PAUL SCHERRER INSTITUT

PSI

Wir schaffen Wissen – heute für morgen

Paul Scherrer Institut
Michael Wedel

Crystallographic code in Mantid

Introduction

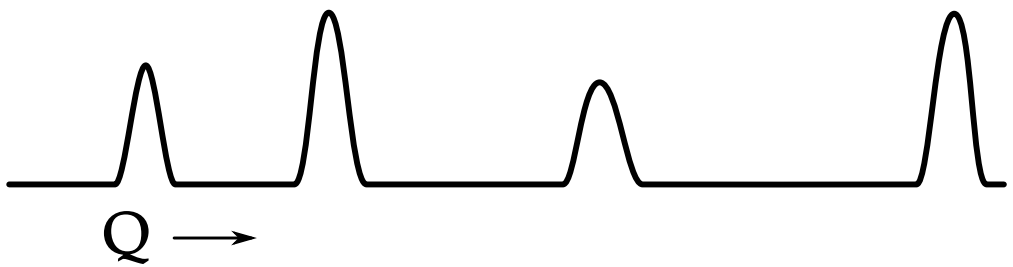
Original problem

- POLDI: Engineering diffractometer at SINQ/PSI
- Typical samples: Metals, alloys, sometimes with impurities
- Bragg peaks must be indexed for analysis

Introduction

Original problem

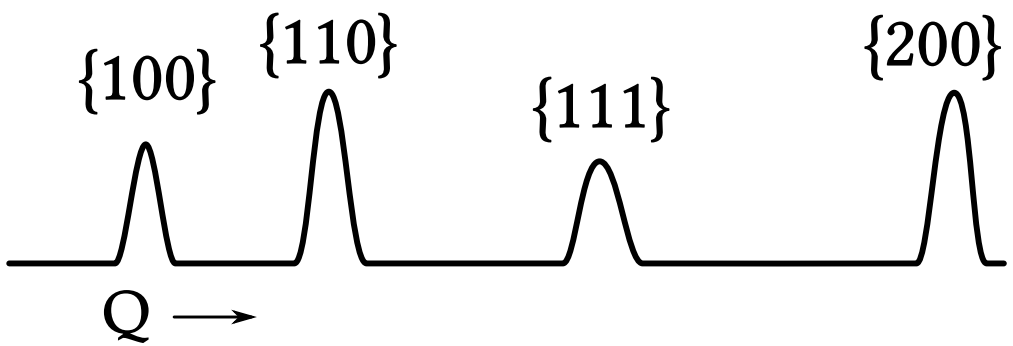
- POLDI: Engineering diffractometer at SINQ/PSI
- Typical samples: Metals, alloys, sometimes with impurities
- Bragg peaks must be indexed for analysis



Introduction

Original problem

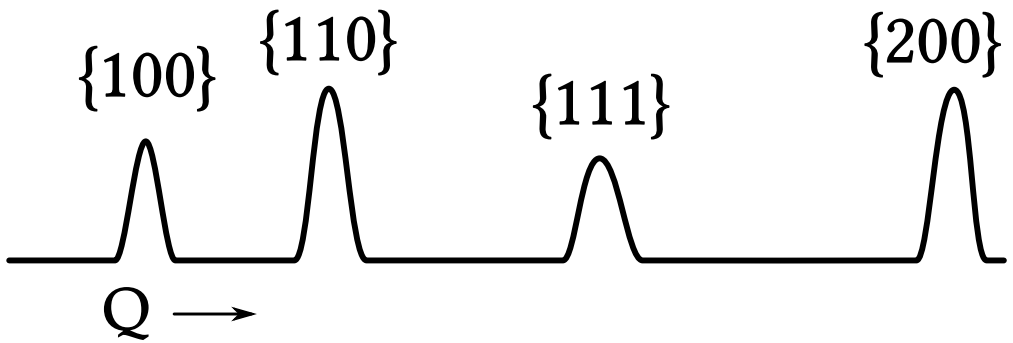
- POLDI: Engineering diffractometer at SINQ/PSI
- Typical samples: Metals, alloys, sometimes with impurities
- Bragg peaks must be indexed for analysis



Introduction

Original problem

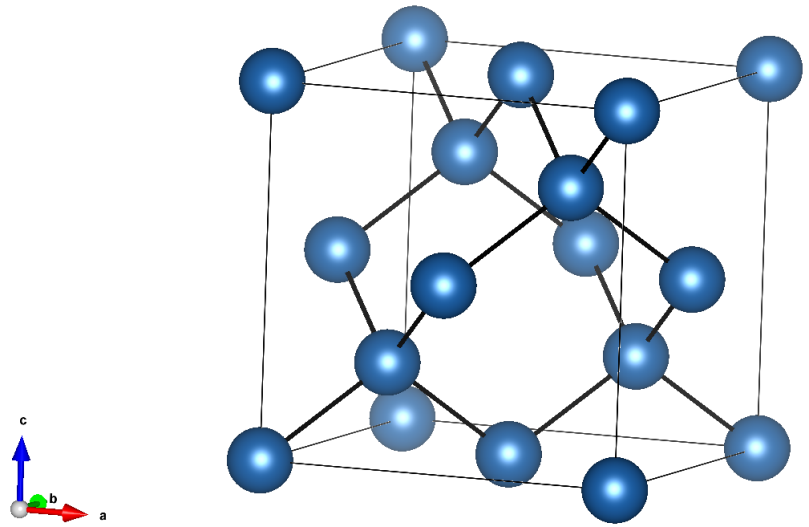
- POLDI: Engineering diffractometer at SINQ/PSI
- Typical samples: Metals, alloys, sometimes with impurities
- Bragg peaks must be indexed for analysis



Boundary conditions

- Crystal structure is known
- Powder diffraction - can not distinguish symmetrically equivalent reflections
- Special reflection conditions should be taken into account

Crystal structure of Silicon



- Space group: $Fd\bar{3}m$
- Unit cell: $a = 5.431$
- Atomic positions:

Element	x	y	z	Occupancy
Si	0	0	0	1.0

Generating Miller indices

```
std::vector<V3D> getHKLs(const UnitCell &cell,
                         double dMin, double dMax) {
  std::vector<V3D> hkls;

  int hMax = static_cast<int>(cell.a() / dMin);
  int kMax = static_cast<int>(cell.b() / dMin);
  int lMax = static_cast<int>(cell.c() / dMin);

  for (int h = -hMax; h <= hMax; ++h) {
    for (int k = -kMax; k <= kMax; ++k) {
      for (int l = -lMax; l <= lMax; ++l) {
        V3D hkl(h, k, l);

        if (    isAllowed(hkl)
             && inRange(cell.d(hkl), dMin, dMax) ) {
          hkls.push_back(hkl);
        }
      }
    }
  }

  return hkls;
}
```

Getting independent reflections

- hkl denotes normal vector to a family of lattice planes
- Crystal symmetry makes certain plane families equivalent
- Cubic: (100), (010), (001), $(\bar{1}00)$, $(0\bar{1}0)$, $(00\bar{1}) \rightarrow \{100\}$

Getting independent reflections

- hkl denotes normal vector to a family of lattice planes
- Crystal symmetry makes certain plane families equivalent
- Cubic: (100), (010), (001), $(\bar{1}00)$, $(0\bar{1}0)$, $(00\bar{1}) \rightarrow \{100\}$
- Could be handled by limiting indices ($h > 0$, $k < h$, $l < k$, ...)

Getting independent reflections

- hkl denotes normal vector to a family of lattice planes
- Crystal symmetry makes certain plane families equivalent
- Cubic: (100), (010), (001), $(\bar{1}00)$, $(0\bar{1}0)$, $(00\bar{1}) \rightarrow \{100\}$
- Could be handled by limiting indices ($h > 0$, $k < h$, $l < k$, ...)
- But: Very inconvenient (many different cases)

Getting independent reflections

- hkl denotes normal vector to a family of lattice planes
- Crystal symmetry makes certain plane families equivalent
- Cubic: (100), (010), (001), $(\bar{1}00)$, $(0\bar{1}0)$, $(00\bar{1}) \rightarrow \{100\}$
- Could be handled by limiting indices ($h > 0$, $k < h$, $l < k$, ...)
- But: Very inconvenient (many different cases)

Describe symmetry by point groups

What's a group?

A group $(G, \cdot)$ is a set G with a binary operation $\cdot$ that satisfies the four group axioms.[1]

[1] https://sites.google.com/a/thewe.net/mathematics/Motivation/What-are-groups-

What's a group?

A group $(G, \cdot)$ is a set G with a binary operation $\cdot$ that satisfies the four group axioms.[1]

1. *Closure*: For all a, b in G the result of $a \cdot b$ is also in G.

[1] https://sites.google.com/a/thewe.net/mathematics/Motivation/What-are-groups-

What's a group?

A group $(G, \cdot)$ is a set G with a binary operation $\cdot$ that satisfies the four group axioms.[1]

1. *Closure*: For all a, b in G the result of $a \cdot b$ is also in G.
2. *Associativity*: For all a, b, c in G, $(a \cdot b) \cdot c = a \cdot (b \cdot c)$.

[1] https://sites.google.com/a/thewe.net/mathematics/Motivation/What-are-groups-

What's a group?

A group $(G, \cdot)$ is a set G with a binary operation $\cdot$ that satisfies the four group axioms.[1]

1. *Closure*: For all a, b in G the result of $a \cdot b$ is also in G.
2. *Associativity*: For all a, b, c in G, $(a \cdot b) \cdot c = a \cdot (b \cdot c)$.
3. *Identity element*: There exists an element e in G such that $e \cdot a = a$.

[1] https://sites.google.com/a/thewe.net/mathematics/Motivation/What-are-groups-

What's a group?

A group $(G, \cdot)$ is a set G with a binary operation $\cdot$ that satisfies the four group axioms.[1]

1. *Closure*: For all a, b in G the result of $a \cdot b$ is also in G.
2. *Associativity*: For all a, b, c in G, $(a \cdot b) \cdot c = a \cdot (b \cdot c)$.
3. *Identity element*: There exists an element e in G such that $e \cdot a = a$.
4. *Inverse element*: For each a in G, there exists an element b in G such that $a \cdot b = e$.

[1] https://sites.google.com/a/thewe.net/mathematics/Motivation/What-are-groups-

Symmetry groups

A symmetry operation describes a transformation of an object x into an image x'.

Symmetry groups

A symmetry operation describes a transformation of an object x into an image x'.

- Represented by a matrix/vector pair:

$$S = (\boldsymbol{W}, \boldsymbol{w})$$

Symmetry groups

A symmetry operation describes a transformation of an object x into an image x'.

- Represented by a matrix/vector pair:

$$S = (\boldsymbol{W}, \boldsymbol{w})$$

- The group operation $\cdot$ is defined as follows:

$$S_1 \cdot S_2 = (\boldsymbol{W}_1 \cdot \boldsymbol{W}_2, (\boldsymbol{W}_1 \cdot \boldsymbol{w}_2) + \boldsymbol{w}_1)$$

Symmetry groups

A symmetry operation describes a transformation of an object x into an image x'.

- Represented by a matrix/vector pair:

$$S = (\boldsymbol{W}, \boldsymbol{w})$$

- The group operation $\cdot$ is defined as follows:

$$S_1 \cdot S_2 = (\boldsymbol{W}_1 \cdot \boldsymbol{W}_2, (\boldsymbol{W}_1 \cdot \boldsymbol{w}_2) + \boldsymbol{w}_1)$$

- Hermann-Mauguin notation (symmetry elements):

$$1, \bar{1}, 2, 2_1, \bar{6}, m, \ldots$$

Symmetry groups

A symmetry operation describes a transformation of an object x into an image x'.

- Represented by a matrix/vector pair:

$$S = (\boldsymbol{W}, \boldsymbol{w})$$

- The group operation $\cdot$ is defined as follows:

$$S_1 \cdot S_2 = (\boldsymbol{W}_1 \cdot \boldsymbol{W}_2, (\boldsymbol{W}_1 \cdot \boldsymbol{w}_2) + \boldsymbol{w}_1)$$

- Hermann-Mauguin notation (symmetry elements):

$$1, \bar{1}, 2, 2_1, \bar{6}, m, \ldots$$

- Jones-faithful notation:

$$(x, y, z), (\bar{x}, \bar{y}, \bar{z}), (\bar{x}, \bar{y}, z), (\bar{x}, \bar{y}, z + {}^1/_2), (y - x, \bar{x}, \bar{z}), (x, y, \bar{z})$$

Geometry::SymmetryOperation

Geometry::SymmetryOperation

- Represented by Jones-faithful notation (x, y, z)

Geometry::SymmetryOperation

- Represented by Jones-faithful notation (x, y, z)
- Supports rational vector components $(x + 1/2, z, -y)$

Geometry::SymmetryOperation

- Represented by Jones-faithful notation (x, y, z)
- Supports rational vector components $(x + 1/2, z, -y)$

Geometry::SymmetryOperation

- Represented by Jones-faithful notation (x, y, z)
- Supports rational vector components $(x + 1/2, z, -y)$
- Operations on V3D, V3R (3×1-vector of rational numbers)

```
SymmetryOperation inv = SymmetryOperationFactory::Instance()
                                              .createSymOp("-x,-y,-z");
SymmetryOperation mir = SymmetryOperationFactory::Instance()
                                              .createSymOp("x,y,-z");
SymmetryOperation twoFoldA = mir * inv;
SymmetryOperation twoFoldB = inv * mir;

assert(twoFoldA == twoFoldB);

// Apply two-fold rotation to V3D
V3D rotated = twoFold * V3D(1,1,1);

// Create several operations at once
std::vector<SymmetryOperation> ops =
                          SymmetryOperationFactory::Instance()
                          .createSymOps("x,y,z; z,x,y");
```

Crystallographic point groups

Example: $2/m$

Crystallographic point groups

Example: $2/m$

- Group elements: $G_{2/m} = \{1, \bar{1}, 2, m\}$

Crystallographic point groups

Example: $2/m$

- Group elements: $G_{2/m} = \{1, \bar{1}, 2, m\}$
- Group table:

	1	$\bar{1}$	2	m
1	1	$\bar{1}$	2	m
$\bar{1}$	$\bar{1}$	1	m	2
2	2	m	1	$\bar{1}$
m	m	2	$\bar{1}$	1

Crystallographic point groups

Example: $2/m$

- Group elements: $G_{2/m} = \{1, \bar{1}, 2, m\}$
- Group table:

	1	$\bar{1}$	2	m
1	1	$\bar{1}$	2	m
$\bar{1}$	$\bar{1}$	1	m	2
2	2	m	1	$\bar{1}$
m	m	2	$\bar{1}$	1

- Example group operation:

$$2 = m \cdot \bar{1}$$

$$\begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \cdot \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

Generating point groups

[2] Shmueli, U. Acta Crystallogr. A 40, 559–567 (1984).

Generating point groups

- A point group is a *cyclic group* or product of cyclic groups[2]

[2] Shmueli, U. Acta Crystallogr. A 40, 559–567 (1984).

Generating point groups

- A point group is a *cyclic group* or product of cyclic groups[2]
- Order k of a symmetry operation:

$$S^k = I$$

[2] Shmueli, U. Acta Crystallogr. A 40, 559–567 (1984).

Generating point groups

- A point group is a *cyclic group* or product of cyclic groups[2]
- Order k of a symmetry operation:

$$S^k = I$$

- Cyclic group:

$$C = \left\{ S^{k-1}, \ldots, S^1, S^0 = I \right\}$$

[2] Shmueli, U. Acta Crystallogr. A 40, 559–567 (1984).

Generating point groups

- A point group is a *cyclic group* or product of cyclic groups[2]
- Order k of a symmetry operation:

$$S^k = I$$

- Cyclic group:

$$C = \left\{ S^{k-1}, \ldots, S^1, S^0 = I \right\}$$

- Product of two groups is again a group:

$$G_{2/m} = G_2 \cdot G_m = C_2 \cdot C_m = \{1, 2\} \cdot \{1, m\}$$

[2] Shmueli, U. Acta Crystallogr. A 40, 559–567 (1984).

Generating point groups

- A point group is a *cyclic group* or product of cyclic groups[2]
- Order k of a symmetry operation:

$$S^k = I$$

- Cyclic group:

$$C = \left\{ S^{k-1}, \ldots, S^1, S^0 = I \right\}$$

- Product of two groups is again a group:

$$G_{2/m} = G_2 \cdot G_m = C_2 \cdot C_m = \{1, 2\} \cdot \{1, m\}$$

All point groups can be generated using symmetry operations!

[2] Shmueli, U. Acta Crystallogr. A 40, 559–567 (1984).

Geometry::PointGroup

- Was introduced in 2012 for checking equivalence of hkls

Geometry::PointGroup

- Was introduced in 2012 for checking equivalence of hkls
- Refactored to use group-theoretical code
- New functionality added

Geometry::PointGroup

- Was introduced in 2012 for checking equivalence of hkls
- Refactored to use group-theoretical code
- New functionality added

```
PointGroup_sptr m3m = PointGroupFactory::Instance()
                                .createPointGroup("m-3m");

std::vector<V3D> equivalents = m3m->getEquivalents(V3D(1,0,0));

// Vector contains all equivalent hkls for (100)
assert(equivalents.size() == 6);

V3D family100 = m3m->getReflectionFamily(V3D(1,0,0));
V3D family010 = m3m->getReflectionFamily(V3D(0,1,0));

// Returns the same value for two equivalent reflections
assert(family100 == family010);
```

Generating independent reflections

```
std::vector<V3D> getHKLs(const UnitCell &cell,
                         const PointGroup_sptr &pointGroup,
                         double dMin, double dMax) {
  // set instead of vector
  std::set<V3D> hkls;

  // lots of nested for loops...

        if (   isAllowed(hkl)
            && inRange(cell.d(hkl), dMin, dMax) ) {
          // Generate reflection family from hkl
          V3D unique = pointGroup->getReflectionFamily(hkl);
          hkls.insert(unique);
        }

  // closing loops...

  return std::vector<V3D>(hkls.begin(), hkls.end());
}
```

Generating independent reflections

```
std::vector<V3D> getHKLs(const UnitCell &cell,
                         const PointGroup_sptr &pointGroup,
                         double dMin, double dMax) {
  // set instead of vector
  std::set<V3D> hkls;

  // lots of nested for loops...

        if (   isAllowed(hkl)
            && inRange(cell.d(hkl), dMin, dMax) ) {
          // Generate reflection family from hkl
          V3D unique = pointGroup->getReflectionFamily(hkl);
          hkls.insert(unique);
        }

  // closing loops...

  return std::vector<V3D>(hkls.begin(), hkls.end());
}
```

Set of independent reflections with `Geometry::PointGroup`

Problem solved?

- Space group $Fd\bar{3}m$ - face centered lattice
- Checking allowed reflections with `Geometry::ReflectionCondition`?

Problem solved?

- Space group $Fd\bar{3}m$ - face centered lattice
- Checking allowed reflections with `Geometry::ReflectionCondition`?
- F allows (222) ($h+k=2n, h+l=2n, k+l=2n$)

Problem solved?

- Space group $Fd\bar{3}m$ - face centered lattice
- Checking allowed reflections with `Geometry::ReflectionCondition`?
- F allows (222) ($h + k = 2n, h + l = 2n, k + l = 2n$)
- Problem: Silicon atoms on Wyckoff-position $8a$

8	*b*	-4 3 *m*	1/2, 1/2, 1/2	1/4, 3/4, 1/4	*hkl* : *h* = 2*n* + 1 or *h* + *k* + *l* = 4*n*
8	*a*	-4 3 *m*	0, 0, 0	3/4, 1/4, 3/4	

Screenshot from ITA online.

Problem solved?

- Space group $Fd\bar{3}m$ - face centered lattice
- Checking allowed reflections with `Geometry::ReflectionCondition`?
- F allows (222) ($h+k=2n, h+l=2n, k+l=2n$)
- Problem: Silicon atoms on Wyckoff-position $8a$

8	*b*	-4 3 *m*	1/2, 1/2, 1/2	1/4, 3/4, 1/4	*hkl* : *h* = 2*n* + 1 or *h* + *k* + *l* = 4*n*
8	*a*	-4 3 *m*	0, 0, 0	3/4, 1/4, 3/4	

Screenshot from ITA online.

$2+2+2=6 \neq 4n$ – (222) is forbidden!

Allowed reflections through structure factors

- Structure factor amplitudes for each hkl:

$$F(hkl) = \sum_j b_j \cdot \exp\left[2\pi i \cdot (hx_j + ky_j + lz_j)\right]$$

- Sum over all atoms j *in the unit cell*

Allowed reflections through structure factors

- Structure factor amplitudes for each hkl:

$$F(hkl) = \sum_j b_j \cdot \exp\left[2\pi i \cdot (hx_j + ky_j + lz_j)\right]$$

- Sum over all atoms j *in the unit cell*
- Si atom at $0, 0, 0$ is mapped to 8 symmetrically equivalent positions:

$0,\ 0,\ 0$	$0,\ 1/2,\ 1/2$	$1/2,\ 0,\ 1/2$	$1/2,\ 1/2,\ 0$
$3/4,\ 1/4,\ 3/4$	$3/4,\ 3/4,\ 1/4$	$1/4,\ 1/4,\ 1/4$	$1/4,\ 3/4,\ 3/4$

Allowed reflections through structure factors

- Structure factor amplitudes for each hkl:

$$F(hkl) = \sum_j b_j \cdot \exp\left[2\pi i \cdot (hx_j + ky_j + lz_j)\right]$$

- Sum over all atoms j *in the unit cell*
- Si atom at $0, 0, 0$ is mapped to 8 symmetrically equivalent positions:

$$\begin{array}{cccc} 0,\ 0,\ 0 & 0,\ 1/2,\ 1/2 & 1/2,\ 0,\ 1/2 & 1/2,\ 1/2,\ 0 \\ 3/4,\ 1/4,\ 3/4 & 3/4,\ 3/4,\ 1/4 & 1/4,\ 1/4,\ 1/4 & 1/4,\ 3/4,\ 3/4 \end{array}$$

- For (222) contributions cancel out – not allowed!

Allowed reflections through structure factors

- Structure factor amplitudes for each hkl:

$$F(hkl) = \sum_j b_j \cdot \exp\left[2\pi i \cdot (hx_j + ky_j + lz_j)\right]$$

- Sum over all atoms j *in the unit cell*
- Si atom at $0, 0, 0$ is mapped to 8 symmetrically equivalent positions:

$0,\ 0,\ 0$	$0,\ 1/2,\ 1/2$	$1/2,\ 0,\ 1/2$	$1/2,\ 1/2,\ 0$
$3/4,\ 1/4,\ 3/4$	$3/4,\ 3/4,\ 1/4$	$1/4,\ 1/4,\ 1/4$	$1/4,\ 3/4,\ 3/4$

- For (222) contributions cancel out – not allowed!
- Implemented in `Geometry::BraggScatterer`

PAUL SCHERRER INSTITUT PSI

Geometry::SpaceGroup

- Generation of equivalent coordinates in the unit cell
- Translational symmetry (screw axes, glide mirror planes, lattice centering)
- Exactly the same generation algorithm as for point groups if $\boldsymbol{w}$ is limited to interval $[0, 1)$
- Algorithmic generation only on first request, aftwards *Prototype* pattern

Geometry::SpaceGroup

- Generation of equivalent coordinates in the unit cell
- Translational symmetry (screw axes, glide mirror planes, lattice centering)
- Exactly the same generation algorithm as for point groups if $\boldsymbol{w}$ is limited to interval $[0, 1)$
- Algorithmic generation only on first request, aftwards *Prototype* pattern

```
SpaceGroup_const_sptr Fd3m = SpaceGroupFactory::Instance()
                                    .createSpaceGroup("F d -3 m");

// Si-atom at (0,0,0)
std::vector<V3D> atoms = Fd3m * V3D(0,0,0);
assert(atoms.size() == 8);
```

Geometry::CrystalStructure

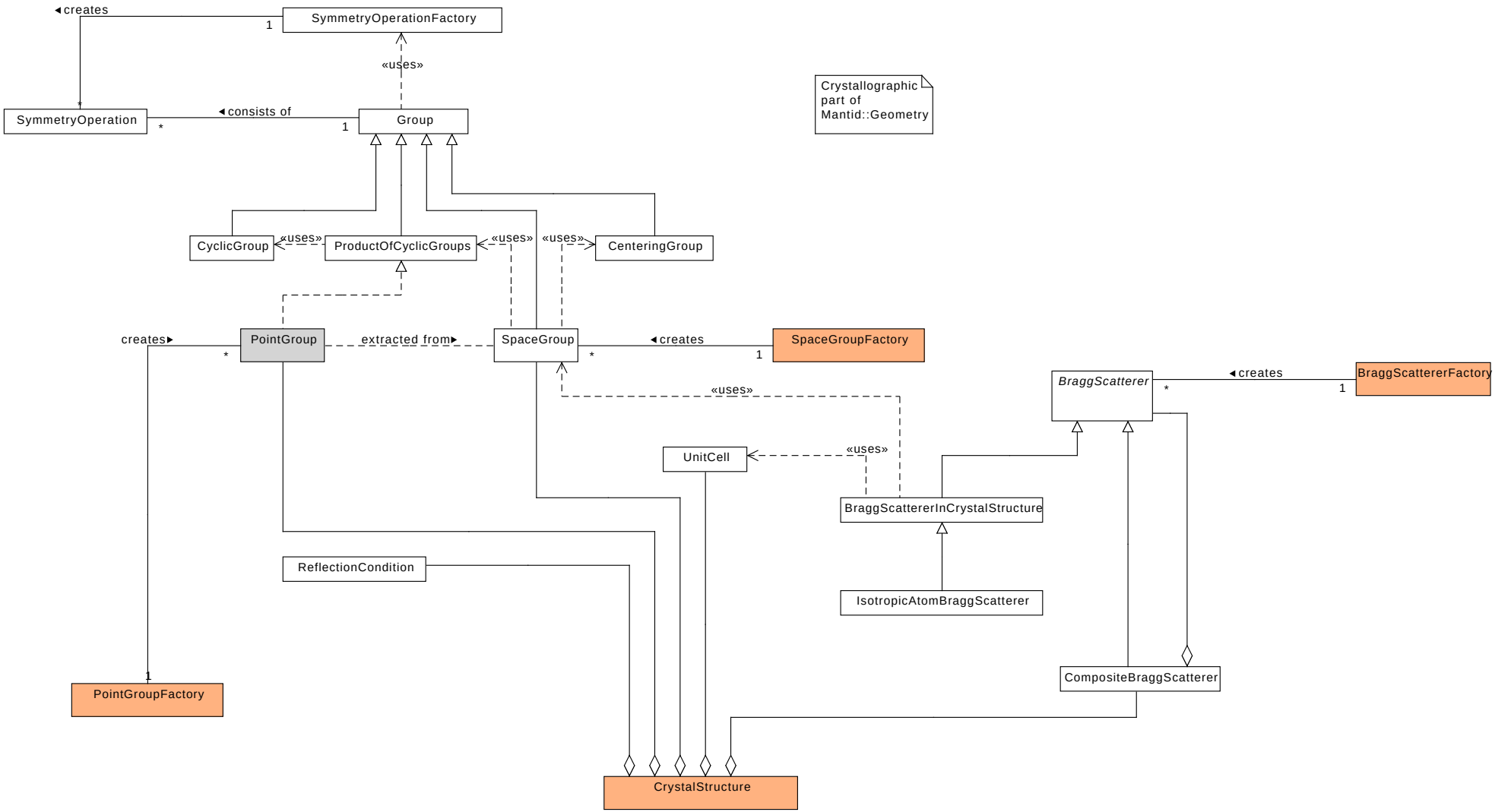
- Combines unit cell, space group and scatterers

Geometry::CrystalStructure

- Combines unit cell, space group and scatterers

```
SpaceGroup_const_sptr Fd3m = SpaceGroupFactory::Instance()
                                    .createSpaceGroup("F d -3 m");

BraggScatterer_sptr SiAtom =
            BraggScattererFactory::Instance()
               .createScatterer("IsotropicAtomBraggScatterer",
                                "Element=Si;U=0.05");

CompositeBraggScatterer_sptr basis =
            CompositeBraggScatterer::create(
               std::vector<BraggScatterer_sptr>(1, SiAtom));

UnitCell cell(5.431, 5.431, 5.431);

CrystalStructure Si(cell, Fd3m, basis);

// Get unique hkls with correct absences
std::vector<V3D> hkls = Si.getUniqueHKLs(0.75,10.0,
                          CrystalStructure::UseStructureFactor);
// Based on centering only, we would get 22
assert(hkls.size() == 15)
```

Class diagram of crystallographic code



Summary

What has been done?

- Extended existing point group code
- Added space groups based on group theoretical approach
- Introduced scatterers (composite patterns - very flexible)
- Crystal structure class
- Lots of unit tests and space group system test

PAUL SCHERRER INSTITUT PSI

Summary

What has been done?

- Extended existing point group code
- Added space groups based on group theoretical approach
- Introduced scatterers (composite patterns - very flexible)
- Crystal structure class
- Lots of unit tests and space group system test

Future improvements

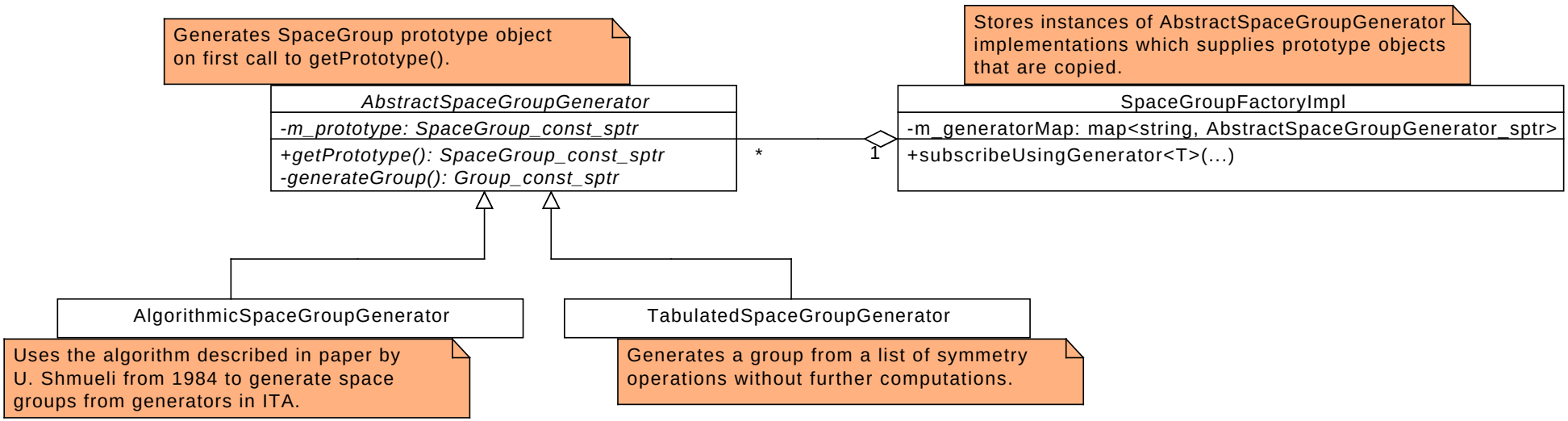
- Refactor point group code
- Better factory for scatterers
- Export everything (?) to Python
- Ticket #10134 - Introduce *Reflection* concept?

Acknowledgements

- My group at PSI: Helena Van Swygenhoven, Steven Van Petegem, Tobias Panzner
- Help from the team, especially: Anders, Andrei, Vicky (point group code & tests)
- Space group help: Dr. Igor Baburin (TU Dresden)
- Literature:
  - *International Tables for Crystallography Volume A*
  - *Symmetry Relationships between Crystal Structures: Applications of Crystallographic Group Theory in Crystal Chemistry* by Ulrich Müller (ISBN: 9780191648809)

Thank you for your attention!

SpaceGroupFactory




```
DECLARE_GENERATED_SPACEGROUP(198, "P 21 3",
            "-x+1/2,-y,z+1/2; -x,y+1/2,-z+1/2; z,x,y")
```