{4}m2$, $P\bar{4}c2$, $P\bar{4}b2$, $P\bar{4}n2$, $I\bar{4}m2$, $I\bar{4}c2$, $I\bar{4}2m$, $I\bar{4}2d$
$4/m2/m2/m$	$P4/m2/m2/m$, $P4/m2/c2/c$, $P4/n2/b2/m$, $P4/n2/n2/c$, $P4/m2_1/b2/m$, $P4/m2_1/n2/c$, $P4/n2_1/m2/m$, $P4/n2_1/c2/c$, $P4_1/m2/m2/c$, $P4_2/m2/c2/m$, $P4_2/n2/b2/c$, $P4_2/n2/n2/m$, $P4_2/m2_1/b2/c$, $P4_2/m2_1/n2/m$, $P4_1/n2_1/m2/c$, $P4_2/n2_1/c2/m$, $I4/m2/m2/m$, $I4/m2/c2/m$, $I4_1/a2/m2/d$, $I4_1/a2/c2/d$
$\underline{3}$	$P3$, $P3_1$, $P3_2$, $R3$
$\bar{3}$	$P\bar{3}$, $R\bar{3}$
32	$P312$, $P321$, $P3_112$, $P3_121$, $P3_212$, $P3_221$, $R32$
$3m$	$P3m1$, $P31m$, $P3c1$, $P31c$, $R3m$, $R3c$
$\bar{3}2/m$	$P\bar{3}1m$, $P\bar{3}1c$, $P\bar{3}m1$, $P\bar{3}c1$, $R\bar{3}m$, $R\bar{3}c$
$\underline{6}$	$P6$, $P6_1$, $P6_5$, $P6_2$, $P6_4$, $P6_3$
$\bar{6}$	$P\bar{6}$
$6/m$	$P6/m$, $P6_3/m$
622	$P622$, $P6_122$, $P6_522$, $P6_222$, $P6_422$, $P6_322$
$\underline{6}mm$	$P6mm$, $P6cc$, $P6_3cm$, $P6_3mc$
$\bar{6}m2$	$P\bar{6}m2$, $P\bar{6}c2$, $P\bar{6}2m$, $P\bar{6}2c$
$6/m2/m2/m$	$P6/m2/m2/m$, $P6/m2/c2/c$, $P6_3/m2/c2/m$, $P6_3/m2/m2/c$
23	$P23$, $F23$, $I23$, $P2_13$, $I2_13$
$2/m\bar{3}$	$P2/m\bar{3}$, $P2/n\bar{3}$, $F2/m\bar{3}$, $F2/d\bar{3}$, $I2/m\bar{3}$, $P2_1/a\bar{3}$, $I2_1/a\bar{3}$
432	$P432$, $P4_232$, $F432$, $F4_132$, $I432$, $P4_332$, $P4_132$, $I4_132$
$\bar{4}3m$	$P\bar{4}3m$, $F\bar{4}3m$, $I\bar{4}3m$, $P\bar{4}3n$, $F\bar{4}3c$, $I\bar{4}3d$
$4/m\bar{3}2/m$	$P4/m\bar{3}2/m$, $P4/n\bar{3}2/n$, $P4_2/m\bar{3}2/n$, $P4_2/n\bar{3}2/m$, $F4/m\bar{3}2/m$, $F4/m\bar{3}2/c$, $F4_1/d\bar{3}2/m$, $F4_1/d\bar{3}2/c$, $I4/m\bar{3}2/m$, $I4_1/a\bar{3}2/d$

*From *International Tables for Crystallography*. 1983. v. A. T. Han, ed: *Space group symmetry*. International Union of Crystallography, Reidel Publ. Co., Boston, USA.