A big thanks to our sponsors, the participants and …

- Thank you!

From Point Groups to Space Groups

What are they and why do we need them?

Andreas Decken, University of New Brunswick

Thanks

To so many people that provided slides

and suggestions


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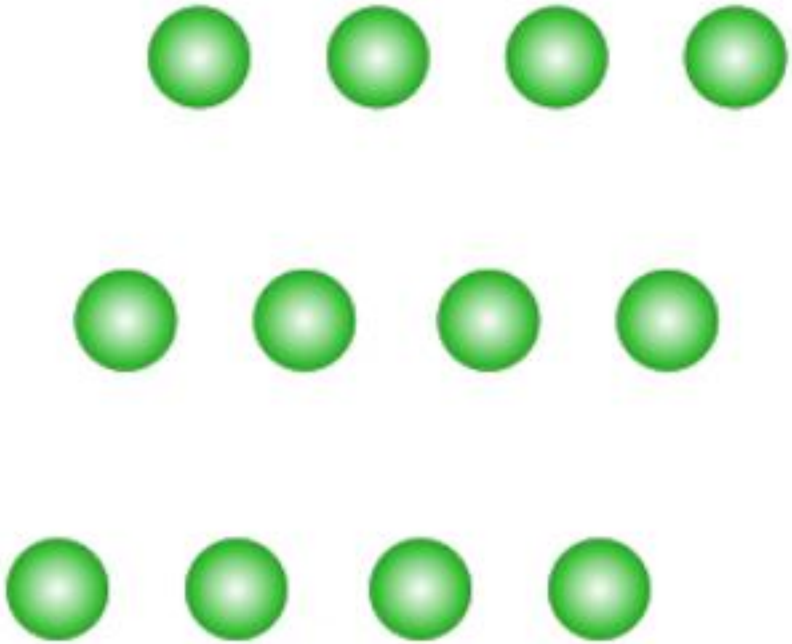
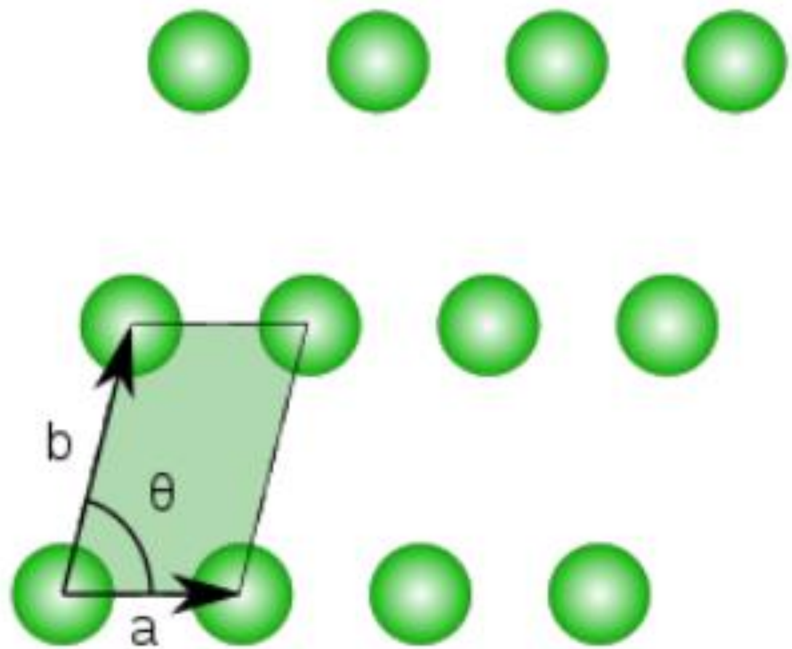
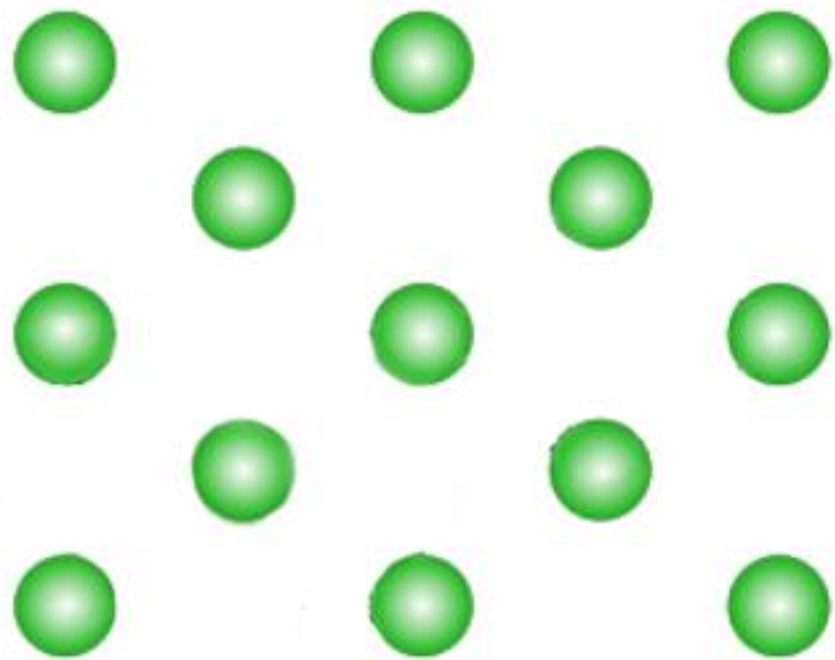
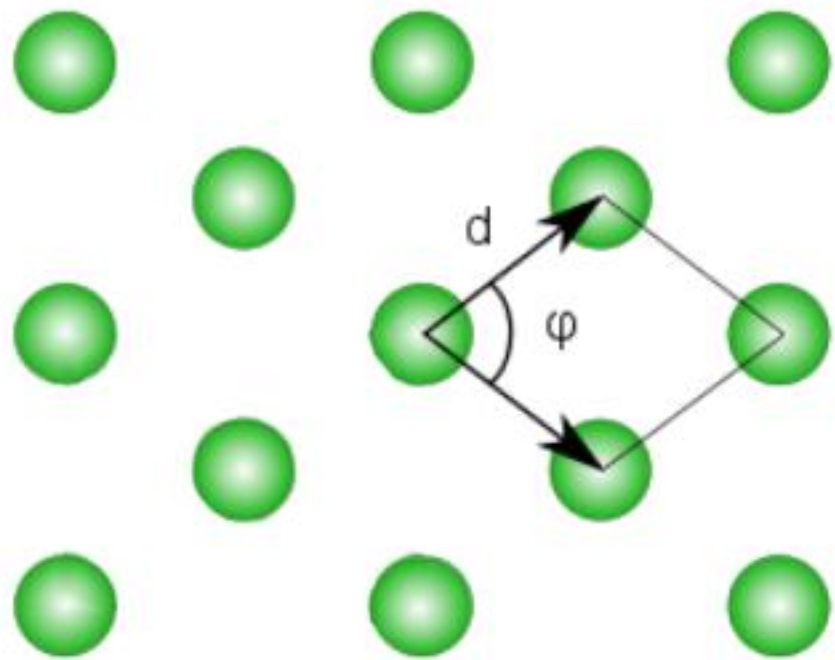




In the absence of symmetry, we can choose every possible unit cell.

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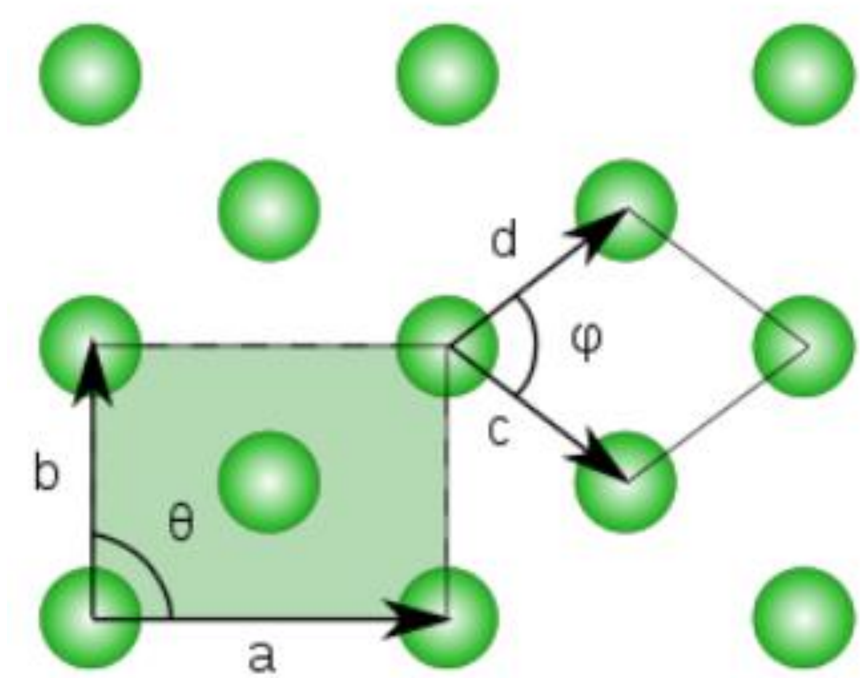
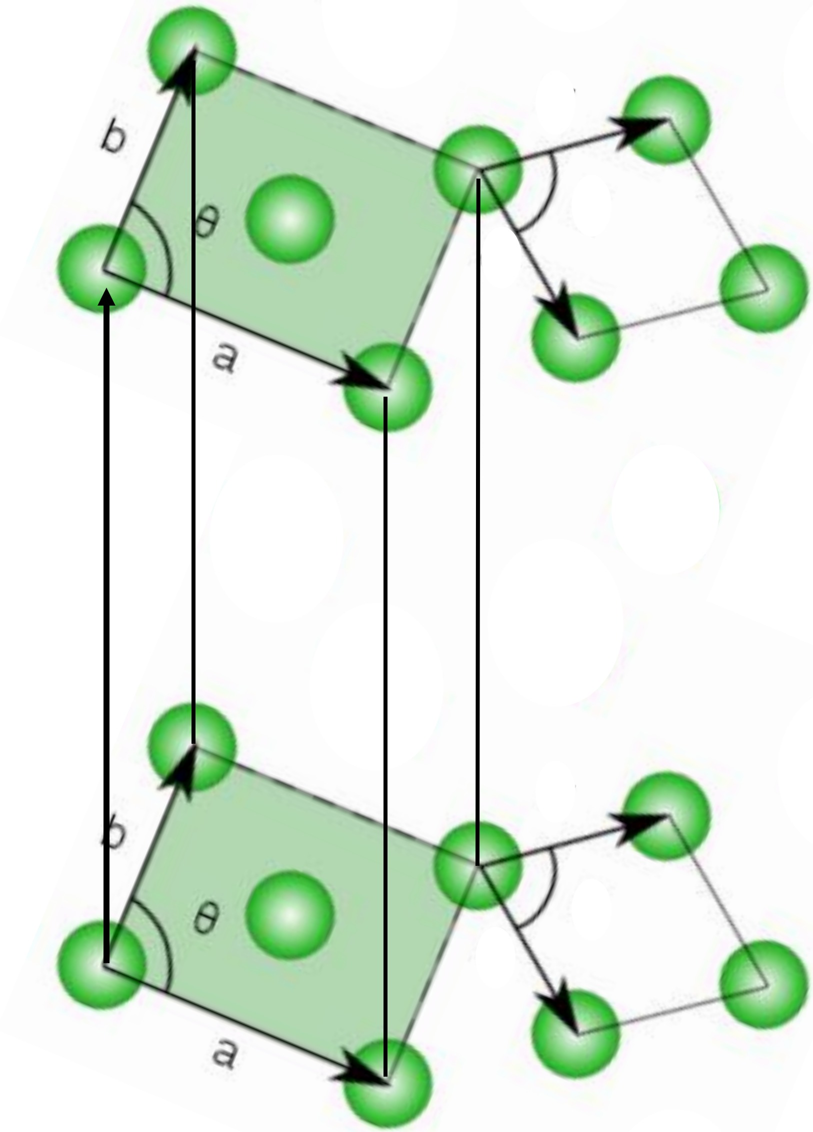


Hein Schaper:

To correctly describe our structure, we have always to choose the highest possible symmetry.



How can we describe a crystal which contains a certain symmetry, for example a mirror plane, but the smallest cells are incompatible with these symmetry elements.

We choose a cell of higher volume, containing more than one lattice point, a so called centered cell. In this example, we have a C-centered cell.

Bravais Lattices

Courtesy: Charles Campana

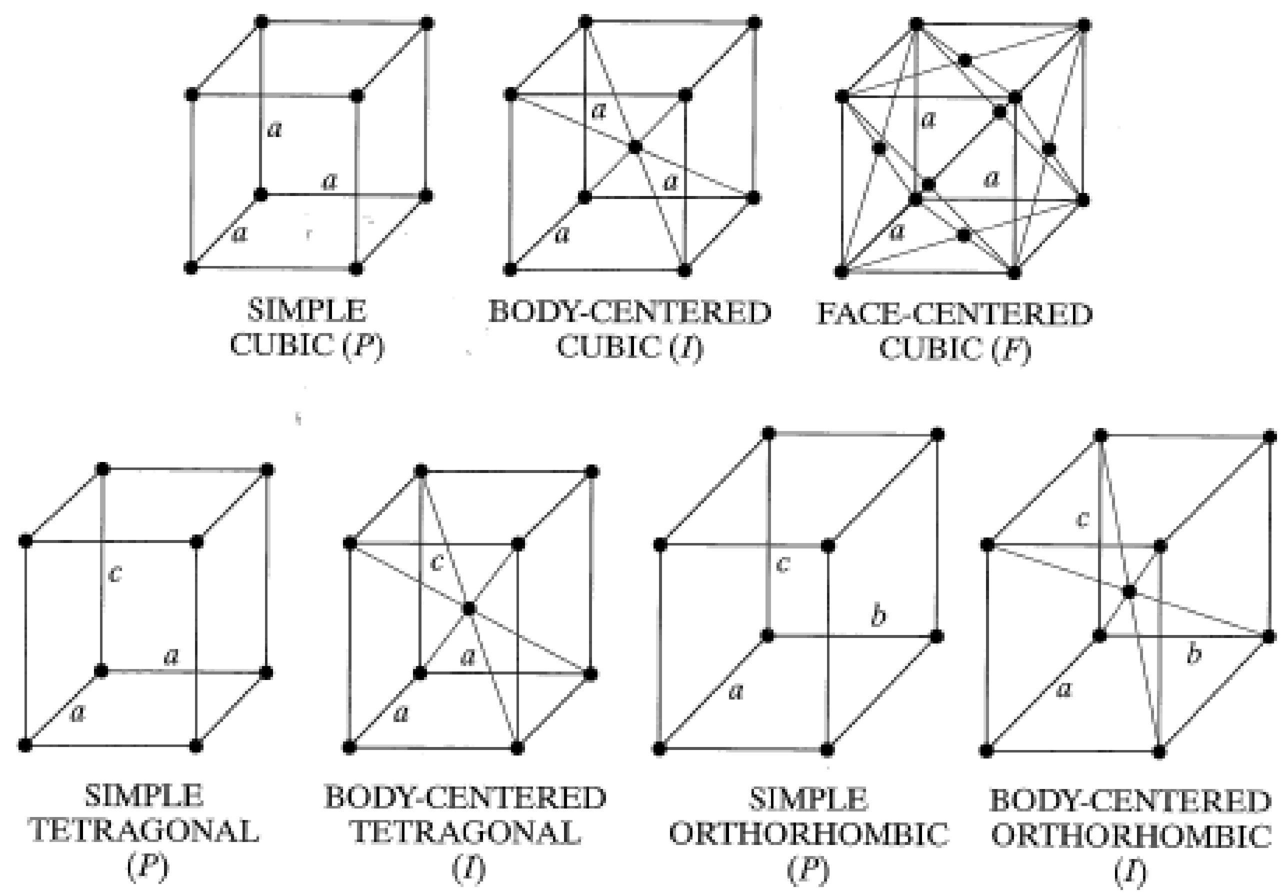
- Within each crystal system, different types of centering produce a total of 14 different lattices.

- P – Simple
- I – Body-centered
- F – Face-centered
- B – Base-centered (A, B, or C-centered)

- All crystalline materials can have their crystal structure described by one of these Bravais lattices.

Bravais Lattices

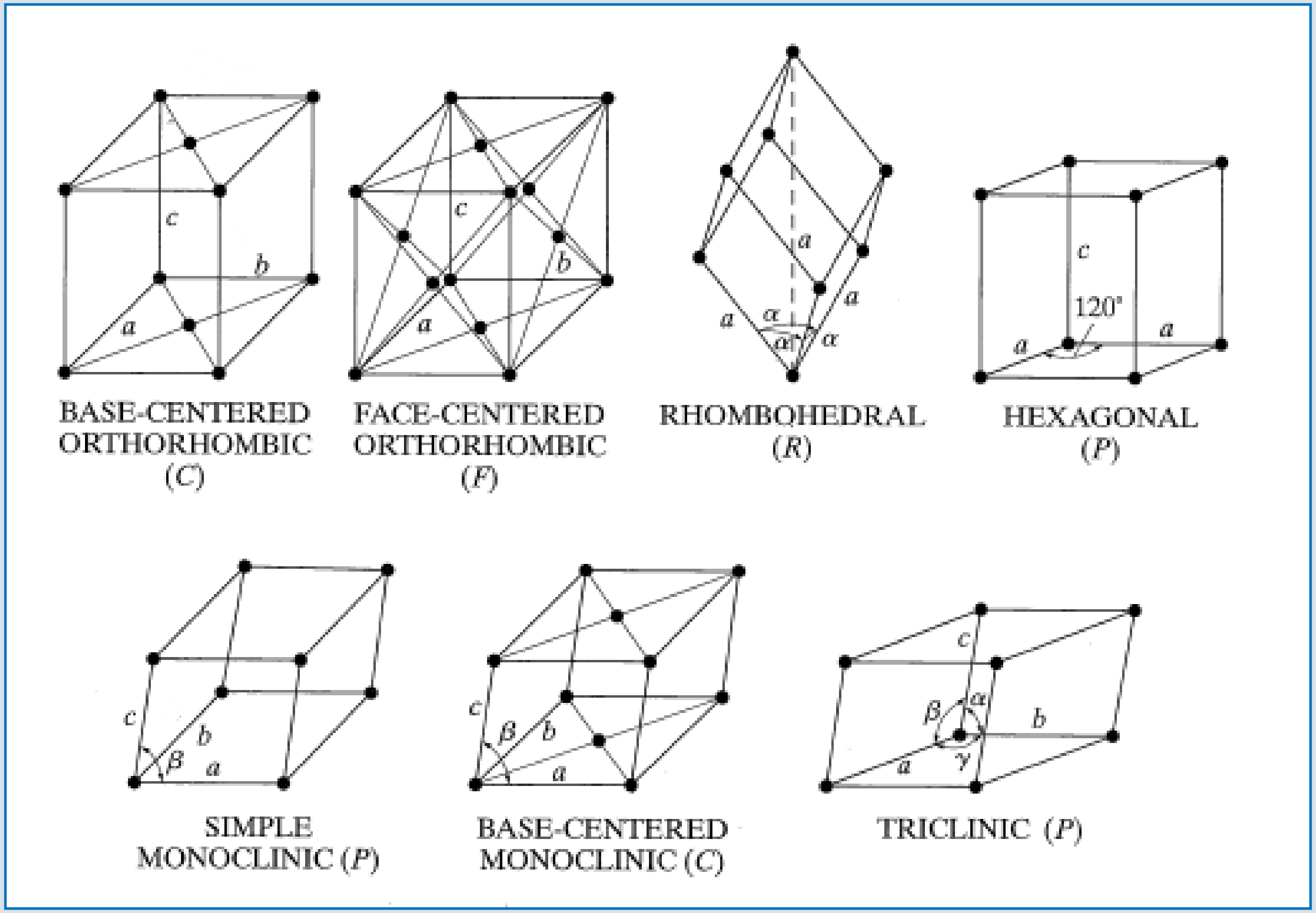
Courtesy: Charles Campana



Cullity, B.D. and Stock, S.R., 2001, Elements of X-Ray Diffraction, 3rd Ed., Addison-Wesley

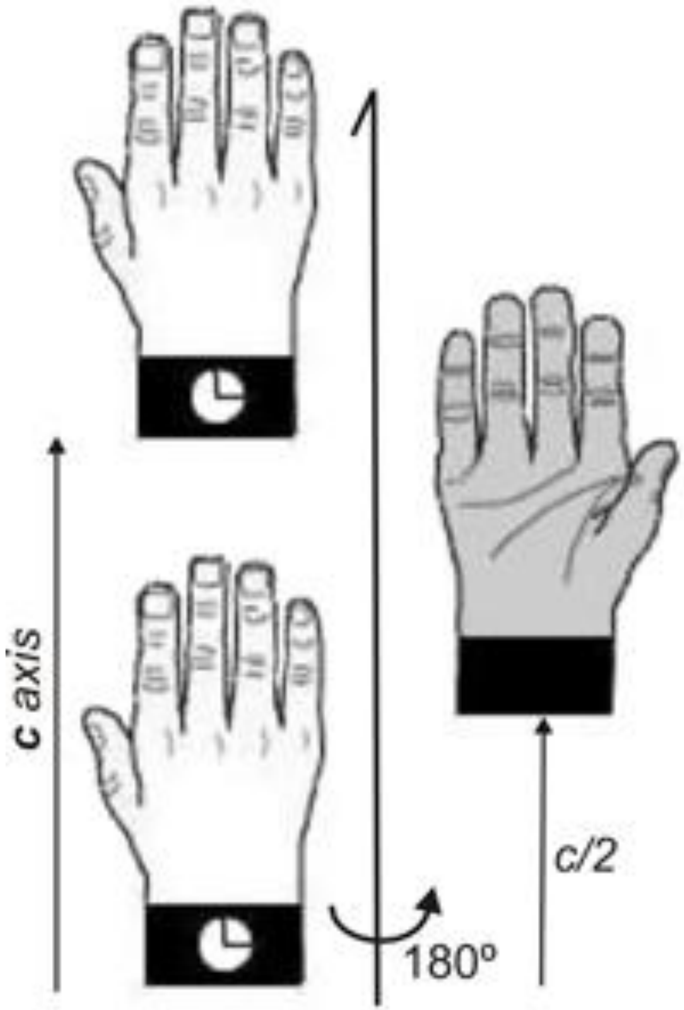
Bravais Lattices

Courtesy: Charles Campana



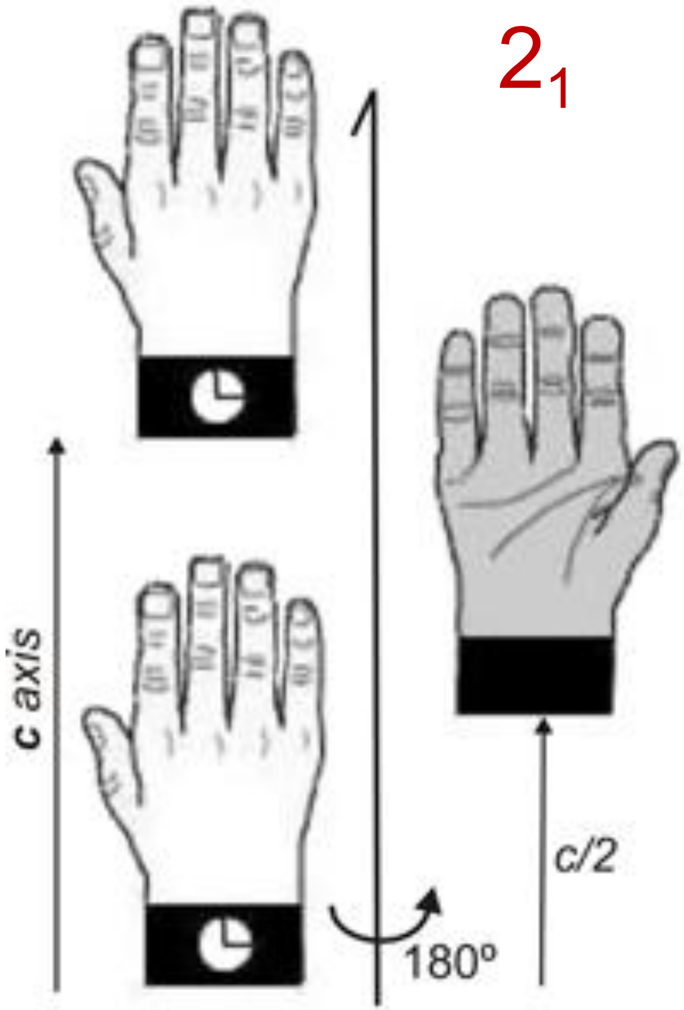
Cullity, B.D. and Stock, S.R., 2001, Elements of X-Ray Diffraction, 3rd Ed., Addison-Wesley

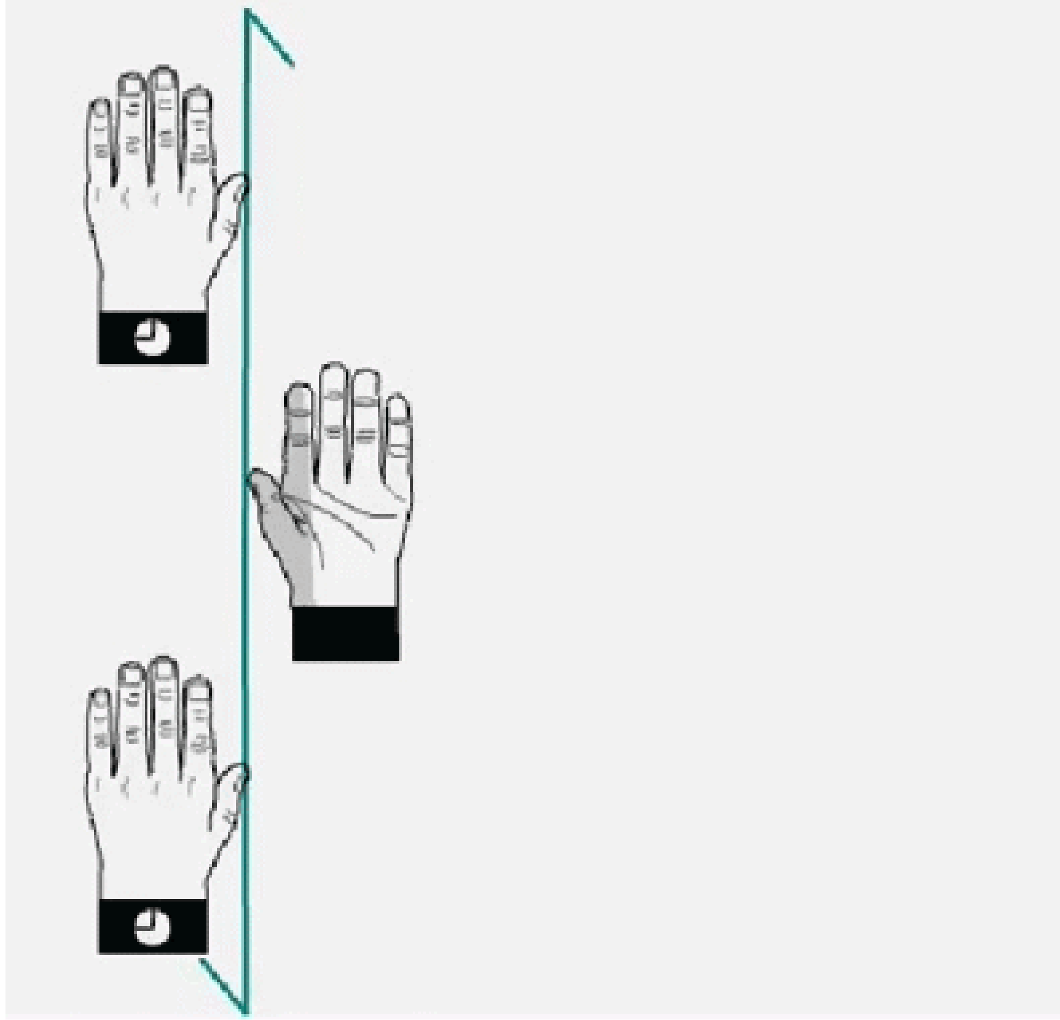
Screw Axes



Credit: [M. Kastner, T. Medlock & K. Brown, Univ. of Bucknell]

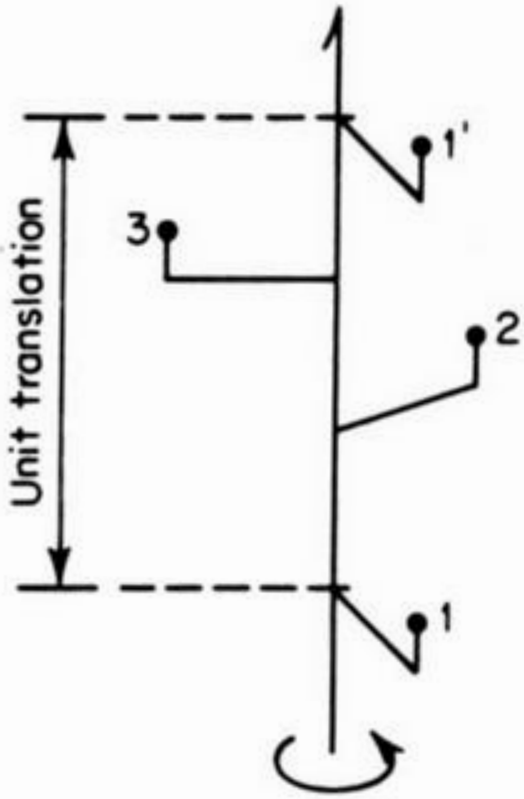
Two-fold Screw Axis



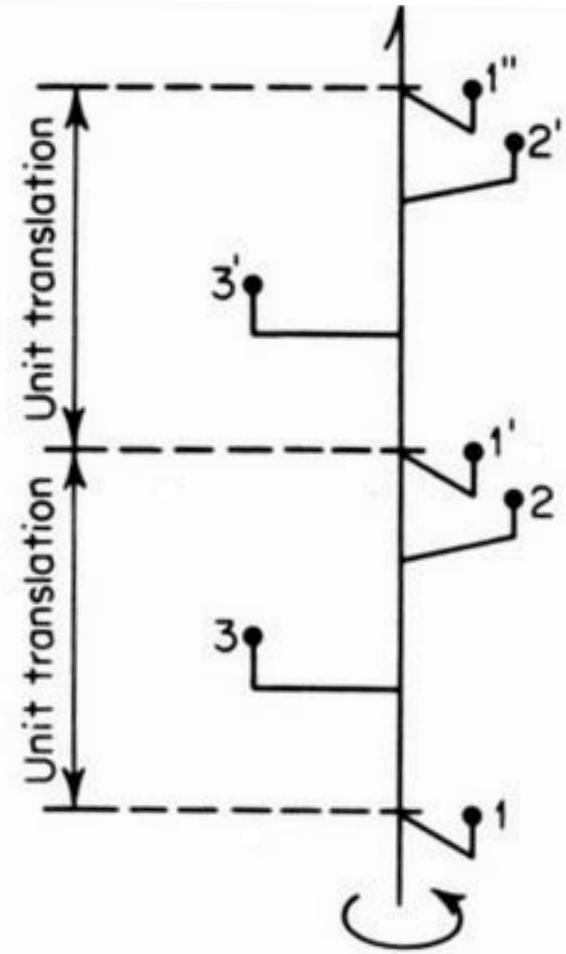


Credit: [M. Kastner, T. Medlock & K. Brown, Univ. of Bucknell]()

Three-fold Screw Axis



3_1



3_2

Source: G.H Stout & L.H. Jensen - X-Ray Structure Determination (A Practical Guide)

Screw Axes

Combination of translation and rotation

Designated as n_m (e.g. 2_1, 3_1, 3_2)

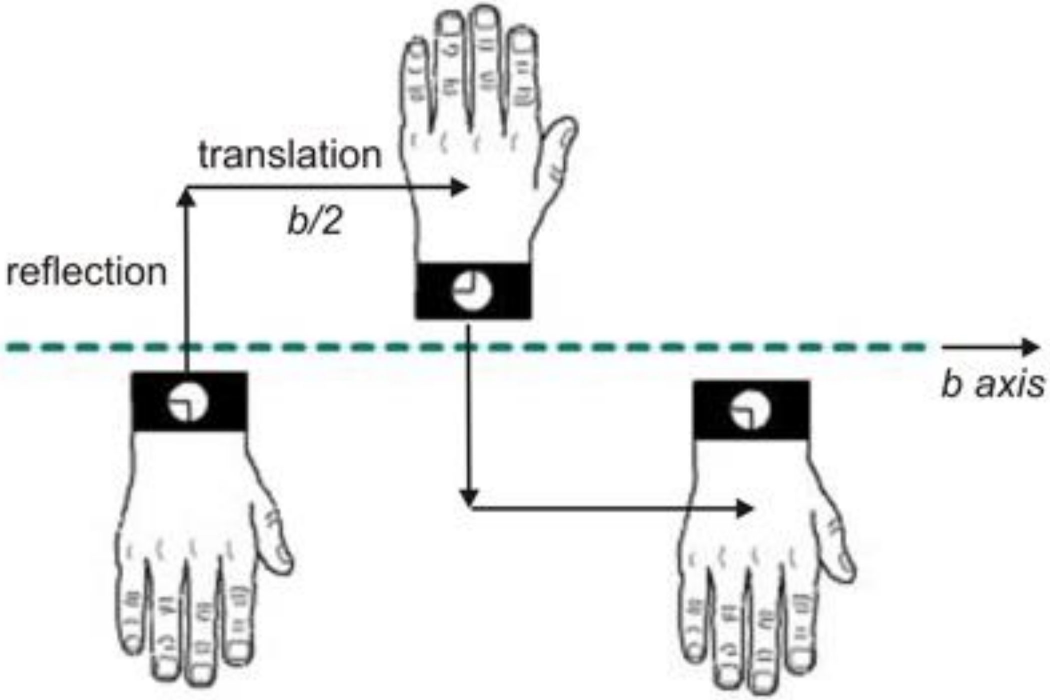
Rotation as $360^o/n$

Translation as m/n of a unit cell

Does not change handedness

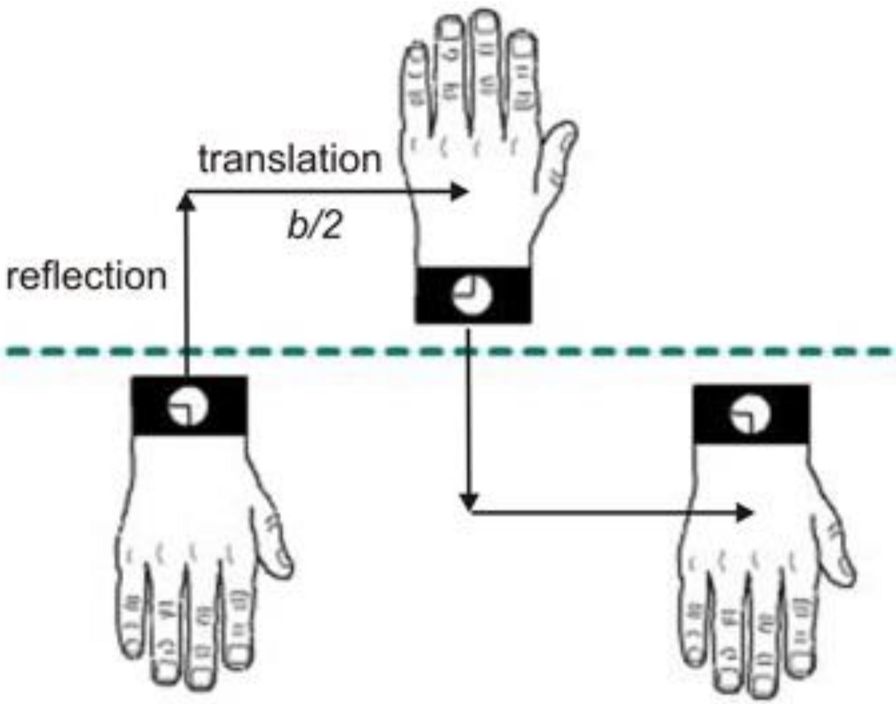
Courtesy: Paul Boyle

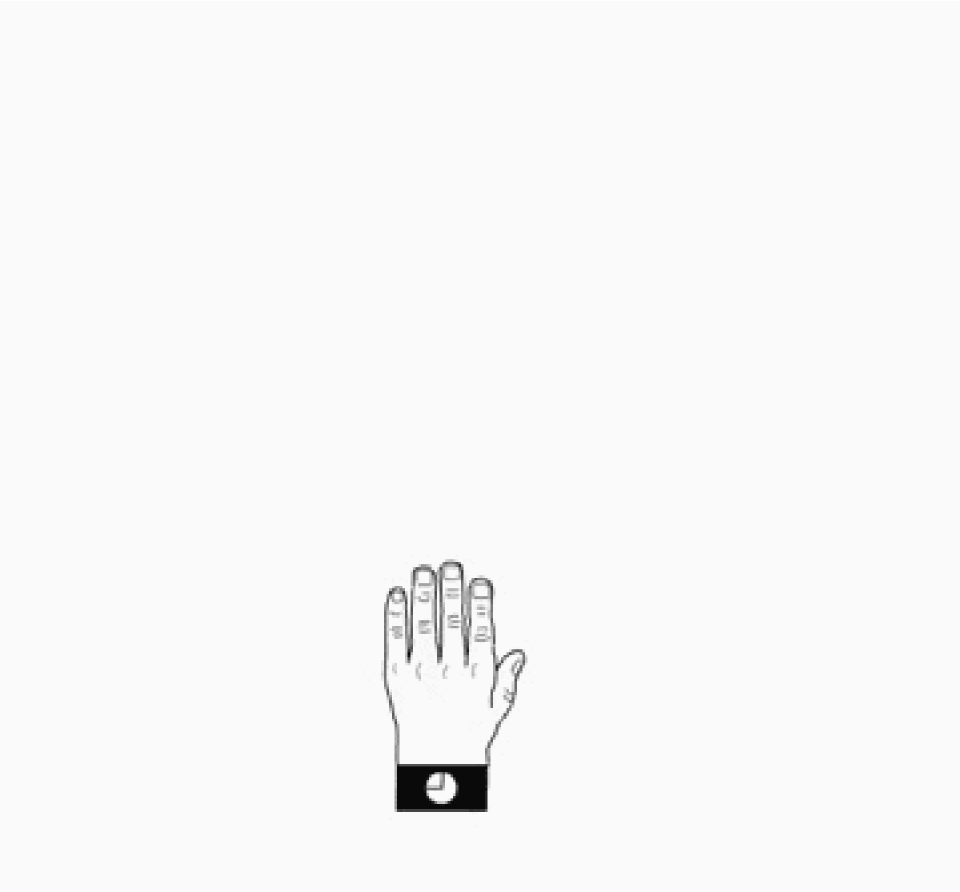
Glide Plane



Credit: [M. Kastner, T. Medlock & K. Brown, Univ. of Bucknell]

Glide Plane





Credit: [M. Kastner, T. Medlock & K. Brown, Univ. of Bucknell]

Glide Planes

Combination of translation and reflection

Designated as *a*, *b*, *c*, *n*, *d*

Translation as *a/2* (a-glide), *b/2* (b-glide)or *c/2* (c-glide)

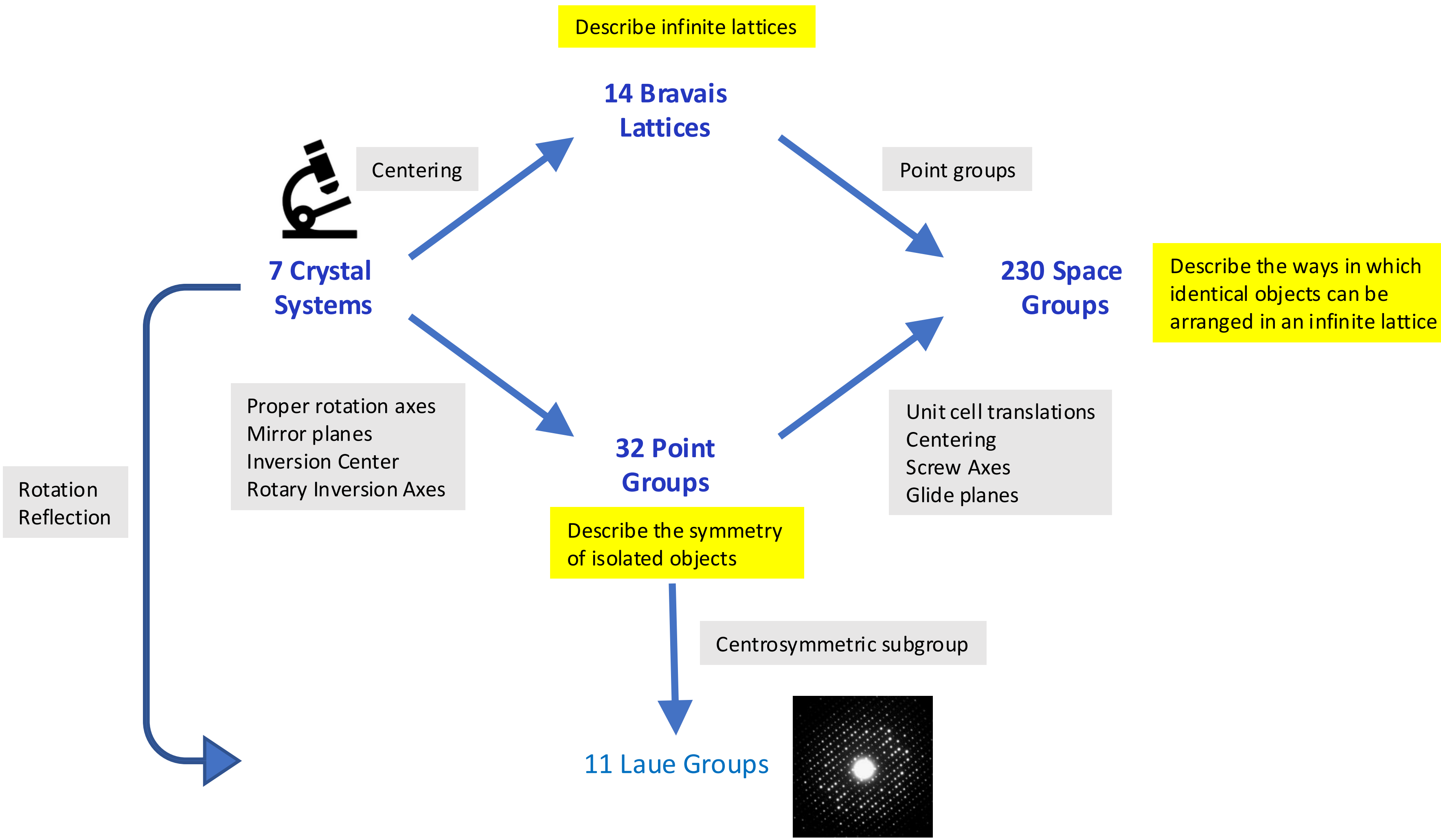
Changes handedness

Courtesy: Paul Boyle

n and *d* Glide Planes

- *n* glides translate along face diagonals, (a+b)/2, (a+c)/2, or (b+c)/2
- *d* glides only occur F and I centred lattices
- *d* glides translate along face diagonals at ¼ along each direction, *i.e.* (a+b)/4, (a+c)/4, or (b+c)/4

Courtesy: Paul Boyle


Describe infinite lattices
14 Bravais Lattices
Centering
Point groups
7 Crystal Systems
230 Space Groups
Describe the ways in which identical objects can be arranged in an infinite lattice
Proper rotation axes
Mirror planes
Inversion Center
Rotary Inversion Axes
Unit cell translations
Centering
Screw Axes
Glide planes
Rotation
Reflection
32 Point Groups
Describe the symmetry of isolated objects
Centrosymmetric subgroup
11 Laue Groups

Systems – Point Groups – Space Groups

System	Point Group	Space Group						
Triclinic	1	$P1$						
	$\bar{1}$	$P\bar{1}$						
Monoclinic	2	$P2$	$P2_1$	$C2$				
	m	Pm	Pc	Cm	Cc			
	$2/m$	$P2/m$	$P2_1/m$	$C2/m$	$P2/c$	$P2_1/c$	$C2/c$	
Orthorhombic	222	$P222$	$P222_1$	$P2_12_12$	$P2_12_12_1$	$C222_1$	$C222$	
		$F222$	$I222$	$I2_12_12_1$				
	$mm2$	$Pmm2$	$Pmc2_1$	$Pcc2$	$Pma2$	$Pca2_1$	$Pnc2$	
		$Pmn2_1$	$Pba2$	$Pna2_1$	$Pnn2$	$Cmm2$	$Cmc2_1$	
		$Ccc2$	$Amm2$	$Abm2$	$Ama2$	$Aba2$	$Fmm2$	
		$Fdd2$	$Imm2$	$Iba2$	$Ima2$			
	mmm	$Pmmm$	$Pnnn$	$Pccm$	$Pban$	$Pmma$	$Pnna$	
		$Pmna$	$Pcca$	$Pbam$	$Pccn$	$Pbcm$	$Pnnm$	
		$Pmmn$	$Pbcn$	$Pbca$	$Pnma$	$Cmcm$	$Cmca$	
		$Cmmm$	$Cccm$	$Cmma$	$Ccca$	$Fmmm$	$Fddd$	
		$Immm$	$Ibam$	$Ibca$	$Imma$			
Tetragonal	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	$P422$	$P42_12$	$P4_122$	$P4_12_12$	$P4_222$	$P4_22_12$	
		$P4_322$	$P4_32_12$	$I422$	$I4_122$			
	$4mm$	$P4mm$	$P4bm$	$P4_2cm$	$P4_2nm$	$P4cc$	$P4nc$	
		$P4_2mc$	$P4_2bc$	$I4mm$	$I4cm$	$I4_1md$	$I4_1cd$	
	$\bar{4}2m$	$P\bar{4}2m$	$P\bar{4}2c$	$P\bar{4}2_1m$	$P\bar{4}2_1c$	$P\bar{4}m2$	$P\bar{4}c2$	
		$P\bar{4}b2$	$P\bar{4}n2$	$I\bar{4}m2$	$I\bar{4}c2$	$I\bar{4}2m$	$I\bar{4}2d$	

	$4/mmm$	$P4/mmm$	$P4/mcc$	$P4/nbm$	$P4/nnc$	$P4/mbm$	$P4/mnc$
		$P4/nmm$	$P4/ncc$	$P4_2/mmc$	$P4_2/mcm$	$P4_2/nbc$	$P4_2/nnm$
		$P4_2/mbc$	$P4_2/mnm$	$P4_2/nmc$	$P4_2/ncm$	$I4/mmm$	$I4/mcm$
		$I4_1/amd$	$I4_1/acd$				
Trigonal/rhombohedral	3	$P3$	$P3_1$	$P3_2$	$R3$		
	$\bar{3}$	$P\bar{3}$	$R\bar{3}$				
	32	$P312$	$P321$	$P3_112$	$P3_121$	$P3_212$	$P3_221$
		$R32$					
	$3m$	$P3m1$	$P31m$	$P3c1$	$P31c$	$R3m$	$R3c$
	$\bar{3}m$	$P\bar{3}1m$	$P\bar{3}1c$	$P\bar{3}m1$	$P\bar{3}c1$	$R\bar{3}m$	$R\bar{3}c$
Hexagonal	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	$P622$	$P6_122$	$P6_522$	$P6_222$	$P6_422$	$P6_322$
	$6mm$	$P6mm$	$P6cc$	$P6_3cm$	$P6_3mc$		
	$\bar{6}m\bar{2}$	$P\bar{6}m2$	$P\bar{6}c2$	$P\bar{6}2m$	$P\bar{6}2c$		
	$6/mmm$	$P6/mmm$	$P6/mcc$	$P6_3/mcm$	$P6_3/mmc$		
Cubic	23	$P23$	$F23$	$I23$	$P2_13$	$I2_13$	
	$m3$	$Pm3$	$Pn3$	$Fm3$	$Fd3$	$Im3$	$Pa3$
		$Ia3$					
	432	$P432$	$P4_232$	$F432$	$F4_132$	$I432$	$P4_332$
		$P4_132$	$I4_132$				
	$\bar{4}3m$	$P\bar{4}3m$	$F\bar{4}3m$	$I\bar{4}3m$	$P\bar{4}3n$	$F\bar{4}3c$	$I\bar{4}3d$
	$m3m$	$Pm3m$	$Pn3n$	$Pm3n$	$Pn3m$	$Fm3m$	$Fm3c$
		$Fd3m$	$Fd3c$	$Im3m$	$Ia3d$		

[a]The 11 Laue symmetries are separated by horizontal lines.

Source: G.H Stout & L.H. Jensen - X-Ray Structure Determination (A Practical Guide)

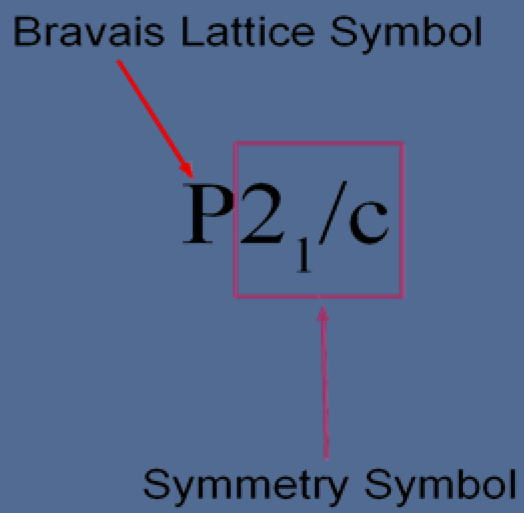
Interpretation of Space Group Symbols

- Space group symbols consist of several parts

  Bravais lattice type

  List of symbols denoting type and orientation of symmetry elements

- Must know the Crystal System in order to correctly interpret the space group symbol



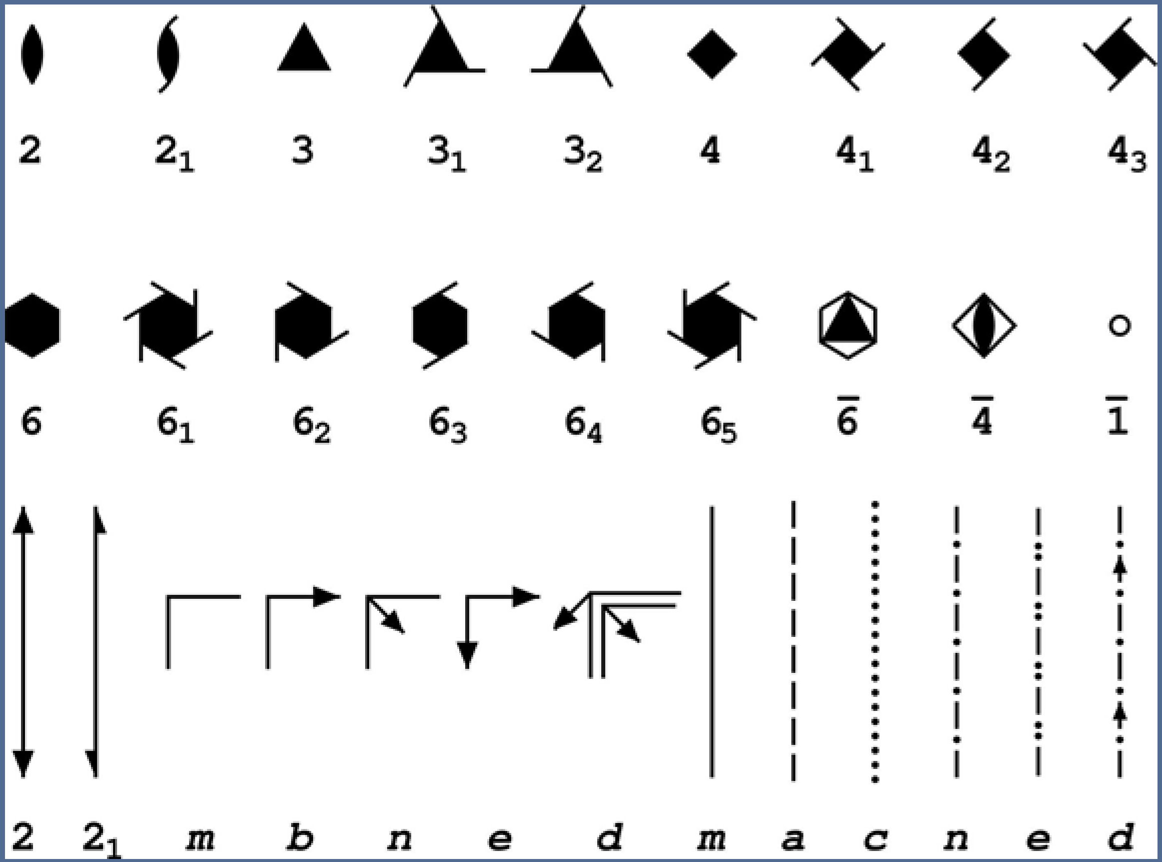
Courtesy: Paul Boyle

Representations of Symmetry

- Graphical Representation
  - Qualitative and Symbolic
  - Non-mathematical
  - Visually intuitive (for the most part)
- Equivalent positions (x,y,z)
  - Simple algebraic expressions
  - Good for humans
- Matrix Representation
  - Easy to transform
  - Numerically oriented
  - Good for computers
- ORTEP Representation
  - Compact notation of symmetry operation and unit cell translations
  - Related representations found in PLATON, XP, and CIF

Graphical Representation of Symmetry Elements

- Proper rotations depicted as symbols with the number of vertices which corresponds to n
- Screw axes have same symbol, but have “tails”



Courtesy: Paul Boyle

Space Groups and Crystallographic Symmetry

A tutorial
Version 1.55m

Fachschule Raumgruppe
Brandeis University

by

Jerry P. Jasinski (Keene state college)

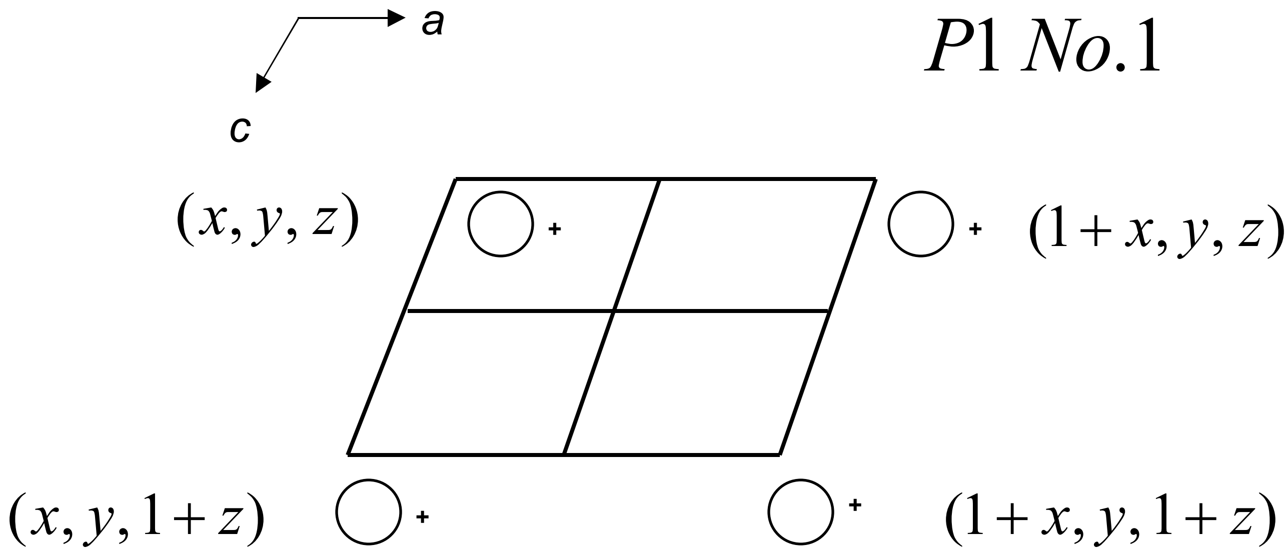
and

Bruce M. Foxman (Brandeis University)

(Mac-compatible version by Ian S. Batson, 2015)

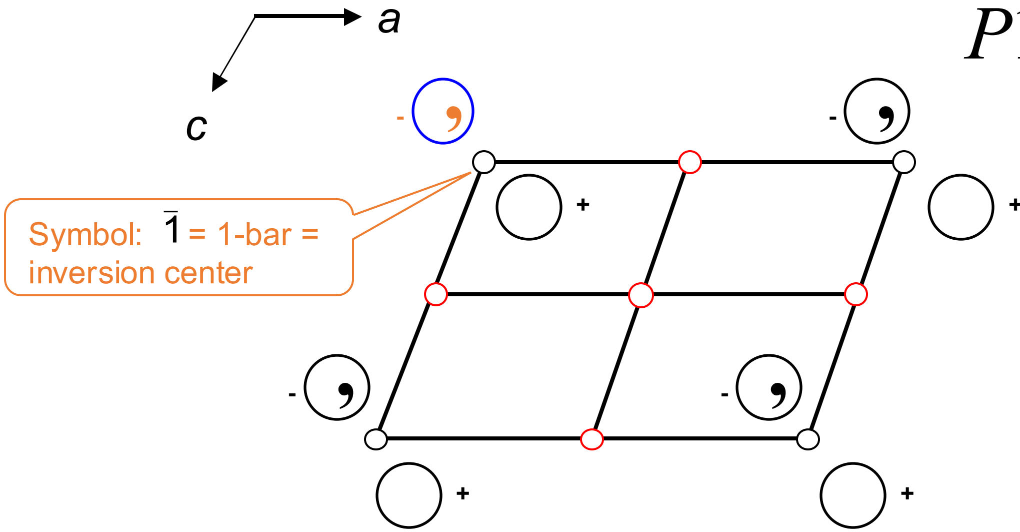
Support by the National science Foundation through grants DMR-0504000 (Brandeis university) and DMR-0303450 (Clemson University) is gratefully acknowledged

$P1$ $No.1$



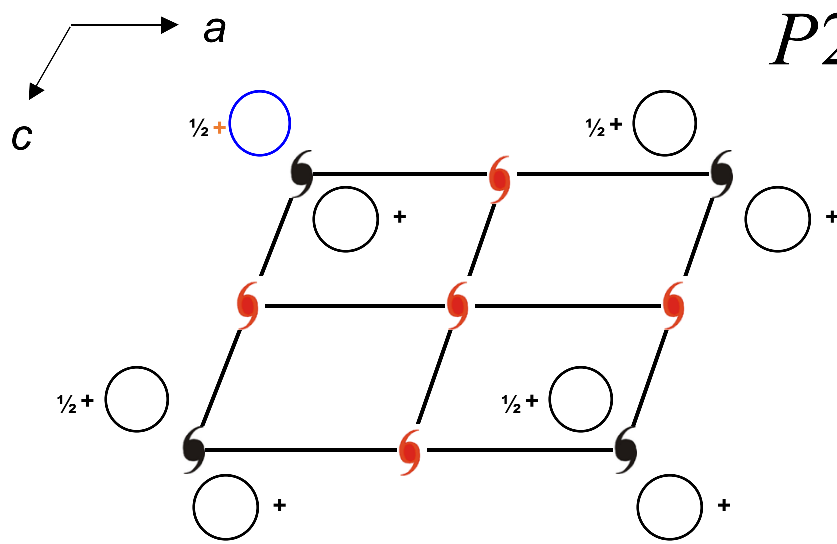
Z=1; (x, y, z)

$P\bar{1}$ *No.2*



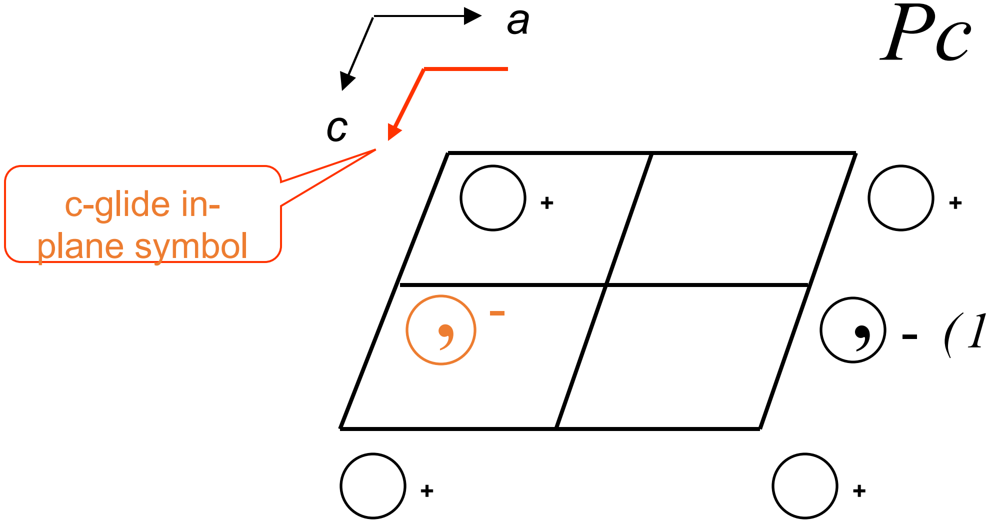
Z=2; (x, y, z) $(\bar{x}, \bar{y}, \bar{z})$

$P2_1$ No.4



$Z=2$; (x, y, z) $(\bar{x}, y+1/2, \bar{z})$

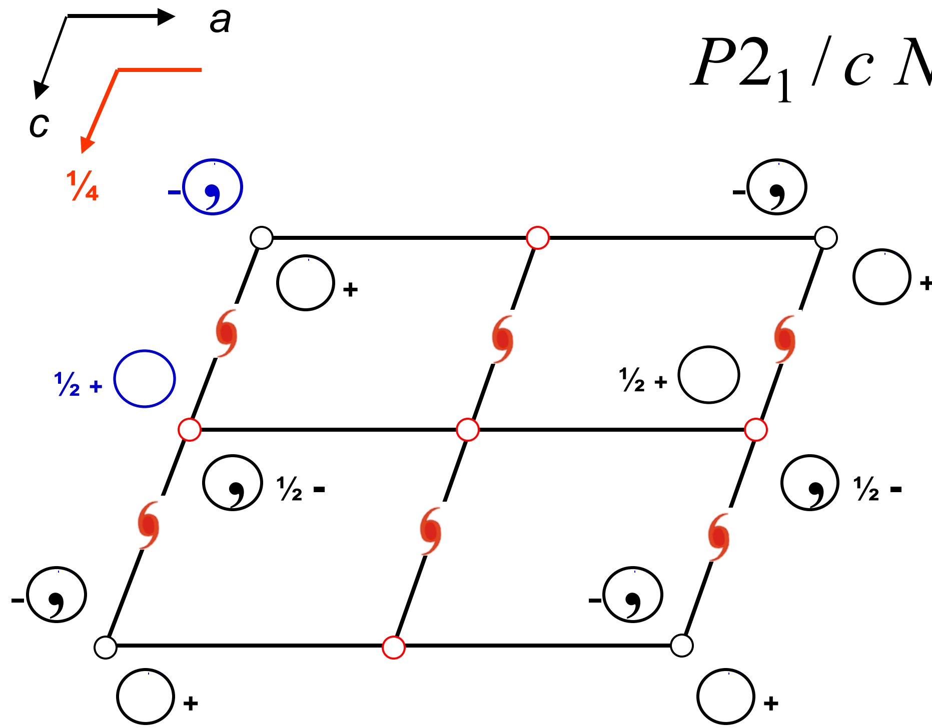
Pc No.7



$(1+x, \bar{y}, z+1/2)$

Z=2; (x, y, z) $(x, \bar{y}, z+1/2)$

$P2_1/c$ $No.14$

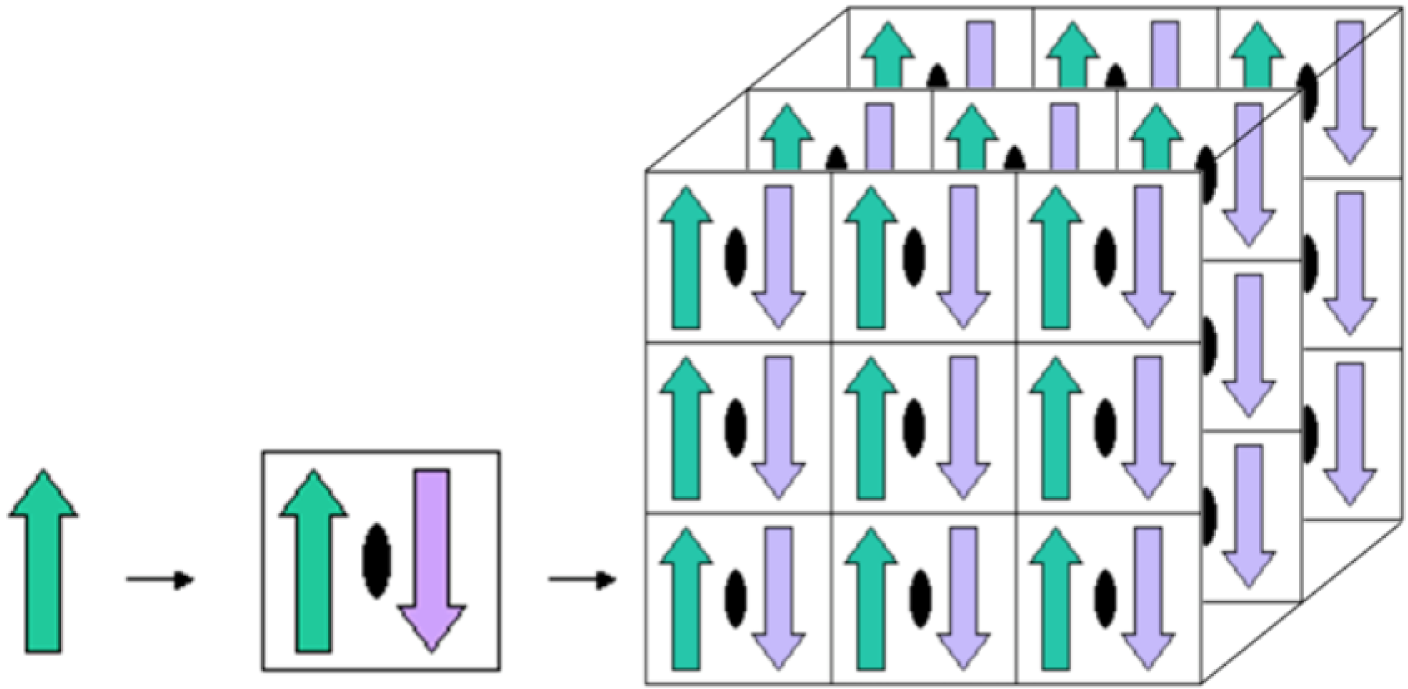


Z=4; (x, y, z) $(x, 1/2-y, 1/2+z)$ $(\bar{x}, \bar{y}, \bar{z})$ $(\bar{x}, 1/2+y, 1/2-z)$

The Asymmetric Unit

The Asymmetric Unit

The asymmetric unit is **the smallest portion of a crystal structure to which symmetry operations can be applied in order to generate the complete unit cell**



Asymmetric Unit

Unit Cell

Entire Crystal

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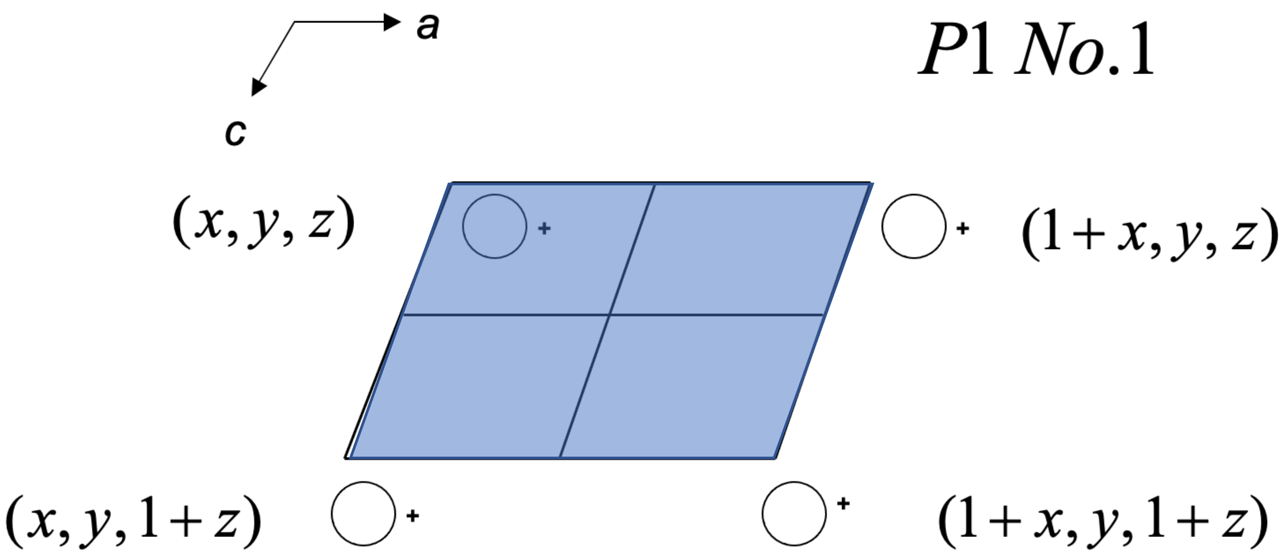
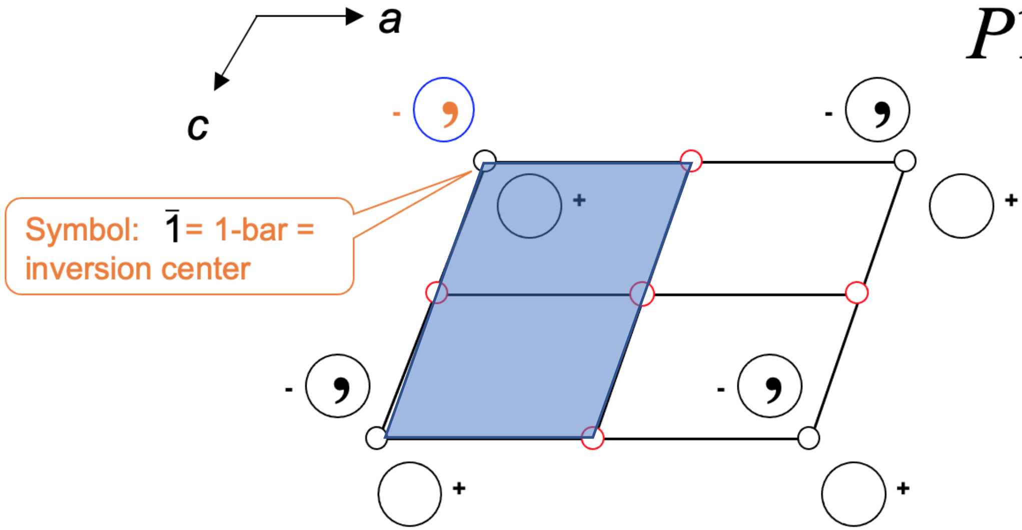
$P1$ $No.1$



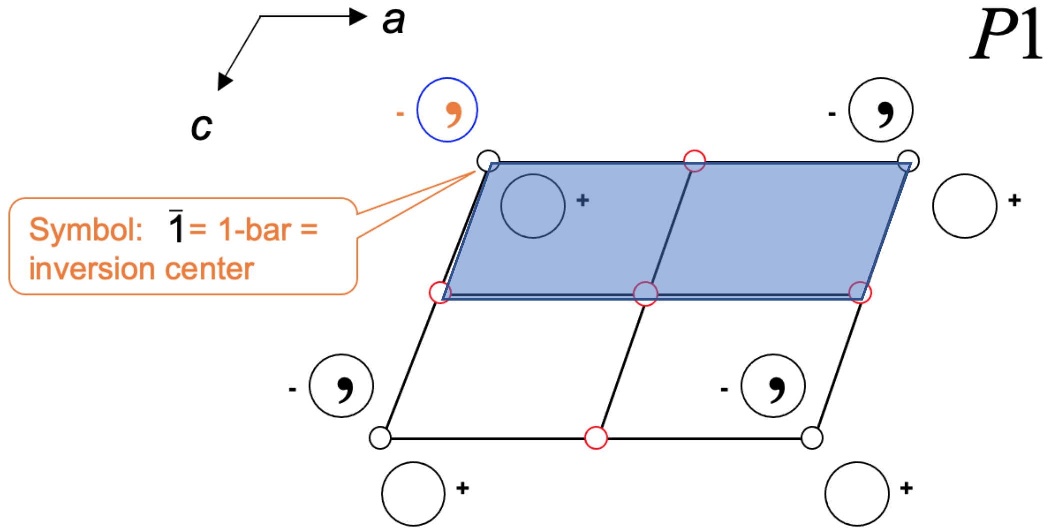
$Z=1$; (x, y, z)

$P\bar{1}$ No.2



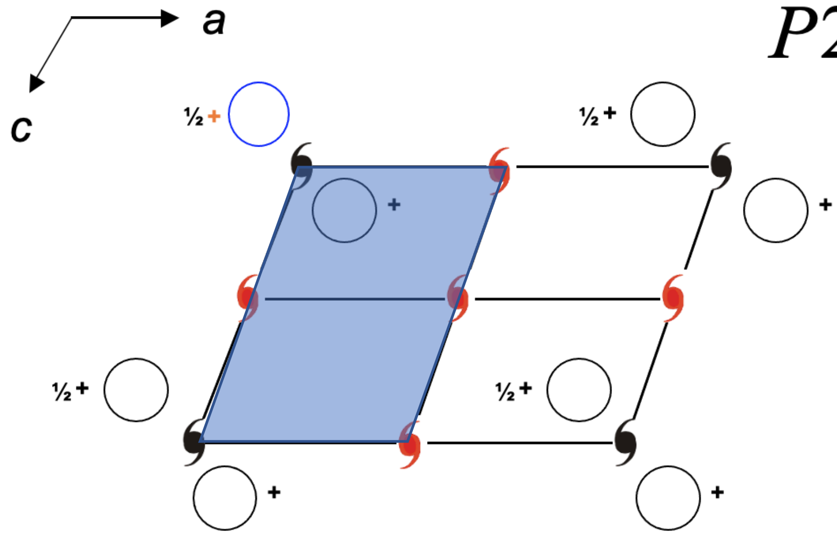
Z=2; (x, y, z) $(\bar{x}, \bar{y}, \bar{z})$

$P\bar{1}$ No.2



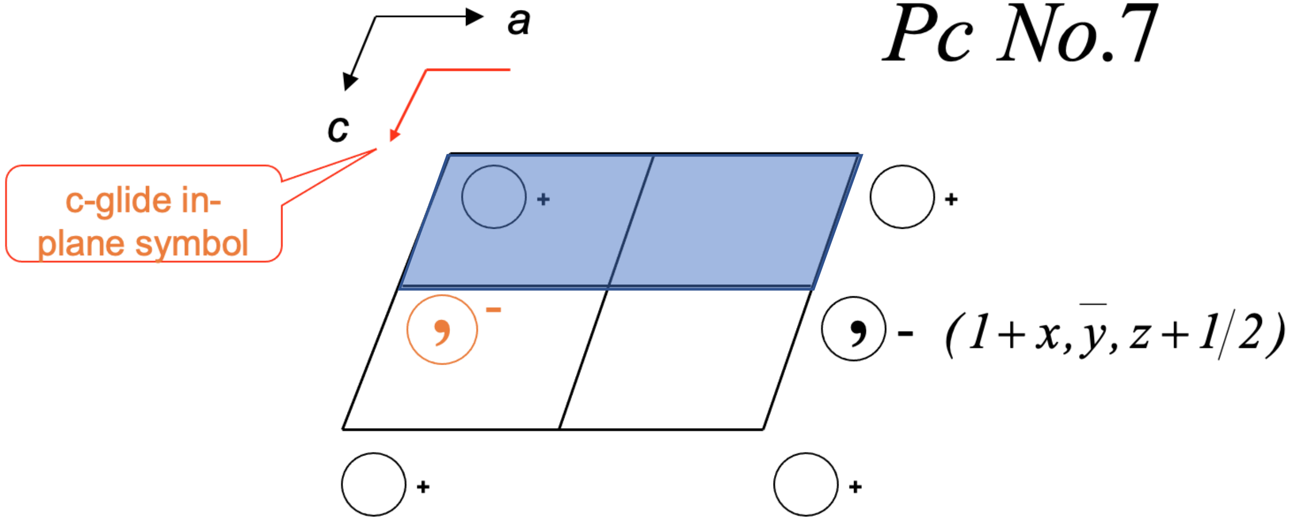
Z=2; (x, y, z) $(\bar{x}, \bar{y}, \bar{z})$

$P2_1$ No.4



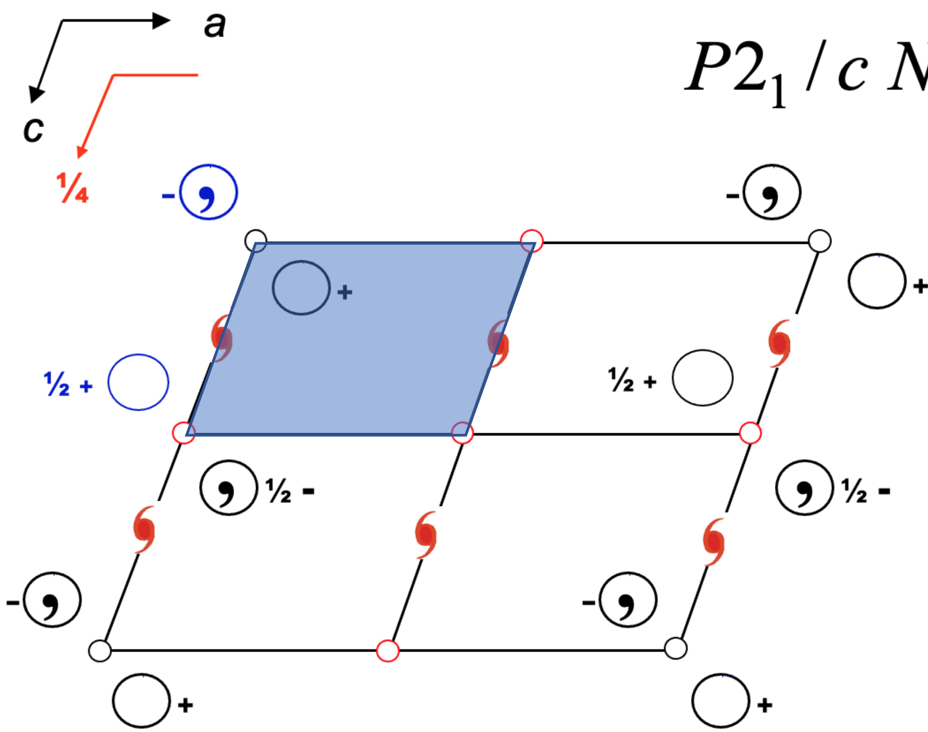
$$Z=2;\quad (x, y, z)\quad (\bar{x}, y+1/2, \bar{z})$$

Pc No.7



Z=2; (x, y, z) $(x, \bar{y}, z+1/2)$

$P2_1/c$ *No.*14



Z=4; (x, y, z) $(x, 1/2-y, 1/2+z)$ $(\bar{x}, \bar{y}, \bar{z})$ $(\bar{x}, 1/2+y, 1/2-z)$

Equivalent Position Representation

- Simple algebraic expressions
- Good for humans

- $P2_1/c$ example

(1) x, y, z

(2) $\bar{x}, y + ½, \bar{z} + ½$

(3) $\bar{x}, \bar{y}, \bar{z}$

(4) $x, \bar{y} + ½, z + ½$

Courtesy: Paul Boyle

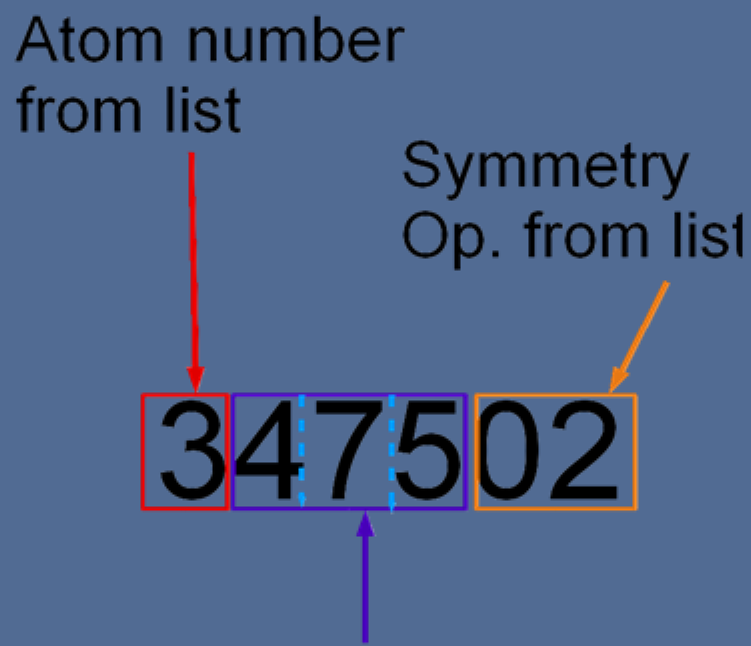
Matrix Representation of Symmetry

- Symmetry operator can be partitioned into a rotational part and a translational part
- Rotations can be described as simple 3x3 matrices. Matrix elements are either 1, 0, or -1
- Translations described as 3x1 matrix
- v' = Rv + t where v = [x,y,z]
- For example, in $P2_1/c$ the equivalent position: $\bar{x}$, y + ½, $\bar{z}$ + ½ looks like this in matrix representation:

$$\begin{bmatrix} x' \\ y' \\ z' \end{bmatrix} = \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} + \begin{bmatrix} 0 \\ 1/2 \\ 1/2 \end{bmatrix}$$

ORTEP Symmetry Representation

- Early days of computing memory was expensive
- Needed compact way to depict symmetry equivalent atomic positions including translations
- Avoid negative numbers in unit cell translations
- “5” is the new “0”
- Example: 347502
- Depends on lists of atoms and symmetry operators elsewhere in the file or the program



$T_x = 5 + (-1) = 4$

$T_y = 5 + 2 = 7$

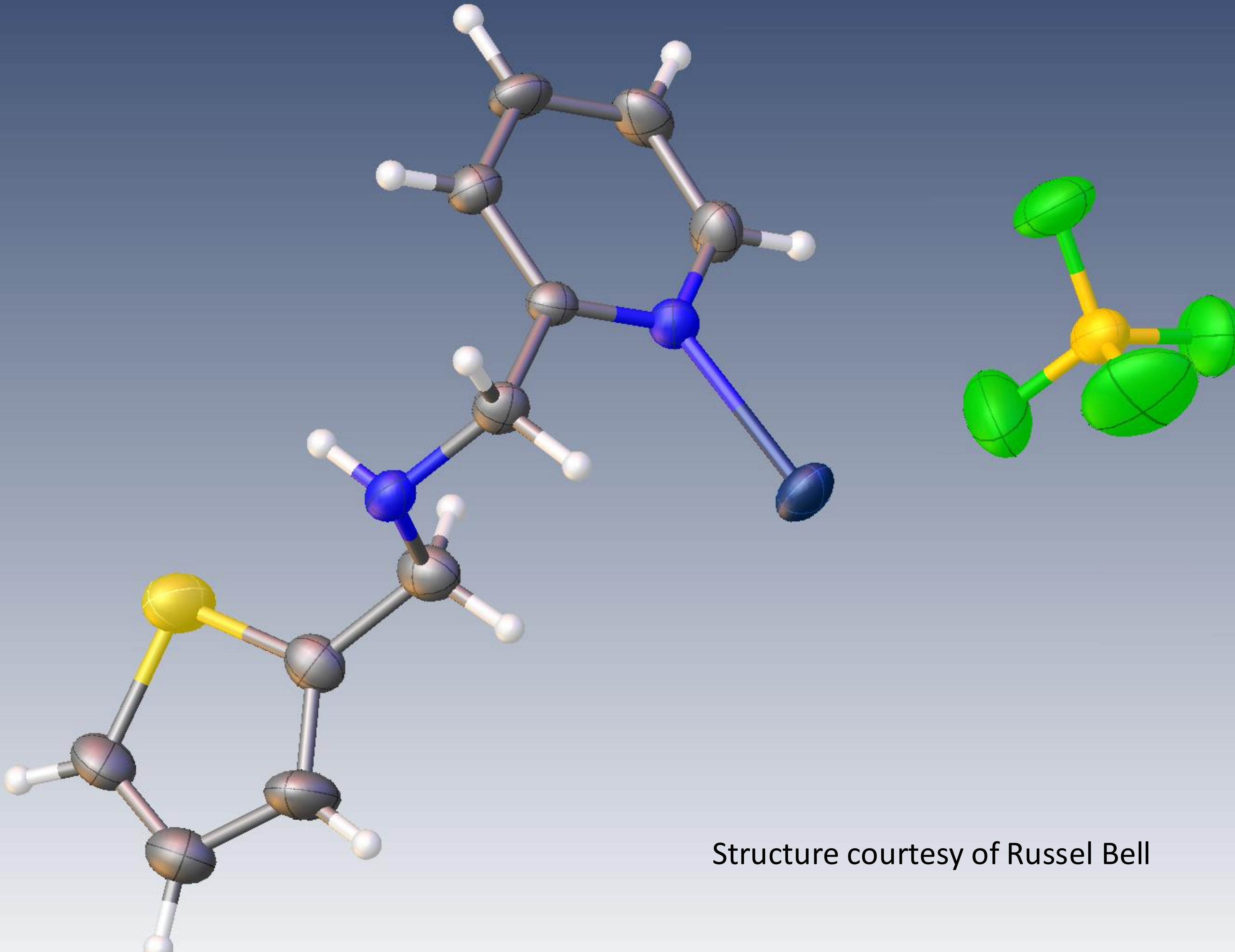
$T_z = 5 + 0 = 5$

Courtesy: Paul Boyle

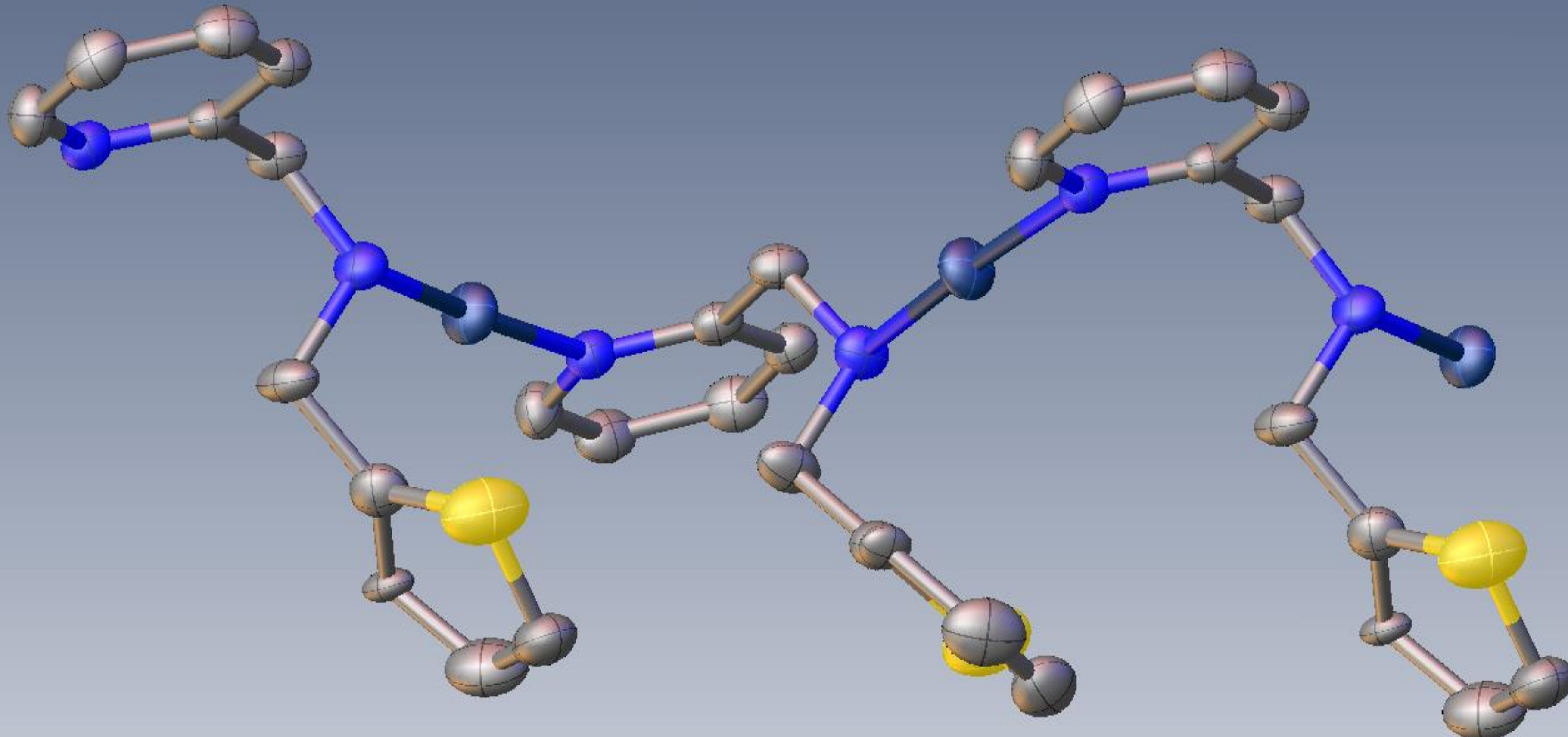
PLATON, XP, and CIF Symmetry Codes

- Derived from original ORTEP scheme, maintains compactness
- PLATON: [sym_op][$T_x T_y T_z$].[residue]
  - *e.g.* 2565.01
- XP: [sym_op][$T_x T_y T_z$]
  - *e.g.* 2565
- CIF: [sym_op]_[$T_x T_y T_z$]
  - *e.g.* 2_565
- SHELX & OLEX combine the symmetry operator and translation

Courtesy: Paul Boyle



Structure courtesy of Russel Bell



Structure courtesy of Russel Bell

Small Molecule Example – a14
Generation of CIF Files

```
_space_group_crystal_system          'monoclinic'
_space_group_IT_number               14
_space_group_name_H-M_alt            'P 1 21/c 1'
_space_group_name_Hall               '-P 2ybc'
loop_
  _space_group_symop_operation_xyz
 'x, y, z'
 '-x, y+1/2, -z+1/2'
 '-x, -y, -z'
 'x, -y-1/2, z-1/2'
```

```
;
loop_
  _geom_bond_atom_site_label_1
  _geom_bond_atom_site_label_2
  _geom_bond_distance
  _geom_bond_site_symmetry_2
  _geom_bond_publ_flag
 Ag01 N005 2.222(3) . ?
 Ag01 N006 2.201(3) 4_575 ?
 S002 C00H 1.720(4) . ?
 S002 C00I 1.638(5) . ?
 F003 B00K 1.449(5) . ?
 F004 B00K 1.364(5) . ?
 N005 H005 0.9900 . ?
 N005 C00A 1.454(5) . ?
 N005 C00F 1.452(5) . ?
 N006 C00B 1.444(5) . ?
 N006 C00D 1.369(5) . ?
```

- All of the crystallographic journals and most of the major chemical journals have now adopted the CIF (Crystal Information Format) for depositing and publishing crystallographic data.
- Most commercial and public-domain structure refinement programs now generate CIF files for validation and deposition.

SHELX output

```
Operators for generating equivalent atoms:
$1   x, -y+3/2, z+1/2
$2   x, -y+3/2, z-1/2


Bond lengths and angles

Ag01 -          Distance        Angles
N006_$2   2.2006 (0.0030)
N005      2.2218 (0.0030)  175.29 (0.11)
                Ag01             N006_$2
```

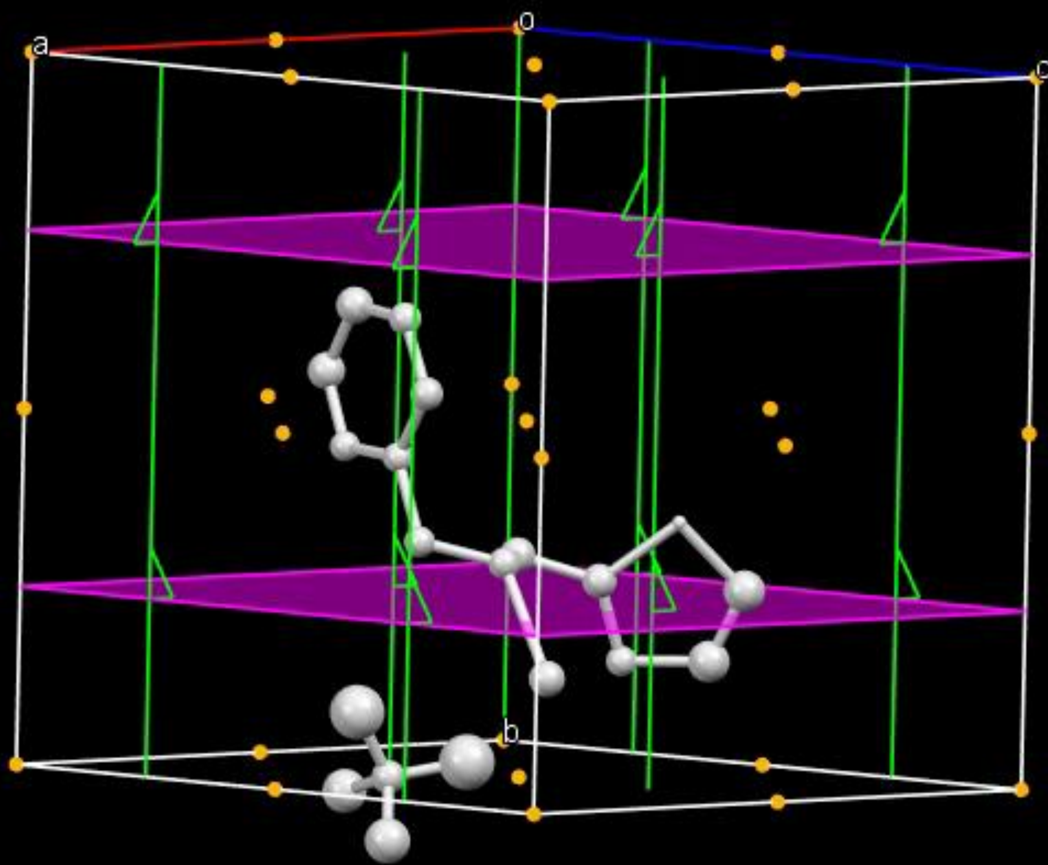
Symm operator: X, –Y – 1/2, Z – 1/2
Trans (575): X, –Y – 1/2 +2, Z – 1/2
Result: X, –Y + 3/2, Z – 1/2

Olex Tables for Publication

Table 4 Bond Lengths for a14.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Ag01	N005	2.222(3)	C008	C00H	1.442(5)
Ag01	N006[1]	2.201(3)	C008	C00J	1.434(6)
S002	C00H	1.720(4)	F009	B00K	1.337(5)
S002	C00I	1.638(5)	C00A	C00B	1.521(5)
F003	B00K	1.449(5)	C00B	C00C	1.428(5)
F004	B00K	1.364(5)	C00C	C00G	1.396(5)
N005	C00A	1.454(5)	C00D	C00E	1.388(5)
N005	C00F	1.452(5)	C00E	C00G	1.491(6)
N006	C00B	1.444(5)	C00F	C00H	1.481(6)
N006	C00D	1.369(5)	C00I	C00J	1.353(6)
F007	B00K	1.329(6)			

[1] X, 3/2 - Y, -1/2 + Z



Mercury view

Courtesy: Jim Britten

International Tables for Crystallography

- Information on crystallographic symmetry and related topics has been codified and published in the *International Tables for Crystallography*
- Originally published in 1935, the work has been revised and expanded to include all sorts of topics relevant to X-ray Crystallography
- We will only concern ourselves with material related to space groups (Volume A)

Courtesy of Paul Boyle

Using the International Tables for X-ray Crystallography

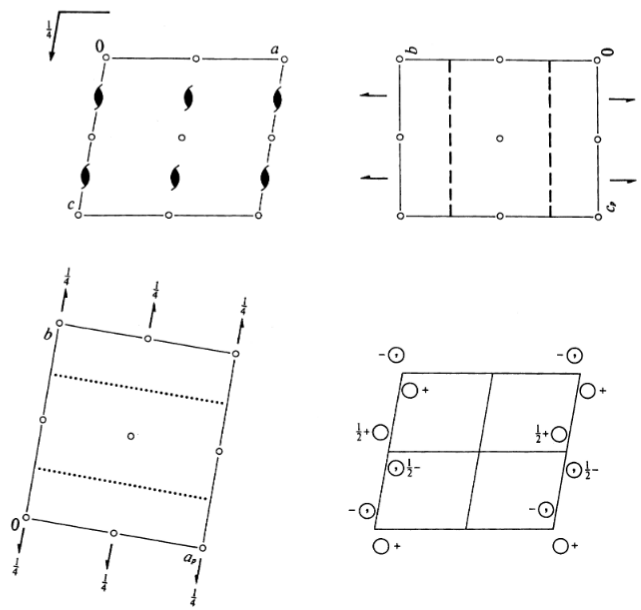
- The *International Tables* (IT) contain information on all space groups
- Most common information used by crystallographers:
  - Graphical depictions
  - Equivalent positions
  - Special positions and site symmetries
  - Systematic absence conditions

Courtesy of Paul Boyle

Example of International Tables Example ($P2_1/c$)

$P2_1/c$	C_{2h}^5	$2/m$	Monoclinic
No. 14	$P\,1\,2_1/c\,1$		Patterson symmetry $P\,1\,2/m\,1$

UNIQUE AXIS b, CELL CHOICE 1



Origin at $\bar{1}$

Asymmetric unit $0 \le x \le 1;\quad 0 \le y \le \frac{1}{4};\quad 0 \le z \le 1$

Symmetry operations

(1) 1 (2) $2(0,\frac{1}{2},0)\quad 0,y,\frac{1}{4}$ (3) $\bar{1}\quad 0,0,0$ (4) $c\quad x,\frac{1}{4},z$

Example of International Tables Example ($P2_1/c$)

CONTINUED No. 14 $P2_1/c$

Generators selected (1); $t(1,0,0)$; $t(0,1,0)$; $t(0,0,1)$; (2); (3)

Positions

Multiplicity, Wyckoff letter, Site symmetry			Coordinates				Reflection conditions
							General:
4	e	1	(1) x,y,z	(2) $\bar{x},y+\frac{1}{2},\bar{z}+\frac{1}{2}$	(3) $\bar{x},\bar{y},\bar{z}$	(4) $x,\bar{y}+\frac{1}{2},z+\frac{1}{2}$	$h0l$: $l=2n$ $0k0$: $k=2n$ $00l$: $l=2n$
							Special: as above, plus
2	d	$\bar{1}$	$\frac{1}{2},0,\frac{1}{2}$	$\frac{1}{2},\frac{1}{2},0$			hkl : $k+l=2n$
2	c	$\bar{1}$	$0,0,\frac{1}{2}$	$0,\frac{1}{2},0$			hkl : $k+l=2n$
2	b	$\bar{1}$	$\frac{1}{2},0,0$	$\frac{1}{2},\frac{1}{2},\frac{1}{2}$			hkl : $k+l=2n$
2	a	$\bar{1}$	$0,0,0$	$0,\frac{1}{2},\frac{1}{2}$			hkl : $k+l=2n$

Symmetry of special projections

Along [001] $p2gm$
$\mathbf{a}'=\mathbf{a}_p$ $\mathbf{b}'=\mathbf{b}$
Origin at $0,0,z$

Along [100] $p2gg$
$\mathbf{a}'=\mathbf{b}$ $\mathbf{b}'=\mathbf{c}_p$
Origin at $x,0,0$

Along [010] $p2$
$\mathbf{a}'=\frac{1}{2}\mathbf{c}$ $\mathbf{b}'=\mathbf{a}$
Origin at $0,y,0$

Maximal non-isomorphic subgroups

I [2] $P1c1$ (Pc, 7) 1; 4
[2] $P12_11$ ($P2_1$, 4) 1; 2
[2] $P\bar{1}$ (2) 1; 3

IIa none

IIb none

Maximal isomorphic subgroups of lowest index

IIc [2] $P12_1/c1$ ($\mathbf{a}'=2\mathbf{a}$ or $\mathbf{a}'=2\mathbf{a},\mathbf{c}'=2\mathbf{a}+\mathbf{c}$) ($P2_1/c$, 14); [3] $P12_1/c1$ ($\mathbf{b}'=3\mathbf{b}$) ($P2_1/c$, 14)

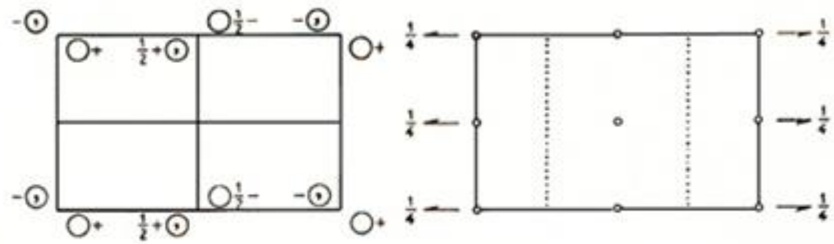
Minimal non-isomorphic supergroups

I [2] $Pnna$ (52); [2] $Pmna$ (53); [2] $Pcca$ (54); [2] $Pbam$ (55); [2] $Pccn$ (56); [2] $Pbcm$ (57); [2] $Pnnm$ (58); [2] $Pbcn$ (60); [2] $Pbca$ (61); [2] $Pnma$ (62); [2] $Cmce$ (64)

II [2] $A12/m1$ ($C2/m$, 12); [2] $C12/c1$ ($C2/c$, 15); [2] $I12/c1$ ($C2/c$, 15); [2] $P12_1/m1$ ($\mathbf{c}'=\frac{1}{2}\mathbf{c}$) ($P2_1/m$, 11); [2] $P12/c1$ ($\mathbf{b}'=\frac{1}{2}\mathbf{b}$) ($P2/c$, 13)

Example of International Tables Example ($P2_1/c$)

Monoclinic 2/*m* $P\,1\,2_1/c\,1$ No. 14 $P\,2_1/c$ C_{2h}^5



Origin at $\bar{1}$; unique axis *b* 2ND SETTING

Number of positions, Wyckoff notation, and point symmetry			Co-ordinates of equivalent positions	Conditions limiting possible reflections
				General:
4	*e*	1	$x,y,z;\ \bar{x},\bar{y},\bar{z};\ \bar{x},\frac{1}{2}+y,\frac{1}{2}-z;\ x,\frac{1}{2}-y,\frac{1}{2}+z.$	*hkl*: No conditions *h0l*: $l=2n$ *0k0*: $k=2n$
				Special: as above, plus
2	*d*	$\bar{1}$	$\frac{1}{2},0,\frac{1}{2};\ \frac{1}{2},\frac{1}{2},0.$	*hkl*: $k+l=2n$
2	*c*	$\bar{1}$	$0,0,\frac{1}{2};\ 0,\frac{1}{2},0.$	
2	*b*	$\bar{1}$	$\frac{1}{2},0,0;\ \frac{1}{2},\frac{1}{2},\frac{1}{2}.$	
2	*a*	$\bar{1}$	$0,0,0;\ 0,\frac{1}{2},\frac{1}{2}.$	

Symmetry of special projections

(001) *pgm*; $a'=a,\ b'=b$ (100) *pgg*; $b'=b,\ c'=c$ (010) *p*2; $c'=c/2,\ a'=a$

- **Thank you**