PROGRAMMING CRYSTALLOGRAPHIC SYMMETRY

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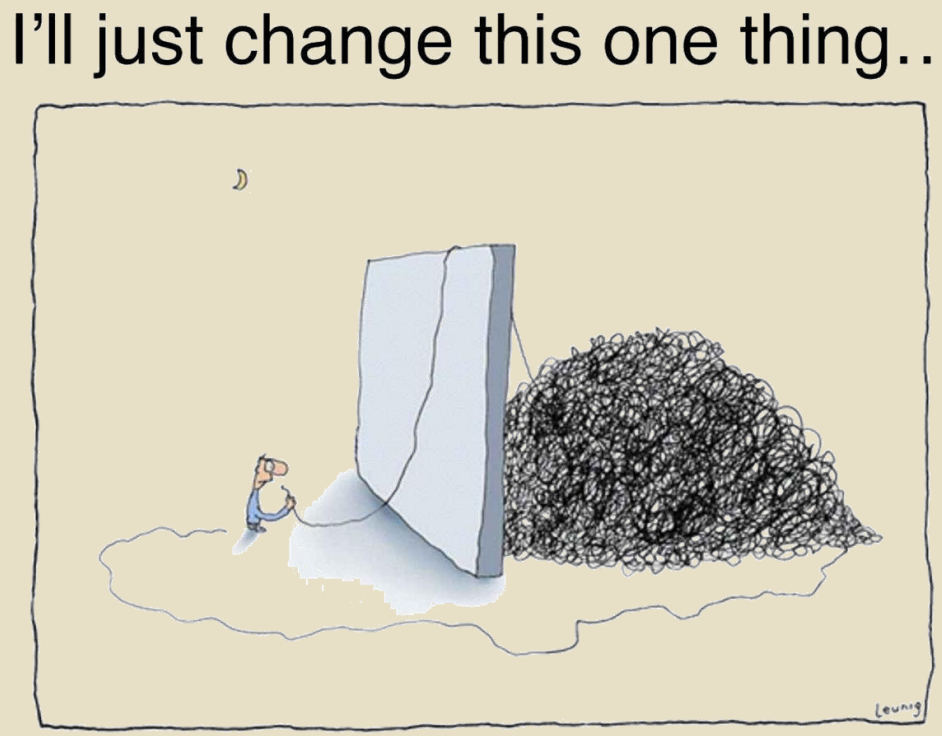
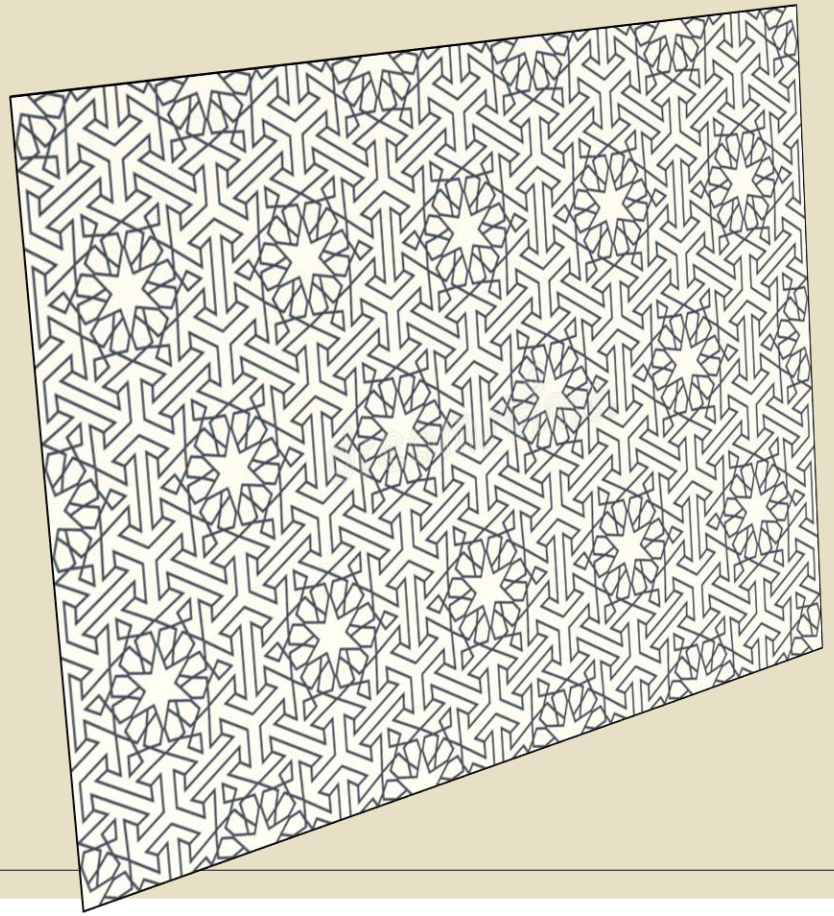
Software libraries hide away complexity, but can also hide useful knowledge.



Symmetry is a threshold concept in crystallography and crystallographic algorithms.



- Notation
- Transformation of coordinate systems
- Example libraries

NOTATION

The International Tables for Crystallography

Groups

- If two operations, a and b, are elements of a group, their product, $c = ab$ is also an element of the group.
- One element of the group will be the identity operation, E, such that $Ea = aE = a$.
- For every element, a, of the group there exists and *inverse* a^{-1}, such that $aa^{-1} = E$.
- Operations are associative: $a(bc) = (ab)c$

Groups are defined by a multiplication table: operations could be symmetry operations (for example).

	E	a	b	c
E	E	a	b	c
a	a	E	c	b
b	b	c	E	a
c	c	b	a	E

Point group operations may involve rotation, reflection or inversion. *E.g.*, point group **2/m**: the multiplication table of point group operations is

	1	*2*	*m*	*-1*
1	*1*	*2*	*m*	*-1*
2	*2*	*1*	*-1*	*m*
m	*m*	*-1*	*1*	*2*
-1	*-1*	*m*	*2*	*1*

Symmetry operations can be expressed as a matrices. They operate on crystallographic coordinates…

$$\begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} x \\ -y \\ z \end{pmatrix}$$

m

Symmetry operations can be expressed as a matrices. They operate on crystallographic coordinates … and on each other.

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

m **2** **-1**

In addition, *space group* operations may contain a translational component. *E.g.*, a 2_1 screw axis is a 180° rotation around an axis, followed by a translation along the same axis.

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

2 (around b-axis) + translation along b

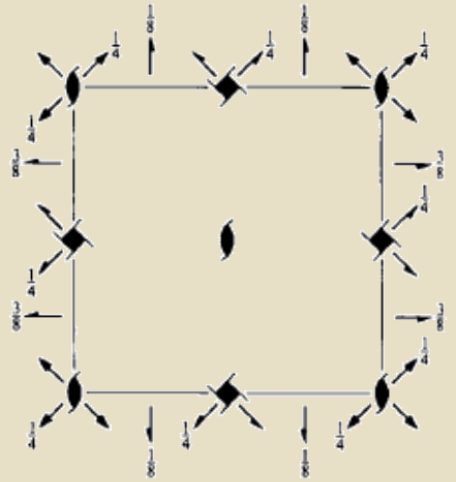
Can be packaged into a 4x4 matrix and extended coordinate vector for easier handling:

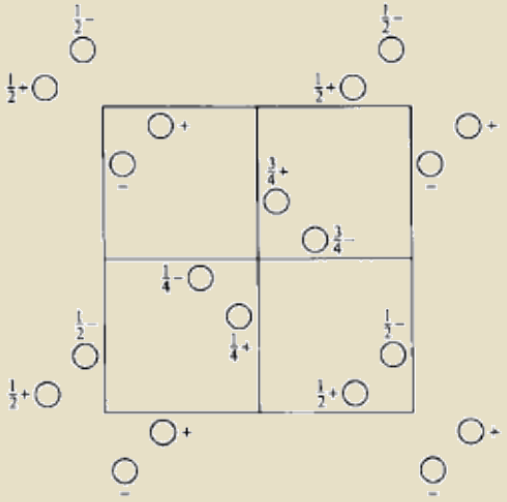
$$\begin{pmatrix} -x \\ y + 1/2 \\ -z \\ 1 \end{pmatrix} = \begin{pmatrix} -1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 1/2 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \\ 1 \end{pmatrix}$$

Based on Seitz notation. Set last line of coordinate vector to 1.
These matrices work as single elements in the group of symmetry operations which define the space group. However we must treat the translational parts using modular arithmetic *e.g.,* (0,1/2, 0) = (0,3/2,1)

$P4_32_12$ D_4^8 422 Tetragonal

No. 96 $P4_32_12$ Patterson symmetry $P4/mmm$





Origin on 2 [1 1 0] at 2, 1 (1, 2)

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

Symmetry operations

(1) 1
(2) $2(0,0,\frac{1}{2})$ $0,0,z$
(3) $4^-(0,0,\frac{1}{4})$ $0,\frac{1}{2},z$
(4) $4\ (0,0,\frac{1}{4})$ $\frac{1}{2},0,z$
(5) $2(0,\frac{1}{2},0)$ $\frac{1}{4},y,\frac{1}{8}$
(6) $2(\frac{1}{2},0,0)$ $x,\frac{1}{4},\frac{1}{8}$
(7) $2\ \ x,x,0$
(8) $2\ \ x,\bar{x},\frac{1}{4}$

Operation:

4- (0,0,¼) ½,0,z

Effect on x,y,z:

y+½ , -x+½, z+¼

Matrix form of op:

$$\begin{pmatrix} 0 & 1 & 0 & 1/2 \\ -1 & 0 & 0 & 1/2 \\ 0 & 0 & 1 & 1/4 \\ 0 & 0 & 0 & 1 \end{pmatrix}$$

The generators can be combined pair-wise to generate all of the operations of a group (no more, no fewer).

Generators selected (1); *t*(1,0,0); *t*(0,1,0); *t*(0,0,1); (2); (3); (5)

	1	*2*	*m*	*-1*
1	*1*	*2*	*m*	*-1*
2	*2*	*1*	*-1*	*m*
m	*m*	*-1*	*1*	*2*
-1	*-1*	*m*	*2*	*1*

TRANSFORMATIONS

Symmetry operations transform real space coordinates

$$\mathbf{x}_s = \mathbf{R}_s\mathbf{x} + \mathbf{t}_s$$

In a structure factor the contribution from a symmetry related atom $\mathbf{x}_s$ is:

$$\mathbf{h}^T\mathbf{x}_s = \mathbf{h}^T\mathbf{R}_s\mathbf{x} + \mathbf{h}^T\mathbf{t}_s = \mathbf{h}_s{}^T\mathbf{x} + \mathbf{h}^T\mathbf{t}_s$$

Inspecting what happens to **h**, we can apply the transformation in reciprocal space:

$$\mathbf{h}^T \mathbf{R}_s \mathbf{x} + \mathbf{h}^T \mathbf{t}_s = \mathbf{h}_s^T \mathbf{x}_r + \mathbf{h}^T \mathbf{t}_s$$

hence:

$$\mathbf{h}^T \mathbf{R}_s = \mathbf{h}_s^T$$

and rearranging,

$$\mathbf{R}_s^T \mathbf{h} = \mathbf{h}_s$$

Reciprocal lattice vectors transform with transposed symm operation.

If an atom position is invariant when a symmetry element is applied we need to take care of structure factor calculation and constraints

In space group P2 if the an atom coordinate is (0,y,0) the symmetry operation 2 has no effect on it. If we are calculating a structure factor by summation then the atom contribution will be added in twice unless action is taken.

$$\begin{pmatrix} 0 \\ 0.217 \\ 0 \end{pmatrix} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \begin{pmatrix} 0 \\ 0.217 \\ 0 \end{pmatrix}$$

The x and z coordinates cannot be refined – the atom must remain stuck on the two-fold axis!

The displacement parameter tensor can be transformed by pre-and post multiplying by the symmetry operation.

$$\begin{pmatrix} \beta_{11} & -\beta_{12} & \beta_{13} \\ -\beta_{21} & \beta_{22} & -\beta_{23} \\ \beta_{31} & -\beta_{32} & \beta_{33} \end{pmatrix} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \begin{pmatrix} \beta_{11} & \beta_{12} & \beta_{13} \\ \beta_{21} & \beta_{22} & \beta_{23} \\ \beta_{31} & \beta_{32} & \beta_{33} \end{pmatrix} \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

An atom on the 2-fold axis must have the same displacement parameters before and after the operation.

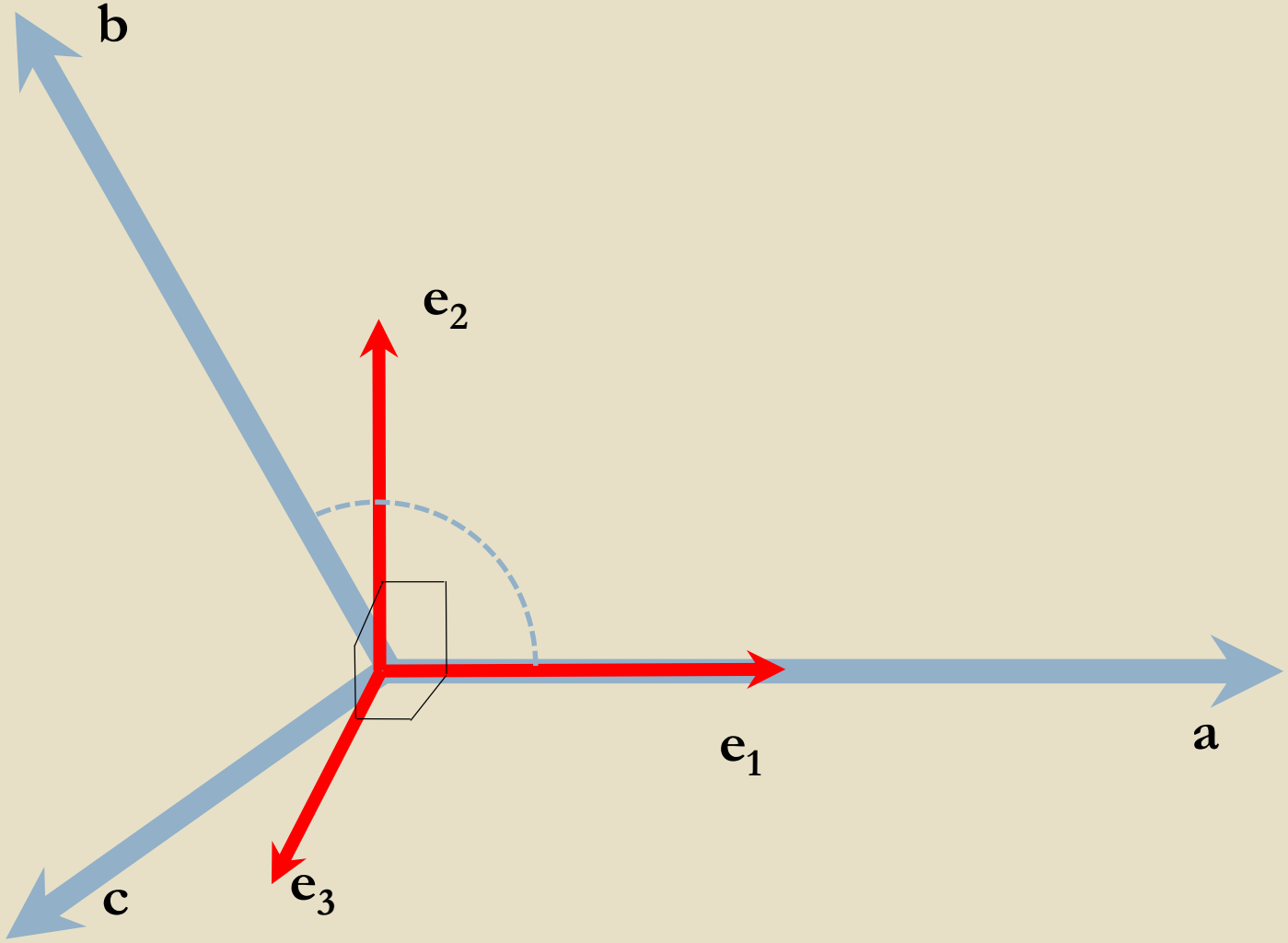
Therefore β_{12} and β_{23} must be zero for this atom.

Start from a definition of a 3x3 matrix, **A**, which converts crystallographic coordinates into an *orthonormal* coordinate system.

$$\begin{pmatrix} x_{orth} \\ y_{orth} \\ z_{orth} \end{pmatrix} = \mathbf{A} \begin{pmatrix} x_{crys} \\ y_{crys} \\ z_{crys} \end{pmatrix}$$

$$\mathbf{A} = \begin{pmatrix} a & b\cos\gamma & c\cos\beta \\ 0 & b\sin\gamma & c\,(\cos\alpha - \cos\beta\cos\gamma)/\sin\gamma \\ 0 & 0 & c\sqrt{1-\cos^2\alpha-\cos^2\beta-\cos^2\gamma+etc,etc\ldots} \end{pmatrix}$$

This is what that the **A** matrix describes:



The real space Metric Tensor is the product the orthogonalisation matrix and its transpose; it's much easier to deal with, in programming, or otherwise:

$$\mathbf{A^T A} = \begin{pmatrix} a^2 & ab\cos\gamma & ac\cos\beta \\ ab\cos\gamma & b^2 & bc\cos\alpha \\ ac\cos\beta & bc\cos\alpha & c^2 \end{pmatrix}$$

It is trivial to extract a cell and angles from this matrix.

The Metric Tensor transforms as a tensor (no surprise).

$$\mathbf{G' = R.G.RT}$$

We saw this earlier in the symmetry operation applied to a atomic displacement factor tensor.

This approach makes it simple to transform unit cells, given any operation, **R.**

Distances must be calculated in an orthonormal coordinate system. The metric tensor simplifies the expression:

$$d^2 = \Delta\mathbf{x}_{\mathbf{orth}}{}^{\mathbf{T}}.\,\Delta\mathbf{x}_{\mathbf{orth}}$$

$$= (\mathbf{A}\Delta\mathbf{x}_{\mathbf{crys}})^{\mathbf{T}}.\,\mathbf{A}\Delta\mathbf{x}_{\mathbf{crys}}$$

$$= \Delta\mathbf{x}_{\mathbf{crys}}{}^{\mathbf{T}}\mathbf{A}^{\mathbf{T}}.\,\mathbf{A}\Delta\mathbf{x}_{\mathbf{crys}}$$

$$= \Delta\mathbf{x}_{\mathbf{crys}}{}^{\mathbf{T}}\,\mathbf{G}\,\Delta\mathbf{x}_{\mathbf{crys}}$$

The reciprocal metric tensor, G^{-1}, can calculate distances in reciprocal space (usually in reciprocal Angstroms)

$$|d^*| = \mathrm{sqrt}(\mathbf{h}^T \mathbf{G}^{-1} \mathbf{h})$$

LIBRARIES

And Tools

CCTBX hides (or exposes?) complexity:

uc_sym_mat3 const & metrical_matrix () const
Access to metrical matrix.

uc_sym_mat3 const & reciprocal_metrical_matrix () const
Access to reciprocal metrical matrix

uc_mat3 const & fractionalization_matrix () const
Matrix for the conversion of cartesian to fractional coordinates.

uc_mat3 const & orthogonalization_matrix () const
Matrix for the conversion of fractional to cartesian coordinates.

FloatType distance (fractional< FloatType > const &site_frac_1, fractional< FloatType > const &site_frac_2) const

uc_mat3 matrix_cart (sgtbx::rot_mx const &rot_mx) const

unit_cell change_basis (sgtbx::rot_mx const &c_inv_r) const

unit_cell change_basis (sgtbx::change_of_basis_op const &cb_op) const
Transformation (change-of-basis) of unit cell parameters.

CrysFML

Real Function Get_Occ_Site (Pto, Spg)
Real(Kind=CP), Dimension(3) Intent(in) Pto Position vector
Type(Space_Group_Type) Intent(in) Spg Space Group
Obtain the occupancy factor (site multiplicity/multiplicity) for **Pto**

Subroutine GET_SO_FROM_GENER (ISystm, ISymCe, IBravl, NG, SS, TS, LatSy, CO, Num_G, SpaceGen)

Calculates the whole set of symmetry operators from a set of given generators

sginfo

http://cci.lbl.gov/sginfo/

```
% sginfo -Hall "-F 4y 2" -Standard

Setting A:
Hall Symbol  -F 4y 2
Point Group  4/mmm
Laue  Group  4/mmm
Tetragonal
Unique Axis  y
Order    64
Order P  16
s.i.Vector  Modulus
  1  1  1   2

Setting B:
Space Group  139  D4h^17  I4/mmm  -I 4 2
Point Group  4/mmm
Laue  Group  4/mmm
Tetragonal
Unique Axis  z
Order    32
Order P  16
s.i.Vector  Modulus
  0  0  1   2

Change of Basis Setting A -> Setting B:
 CBMx = x+z, x-z, y
InvCBMx = 1/2*x+1/2*y, z, 1/2*x-1/2*y
```

Bilbao crystallographic server

Generators of the Group 14 ($P2_1/c$) [unique axis b]

No.	(x,y,z) form	Matrix form	Symmetry operation	
			ITA	Seitz
1	x,y,z	$\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix}$	1	{ 1 | 0 }
2	-x,y+1/2,-z+1/2	$\begin{pmatrix} -1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 1/2 \\ 0 & 0 & -1 & 1/2 \end{pmatrix}$	2 (0,1/2,0) 0,y,1/4	{ 2_{010} | 0 1/2 1/2 }
3	-x,-y,-z	$\begin{pmatrix} -1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & -1 & 0 \end{pmatrix}$	-1 0,0,0	{ -1 | 0 }

Links

How to read (and understand) Volume A of International Tables for Crystallography: an introduction for nonspecialists

Zbigniew Dauter and Mariusz Jaskolski *J. Appl. Cryst.* (2010) **43**, 1150-1171.

sginfo http://cci.lbl.gov/sginfo/

Vectors and Tensors in Crystallography, Donald E. Sands (Addison-Wesley, 1982)

Mathematical Techniques in Crystallography and Materials Science, Edward Prince (Springer-Verlag, 1994 – 2nd ed)

International Tables for Crystallography Volume A, IUCr.