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Space Groups: A primer on topics significant for powder diffraction

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Outline

This talk covers topics important for Rietveld analysis, particularly of inorganic materials, and assumes knowledge of symmetry operations and space groups, as covered in any crystallography textbook.

- Space group naming
  - Nomenclature
- Common tripping hazards
  - Rhombohedral vs. hexagonal settings
  - Origin 1 vs. Origin 2
  - Inputting space groups to GSAS
- Phase transformations
  - Terminology & relation to symmetry
  - Subgroups & Supergroups
  - Systematic absences

Understanding Space Group Symbols

Traditionally we use **short** Hermann-Mauguin space group names ($P2_1/c$), as opposed to full H-M names ($P\ 1\ 2_1/c\ 1$).
- Full name lists symmetry along *a* (1), *b* (2_1 & *c*-glide _|_ *b*) and *c* (1)
- Short name lists minimum symmetry (*b*-axis is implied)

Decoding Hermann-Mauguin space group names:
- 1st letter: Centering (P, A, B, C, F, I, R)
- Space group names list symmetry elements along the unique axes
  - In short names, the number of unique axes depends on unit cell type

Unique axes in space group names (1)

- Triclinic
  - Only 2 choices: *P*1 & *P*-1

  Note that non-standard settings (e.g. *C*–1,…) are occasionally used.

Recognize by presence of no more than -1

- Monoclinic
  - (*b* unique, $\beta \neq 90°$)
  - Names: Ω*y*, Ω = *P* or *C*
  - *y* specifies symmetry along *b*
    - *y*=2, 2_1, *m*, *c* or *2/m*…

  Note that older (or non-standard) usage can have *a*- or *c*-unique

Recognize by presence of no more than one 2-fold or glide

- Orthorhombic
  - Ω*xyz*, Ω = *P, A, C, F, I*
    - x,y,z *specifies symmetry along* a, b & c
    - x,y,z= 2, 2_1, *m, n, c, d, 2/m*…

Recognize by presence of no more than 2-fold or glides on 3 axes

- Tetragonal
  - Ω*xyz*, Ω = *P, I*
    - x,y,z *specifies symmetry along c,* a, & a+b
    - x = 4, -4, 4_1, 4_2, 4_3, *4/m*…
    - *y,z = m, c or* 2, 2_1…

Recognize by presence of a 4-fold on 1st axis

Unique axes in space group names (2)

- Trigonal/Rhombohedral
  - Trigonal: hexagonal cell
  - Rhombohedral: two possible cells
    - *Triply centered hexagonal cell*
    - *Primitive rhombohedral cell (a=b=c α=β=γ)*
  - Ωxyz, Ω = *P*, *R*
    - x,y,z *specifies symmetry along c*, a, *&* a+b
    - x = *3, -3, 3_1, 3_2*
    - y,z = *m, c, 2, 2_1…*

Recognize by presence of 3-fold on 1st axis

- Hexagonal
  - P*xyz*
    - x,y,z *specifies symmetry along c*, a, *&* a+b
    - x = *6, -6, 6_1, 6_2, 6_3, 6_4, 6_5, 6/m*
    - y,z = *m, c, 2, 2/m, 2/c*

Recognize by presence of 6-fold on 1st axis

- Cubic
  - P*xyz*, I*xyz* or F*xyz*
    - x,y,z *specifies symmetry along* a, a+b+c *&* a+b
    - x = *2, 2_1, m, n, a, d, 4, -4, 4_1, 4_2, 4_3, 2_1/a*
    - y = *3 or –3*
    - z = *2, m, n, c, d*

Recognize by presence of 3-fold on 2nd axis combined with symmetry on other 2 axes

Deducing cell type by inspection of H-M name

The cell type can be discerned from a space group name from simple rules:

- *P*x3y or *P*x-3y: cubic (y can be missing)
- *P*4xy, *P*-4xy, $P4_n$xy: tetragonal
- *P*6xy, *P*-6xy, $P6_n$xy: hexagonal
- *P*3xy, *P*-3xy, $P3_n$xy: trigonal
- *R*3xy, R-3xy: rhombohedral
- Ωxyz (xyz not 3,4 or 6-fold): orthorhombic
- Ωx (other than *P*1 or *P*-1): monoclinic

Common Stumbling Points

Confusing aspects of space group nomenclature are:

- Structures with rhombohedral space groups can be set in hexagonal or rhombohedral unit cells
- Some centrosymmetric space groups have symmetry defined in more than one setting (origin 1 vs. origin 2)
- Converting Hermann-Mauguin names to input for GSAS

Rhombohedral Symmetry: Hexagonal vs. Rhombohedral Unit Cells

- A rhombohedral unit cell can be expanded into a hexagonal unit cell with a tripled volume
  - (111) direction in rhombohedral cell becomes (001) direction in hexagonal cell
  - Hexagonal setting has three times as many symmetry operations
- Rhombohedral setting is usually simpler to specify & understand
  - but as α>>90° (or α<<90°) correlation between axes increases
  - refinement using hexagonal cell is usually more stable
- For rhombohedral space groups: be sure to use symmetry operations for correct cell type
  - R3x space groups only (P3x and P6x are hexagonal only)

Origin choice

- Some centrosymmetric space groups may have a higher symmetry site than the –1 site
  - If so, the Internationals Tables offer two origin choices:
    - *Origin 1: origin at highest symmetry site*
    - *Origin 2: origin at center of symmetry*
      - Origin 2: Simplest computationally
      - Origin 2: Has –x,-y,-z symmetry position
- Almost all crystallographic programs require origin 2 unless you are offered both choices:
    - *Exceptions: PowderCell & Cerius²*
    - *Programs that accept symmetry operators as input will probably work fine in either setting*
  - GSAS requires Origin 2 for space groups that have both settings
- If you input coordinates and get the wrong site multiplicities (unit cell contents), suspect origin choice as an error.

Space groups with two origin settings

- Orthorhombic
  - ***Pnnn*** (#48) -¼ -¼ -¼
  - ***Pban*** (#50) -¼ -¼ 0
  - ***Pmmn*** (#59) -¼ -¼ 0
  - ***Ccca*** (#68) 0 -¼ -¼
  - ***Fddd*** (#70) ⅛ ⅛ ⅛
- Cubic
  - ***Pn-3*** (#201) ¼ ¼ ¼
  - ***Fd-3*** (#203) ⅛ ⅛ ⅛
  - ***Pn-3n*** (#222) ¼ ¼ ¼
  - ***Pn-3m*** (#224) ¼ ¼ ¼
  - ***Fd-3m*** (#227) ⅛ ⅛ ⅛
  - ***Fd-3c*** (#228) ⅜ ⅜ ⅜
- Tetragonal
  - ***P4/n*** (#85) ¼ -¼ 0
  - ***$P4_2/n$*** (#86) ¼ ¼ ¼
  - ***$I4_1/a$*** (#88) 0 ¼ ⅛
  - ***P4/nbm*** (#125) ¼ ¼ 0
  - ***P4/nnc*** (#126) ¼ ¼ ¼
  - ***P4/nmm*** (#129) ¼ -¼ 0
  - ***P4/ncc*** (#130) ¼ -¼ 0
  - ***$P4_2/nbc$*** (#133) ¼ -¼ ¼
  - ***$P4_2/nnm$*** (#134) ¼ -¼ ¼
  - ***$P4_2/nmc$*** (#137) ¼ -¼ ¼
  - ***$P4_2/ncm$*** (#138) ¼ -¼ ¼
  - ***$I4_1/amd$*** (#141) 0 -¼ ⅛
  - ***$I4_1/acd$*** (#142) 0 -¼ ⅛

Add this shift to coordinates to convert from origin 1 to origin 2
EXPGUI can do this in the **xform atoms** *window*

Space Group Naming in GSAS

Properly specifying space groups as input for GSAS is a common stumbling point. GSAS allows input of many types of non-standard settings, but this flexibility allows for confusion.

Symmetry elements are converted to standard ASCII. Example: 6_3: `63`

GSAS requires at least a single space between the centering symbol & between symmetry elements for each axis. Examples:

- *P*-1: `P -1`
- *P*4/*mmm*: `P 4/m m m`
- *P*6_3/*mcm*: `P 63/m c m`

A hexagonal cell is assumed for Rhombohedral space groups, unless a “R” is added to the space group name:

- Hexagonal cell: `R -3 c`
- Rhombohedral cell: `R -3 c R`

Phase transformations

One of the most common uses of powder diffraction is to follow phase transformations in solids in response to temperature, pressure, strain, magnetic or electric fields,…

Nomenclature of phase transformations is complex.

Recommended reference: Clark et al, Definition of terms relating to phase transitions of the solid state (IUPAC Recommendations 1994), *Pure and Applied Chemistry*, **66** 571-594 (1994).

http://www.iupac.org/publications/pac/1994/pdf/6603x0577.pdf

http://goldbook.iupac.org/src_PAC199466577.html

Important concepts for phase changes

- Diffusional vs. Diffusionless Transitions:
  - Some phase changes require major reorganization of the atomic structure, such as freezing of a liquid to a crystalline solid or conversion of diamond to graphite. These phase changes are called *diffusional* as atoms must diffuse to form the lattice to complete the phase change
  - Most solid-to-solid phase changes occur with reorganization of symmetry but without major changes local changes in atomic arrangement greater than bonding distances: *diffusionless transitions*
- First vs. Second Order Transitions
  - A *first order transition* is accompanied by release or absorption of energy (heat). The two phases co-exist for some period
  - In a *second order transition* the structure undergoes a continuous change. No energy is absorbed or released

Landau theory relates transition order to changes in symmetry

Symmetry transformations: Subcells & Supercells

- Most phase transformations between crystalline phases are diffusionless transitions. Diffusionless transitions have only straightforward changes in symmetry: *e.g.* symmetry operations are gained or lost
  - Note: symmetry changes may cause a change in unit cell type
    - *Example: loss of 4-fold axis reduces tetragonal to orthorhombic (or monoclinic)*
- Removal (or addition) of symmetry to a space group can only occur in specific ways that are classified in the International Tables vol. A (or A1)
  - Subgroups: removal of symmetry elements
    - *Three types of subgroups:*
      - I: no change in centering
      - IIa: loss of centering
      - IIb & IIc: cell expansion
  - Supergroups: imposition of additional symmetry

Reference on subgroup-supergroup relationships: Burns & Glazer, Space Groups for Solid State Scientists (Academic Press, NY, 1990).

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] $p2gm$ $\mathbf{a}'=\mathbf{a}_c$ $\mathbf{b}'=\mathbf{b}$ Origin at $0,0,z$

Along [100] $p2_1gg$ $\mathbf{a}'=\mathbf{b}$ $\mathbf{b}'=\mathbf{c}_c$ 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] $P12_1/1$ ($P2_1/c$, 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)

Performing Subgroup Transformations on cells and coordinates

- Volume A of the International Tables tabulates subgroups and supergroups relationships, but not how to transform cells or coordinates
  - Example: *I4/mmm* ➔ *Fmmm*
    - *Cell transform! Origin transform? (getting this right takes some effort)*
- Volume A1 of the International Tables tabulates transformations associated with subgroups and supergroups relationships
- *Software exists for subgroup transformations*
  - PowderCell (free!)
    - *www.ccp14.ac.uk/ccp/web-mirrors/powdcell/a_v/v_1/powder/e_cell.html*
  - Bilboa "electronic vol. A" web site: www.cryst.ehu.es
  - Materials version of Insight-II, Acclerys (probably not available)

Systematic Absences

Systematic absences (extinctions) are classes of reflections that have zero intensity due to symmetry constrains. They provide information on space group changes.

Example of how a class of reflections has zero intensity due to symmetry

- Consider 2_1 screw along *a*
  - Generates positions *x,y,z* & *x+1/2,-y,-z*

- Structure factor $F_{hkl} \sim \Sigma f[\exp(2\pi i[hx+ky+lz])]$
- For h00 reflections expanding sum over *x,y,z* and *x+1/2,-y,-z*
  - $F_{h00} = c \Sigma f[\exp(2\pi i hx) + \exp\{2\pi i h(x+1/2)\}]$
    $= c \Sigma f[\exp(2\pi i hx) + \exp(\pi i h)\exp(2\pi i hx)]$

thus,

$F_{h00} \sim \Sigma 2f \exp(2\pi i hx)$ when h is **even** $[\exp(\pi i 2n) = 1]$
$F_{h00} = 0$ when h is **odd** $[\exp(\pi i\{2n+1\}) = -1]$

Systematic absences

- Only translational symmetry causes systematic absences:
  - Centering: A,B,C,F,I,R
  - Screw axes: *e.g.* 2_1 (not 2 or –2)
  - Glide planes: *e.g. c* _|_ *a*

- As the unit cell symmetry is changed (e.g. tetragonal to cubic) classes of reflections will overlap, but reflections do not become extinct due to the unit cell class.

Presence of systematic absences can be deduced from space group name

- If translation symmetry is present, it appears in the short space group name
- Extinctions by inspection:
  - *Fd*–3*m* & *Fd*–3 have same extinctions
  - *Pm*–3*m* has no extinctions
    - *If you are working in* Pm–3m *& see extra lines, investigate a larger cell*

Visualizing changes in powder diffraction patterns

CMPR is a good tool for seeing where how a pattern changes due to addition of extinctions or due to a change in unit cell

http://www.ncnr.nist.gov/xtal/software/cmpr