Domain structures

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Basic definitions
Crystal pattern vs. crystal structure

An object in the n-dimensional Euclidean space $E^n$ is called an n-dimensional crystallographic pattern or, for short, crystal pattern if among its symmetry operations:

- there are **n translations**, the translation vectors $t_1, \ldots, t_n$ of which are linearly independent;
- all translation vectors, except the zero vector $0$, have a length of at least $d > 0$.

When the crystal pattern consists of **atoms**, it takes the name of crystal structure. The crystal pattern is thus the generalization of a crystal structure to any pattern, concrete of abstract, in any dimension, which obeys the conditions of periodicity and discreteness expressed above.
Crystal structure/pattern vs. crystal lattice

Crystal

Molecule or coordination polyhedron

Crystal pattern (crystal structure)

Unit cell

Lattice nodes

Translations
How a structure differs from a pattern?

An n-dimensional crystal pattern is **periodic** and **homogeneous** in the n-dimensional space. A crystal structure differs from a crystal pattern because of its **atomic nature** and because it is *not rigorously* periodic and homogeneous.

The departure of a crystal pattern from the ideal features of a crystal pattern is accounted for by the concept of **defects**, which are usually ignored when describing the structure.

The concrete object on which we perform experimental studies is a **real, imperfect crystal**, whereas the model we use to describe it, is an **ideal crystal**.
Ideal crystal:

Perfect periodicity, no static (vacancies, dislocations, chemical heterogeneities, even the surface!) or dynamic (phonons) defects.

Real crystal:

A crystal whose structure differs from that of an ideal crystal for the presence of static or dynamic defects.

Perfect crystal:

A real crystal whose structure contains only equilibrium defects.

Imperfect crystal:

A real crystal whose structure contains also non-equilibrium defects (dislocations, chemical heterogeneities...).
What do we get from a (conventional) diffraction experiment?

**Time and space averaged structure!**

*“Time-averaged” because the time span of a diffraction experiment is much larger than the time of an atomic vibration.*

The instantaneous position of an atom is replaced by the envelop (most often an ellipsoid) that describes the volume spanned by the atom during its vibration.

*“Space-averaged” because a conventional diffraction experiment gives the average of the atomic position in the whole crystal volume, which corresponds to “the” position of the atom only if perfect periodicity is respected.*

**Importance of studying the “ideal” crystal**

**Domains are defects that cannot be ignored but must be accounted for!**
Isomorphic substitution and substitutional disorder

figure drawn with VESTA (http://jp-minerals.org/vesta/en/)
Isomorphic substitution and substitutional disorder

figure drawn with VESTA (http://jp-minerals.org/vesta/en/)
Domain structures

Domain structures are heterogeneous structures composed of homogeneous regions, called (you guess it!).... domains!

A homogeneous structure

A heterogeneous structure composed of two domain states (variants), occurring as N domains physically separated in space
Types of domain states

Depending on the type of heterogeneity, domain states can be classified as follows:

- **chemical domains**: the domain states differ for their chemical composition;
- **ferroelectric domains**: the domain states differ for the direction of the polarization vector;
- **magnetic domains**: the domain states differ for the orientation of the magnetic dipole moments;
- **translation domains**: the domain states differ for their relative position, not related by a translation vector of the structure;
- **orientation domains**: the domain states differ for their relative orientation, not related by a (proper or improper) rotation operation of the structure.
Domain structures in which the chemical composition of the domain states may or may not bear a crystallographic relation between the domain states. If no such relation exists, the domain structure is called a **polycrystal** (*bicrystal* if only two domain states exist). Otherwise, the domain structure is called:

- **Epitaxy**, in case of overgrowth;
- **Metataxy/Syntaxy**, in case of intergrowth.

Chemical domains may form by:

- **Topotaxy**, when a phase has grown on/in the other such that dimensional and structural correspondences in the three axial directions exist;
- **Exsolution**, when a solid solution becomes thermodynamically unstable and separates in two (or more) phases.
Chemical domains: example of exsolution

Goldschmidt rules: two ions can substitute in the same site if their charge does not differ by more than one unity and if their ionic radius does not differ by more 15%; between 15% and 30% the substitution is partial.

Na$^+$: ionic radius 1 Å
K$^+$: ionic radius 1.33 Å
Ca$^{2+}$: ionic radius 1 Å
Any atom in a crystal structure above 0K is not at rest but vibrates about its equilibrium position. The volume spanned by an atom depends on:

- the **size** of the atom;
- the **mass** of the atom;
- the **temperature**.

In general, lighter atoms vibrate more than heavy atoms. At higher temperature, the volume spanned by lighter atoms approach that spanned by heavy atoms. At lower temperature, the difference in the volumes spanned by different atoms increases.

When the temperature decreases, atoms that substituted without difficulty can no longer share the same site and move away (separate) to produce domains (typically, exsolution lamellae).
Chemical domains: example of exsolution

- K/Na anywhere
- Long distance
- Huge kinetic barrier, never realized

- Short distance
Example of perthites (K/Na lamellae), TEM image

source: www.geo.arizona.edu/xtal/geos306/perthite.gif
Example of magnetic domains

Microcrystalline grains within a piece of NdFeB (the alloy used in neodymium magnets) with magnetic domains made visible with a Kerr microscope. The domains are the light and dark stripes visible within each grain.

source: https://upload.wikimedia.org/wikipedia/commons/b/b4/NdFeB-Domains.jpg
Antiphase domains

figure drawn with VESTA (http://jp-minerals.org/vesta/en/)
Antiphase domains

figure drawn with VESTA (http://jp-minerals.org/vesta/en/)

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Antiphase domains

figure drawn with VESTA (http://jp-minerals.org/vesta/en/)
The operation mapping the orientation of one domain state onto that of another domain state is a **crystallographic** operation not belonging to the point groups of the domains

- Oxygen
- Carbon
- Ca above the CO$_3$ plane
- Ca below the CO$_3$ plane

Aragonite, CaCO$_3$, twinned on (110)

$$H_i = \text{point group of the } i\text{-th domain state } D_i$$

$$\varphi_i = \text{operation mapping } D_1 \rightarrow D_i$$

$$H_i = \varphi_i H_1 \varphi_i^{-1}$$
Indices of directions and planes
Coordinates of lattice nodes, direction indices \([uvw]\)

Use the coordinates of the first node after the origin as indices of direction.

- \([01w]\)
- \([13w]\)
- \([10w]\)
- \([11w]\)
Planes passing through lattice nodes are called "rational planes".

The values $h$, $k$ and $l$ are called the **Miller indices** of the lattice plane and give its orientation. All lattice planes in the same family have the same orientation. → $(hkl)$ represents the whole family of lattice planes.

Parametric equation of the plane:

$$\frac{x}{p} + \frac{y}{q} + \frac{z}{r} = 1$$

$$(qr)x + (pr)y + (pq)z = pqr$$

$$hx + ky + lz = m$$

Making $m$ variable, we obtain a family of lattice planes, $(hkl)$, where $h$, $k$ and $l$ are called the Miller indices.

First plane of the family $(hkl)$ for $m = 1$

$$hx + ky + lz = 1$$

Intercepts of the first plane of the family $(hkl)$ on the axes

$$p = \frac{pqr}{qr} = \frac{m}{qr} = \frac{1}{h}$$

$$q = \frac{pqr}{pr} = \frac{m}{pr} = \frac{1}{k}$$

$$r = \frac{pqr}{pq} = \frac{m}{pq} = \frac{1}{l}$$
Dual spaces
In crystallography we constantly switch between two spaces that are one the dual of the other.

A is the dual of B if when $\mathcal{T}$ transforms A to B, then $\mathcal{T}^{-1}$ transforms B to A.

![Diagram showing the relationship between direct and reciprocal spaces and their respective transforms.](image-url)
Direct and reciprocal lattice

Direct lattice vectors: \( \mathbf{a}, \mathbf{b}, \mathbf{c}: \mathbf{v}_i, i = 1, 3 \)

Reciprocal lattice vectors: \( \mathbf{a}^*, \mathbf{b}^*, \mathbf{c}^*: \mathbf{v}_i^*, i = 1, 3 \)

\[
\mathbf{v}_i \cdot \mathbf{v}_j^* = \delta_{ij}
\]

\((hkl) \rightarrow [hkl]^* \)

\([uvw] \rightarrow (uvw)^* \)
Probing crystals
How do we get structural information?

Example of Transmission Electron Microscope

Here we get the diffraction pattern

Here we get the image

source: I could not recover it, sorry!
How do we get diffraction?

Elementary idealized model: one-dimensional grid

Spherical waves originate at each point of a periodic grid and interfere positively when their phase differ by an integer number of wavelengths. A difference of $n$ wavelengths corresponds to diffraction of order $n$.

Figure modified after M.J. Burger, X-ray crystallography
Examples of diffraction pattern
How do we interpret a diffraction pattern?

Each diffraction ("spot") is characterized by a position in space and an intensity and is the result of a wave arriving on a recording medium. The wave is obtained by positive interference of the waves scattered by each “scatterer” (atom) in the crystal structure.

A wave is characterized by an amplitude and a phase:

$$a$$

$$\varphi_0$$

$$\varphi(t_0) = \varphi_0$$

$$\varphi(t_0 + \tau) = \varphi_0 + \omega \tau$$

If we know the structure, we can compute amplitude and phase. If we measure the intensity $$I$$, we can compute the amplitude $$A$$ (proportional to $$I^{1/2}$$) but not the phase: we have to “guess” the structure.
A crystal (periodic structure) is described as consisting of two functions ($\mathbf{r}$ is a vector spanning the direct space):

1. the real (direct) **periodic** lattice function $f_L(\mathbf{r})$, which is unity at each lattice node and zero elsewhere;

2. the **finite** electron density function $\rho(\mathbf{r})$, describing the content of a unit cell.

The crystal structure is the convolution of the periodic function $f_L(\mathbf{r})$ and the finite function $\rho(\mathbf{r})$

$$f_C(\mathbf{r}) = f_L(\mathbf{r}) \ast \rho(\mathbf{r})$$

The **Fourier transform** of the crystal structure gives the **diffraction pattern** produced when a radiation with suitable wavelength is sent onto the crystal. It is the product of the Fourier transforms of the lattice and of the unit cell content ($\mathbf{r}^* \text{ is a vector spanning the reciprocal space}$)

$$F_C(\mathbf{r}^*) = T[f_L(\mathbf{r})^* \rho(\mathbf{r})] = T[f_L(\mathbf{r})] \cdot T[\rho(\mathbf{r})] = F_L(\mathbf{r}^*) \cdot F(\mathbf{r}^*)$$

$$F_L(\mathbf{r}^*) = T[f_L(\mathbf{r})] = \frac{1}{V} \sum_{h,k,l=\sim \infty}^\infty \delta(\mathbf{r}^* - \mathbf{r}^*_{hkl}) \quad F(\mathbf{r}^*) = T[\rho(\mathbf{r})] = \sum_{j=1}^N f_j(\mathbf{r}^*) \exp(2\pi i \mathbf{r}^* \cdot \mathbf{r}_j)$$
Fourier transform of the content of the crystal

\[ F_C(r^*) = F_L(r^*) \cdot F(r^*) \]

\[ F_L(r^*) = \frac{1}{V} \sum_{h,k,l=-\infty}^{\infty} \delta(r^* - r_{hkl}^*) \]

\[ F(r^*) = \sum_{j=1}^{N} f_j(r^*) \exp(2\pi ir^* \cdot r_j) \]

atomic nature  \hspace{1cm} atomic positions

zero outside reciprocal lattice nodes

\[ \int F(r^*) \delta(r^* - r_{hkl}^*) dV_{r^*} = F(r_{hkl}^*) = \]

\[ = \sum_{j=1}^{N} f_j(r_{hkl}^*) \exp(2\pi i r_{hkl}^* \cdot r_j) \]

atomic nature \hspace{1cm} diffraction spot positions \hspace{1cm} atomic positions
The phase problem

\[ \sum_{j=1}^{N} f_j (r_{hkl}^*) \exp \left( 2\pi i r_{hkl} \cdot r_j \right) = \]

\[ \sum_{j=1}^{N} f_j (hkl) \cos 2\pi (hkl | xyz) + i \sum_{j=1}^{N} f_j (hkl) \sin 2\pi (hkl | xyz) = \]

\[ A(hkl) + iB(hkl) = |F(hkl)| \exp \left[ i\phi(hkl) \right] \]

Amplitude Phase

\[ I(hkl) \propto |F(hkl)|^2 \]

The information on the phase is not retrieved from a diffraction experiment!
Effect of translation on Fourier Transform

\[ \rho_T(r) = \rho(r-t) \quad t = \text{translation vector} \quad F_T(r^*) = T[\rho_T(r)] \]

\[ F_T(r^*) = \int \rho(r - t) \exp(2\pi ir^* \cdot r) dV_r = \]

\[ = \exp(2\pi ir^* \cdot t) \int \rho(r - t) \exp(2\pi ir^* \cdot r - t) dV_r = \]

\[ = F(r^*) \exp(2\pi ir^* \cdot t) \]

Translation of \( \rho(r) \) by a vector \( t \) in direct space is equivalent to modifying the Fourier transform by the phase factor \( \exp(2\pi ir^* \cdot t) \) in reciprocal space, without change in the modulus \( |F(r^*)| \), but the real and imaginary part of \( F(r^*) \) are multiplied by \( \cos(2\pi r^* \cdot t) \) and \( \sin(2\pi r^* \cdot t) \) respectively. A description of a transform is thus origin dependent.
How can we see domain states?

\[ F_T (r^*) = F (r^*) \exp (2\pi i r^* \cdot t) \]

\[ I(hkl) \propto |F(hkl)|^2 \]

- **Twin domains** (differing by orientation)
  - *Visible* in the diffraction pattern, which shows the overlap of two (or more) lattices differently oriented.

- **Antiphase domains** (differing by position)
  - *Invisible* in the diffraction pattern (effect on the *phase*)
  - *Visible* by electron microscopy

- **Translationengleiche** subgroup (same lattice, lower point group)
- **Klassengleiche** subgroup (sublattice, same point group)
Transformation domains. Driving force: symmetry change following a phase transition.

Group-subgroup relation:

- **High-symmetry (parent) phase**
  - \( i = \frac{|G|}{|H|} = \text{No. of domain states} \)
  - \( i = i_p i_L, \ i_p = \text{index of the point group}, \ i_L = \text{index of the sublattice} \)
  - \( i_p = \text{number of twin domain states} \)
  - \( i_L = \text{number of antiphase domain states} \)

- **Low-symmetry (daughter) phase**
Mechanical domains. Driving force: the application of an external force

Result: twins or parallel growths. In general, no precise symmetry relation between the original crystal and the resulting domain structure.
Growth domains. Driving force: the “randomness” (errors in crystal growth or coalescence of nano or macrocrystals).

Result: twins or parallel growths. No symmetry relation between the single crystal and the oriented attachment.

For the formation of the twin, the of the interface is important: a substructure must continue, precisely or approximately, across the interface.
Twinning
Reticular classification of twinning

- Twinning is governed by the structural match at the interface of the individuals.

- To study this structural match means to investigate twins case by case.

- The reticular theory abstracts from the structure and concentrates on the lattice.

- This approach is reasonable, although approximate, because the lattice represents the periodicity of the structure.

- A good lattice match is a necessary, although not sufficient, condition for a good structural match.
Probability occurrence of twins in term of the reticular theory

- A twin is a “mistake” or a “compromise”.
- A coherent or semi-coherent interface is necessary for a twin to form.
- The better is the “atomic restoration” the higher is the probability that a twin occurs.
- The analysis of the atomic restoration reduces the study of twins almost to a “case-by-case” investigation.
- The reticular theory allows a general approach in terms of lattice restoration as a necessary (not sufficient) condition.
- We need parameters to evaluate the degree of lattice restoration: these are the twin index and the obliquity.
Twinning by merohedry

All nodes are restored by the twin operation: we say that the twin index is $n = 1$
All nodes are quasi-restored by the twin operation: we say that the twin index is $n = 1$.
Definition of obliquity
Twinning by reticular merohedry

One node out of three is restored by the twin operation: we say that the twin index is $n = 3$
Twinning by reticular pseudo-merohedry

One node out of three is quasi-restored by the twin operation: we say that the twin index is $n = 3$.
The twin lattice is the sublattice common to the twinned domain states based on the twin element (plane, axis) and the (quasi)-perpendicular lattice element (direction, plane).

Let us see how to compute the cell parameters of the twin lattice.
Covariant and contravariant quantities

Rotation of the red vector by 20º counterclockwise

Covariant quantities change like the basis and are written as row matrices

\[
\begin{pmatrix}
abc \\
hkl
\end{pmatrix}
\]

Contravariant quantities change like the vector and are written as column matrices

\[
\begin{pmatrix}
a^* \\
b^* \\
c^*
\end{pmatrix}
\begin{pmatrix}
x \\
y \\
z
\end{pmatrix}
\begin{pmatrix}
u \\
v \\
w
\end{pmatrix}
\]
Classical (Cartesian) expression of the dot (inner, scalar) product

\[ \mathbf{r}_1 \cdot \mathbf{r}_2 = ||\mathbf{r}_1|| \cdot ||\mathbf{r}_2|| \cos \varphi \]

\[ \mathbf{r}_1 \cdot \mathbf{r}_2 = x_1 x_2 + y_1 y_2 + z_1 z_2 = (x_1 \quad y_1 \quad z_1) \begin{pmatrix} x_2 \\ y_2 \\ z_2 \end{pmatrix} = (x_1, y_1, z_1) \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x_2 \\ y_2 \\ z_2 \end{pmatrix} = (x_1, y_1, z_1) \begin{pmatrix} i \\ j \\ k \end{pmatrix} \begin{pmatrix} x_2 \\ y_2 \\ z_2 \end{pmatrix} \]

\[ \mathbf{r}_1^T \cdot \mathbf{r}_2 \]
General expression of the dot product

$$r_1 \cdot r_2 = ||r_1|| \cdot ||r_2|| \cos \phi$$

$$r_1^T \cdot r_2 = (x_1 \ y_1 \ z_1) \begin{pmatrix} a & b & c \\ x_2 \\ z_2 \end{pmatrix} = (x_1 \ y_1 \ z_1) \begin{pmatrix} a \cdot a & a \cdot b & a \cdot c \\ b \cdot a & b \cdot b & b \cdot c \\ c \cdot a & c \cdot b & c \cdot c \end{pmatrix} \begin{pmatrix} x_2 \\ y_2 \\ z_2 \end{pmatrix}$$

Because the dot product is commutative, the metric tensor is symmetric w.r.t. the main diagonal

---

Metric tensor
Unit cell transformation

\[
(a \ b \ c) P = (a' \ b' \ c')
\]

\[
G' = \begin{pmatrix} a' \\ b' \\ c' \end{pmatrix} (a' \ b' \ c') = P^t \begin{pmatrix} a \\ b \\ c \end{pmatrix} (a \ b \ c) P = P^t G P
\]

\[
P = \begin{bmatrix}
    a'_{\ a} & b'_{\ a} & c'_{\ a} \\
    a'_{\ b} & b'_{\ b} & c'_{\ b} \\
    a'_{\ c} & b'_{\ c} & c'_{\ c}
\end{bmatrix}
\]

But check the determinant!
In reciprocal space

\[
P^* t \left( \begin{array}{c} a^* \\ b^* \\ c^* \end{array} \right) = \left( \begin{array}{c} a'^* \\ b'^* \\ c'^* \end{array} \right)
\]

\[
G'^* = \left( \begin{array}{ccc} a'^* \\ b'^* \\ c'^* \end{array} \right)
\]

\[
= P^* t \left( \begin{array}{ccc} a^* \\ b^* \\ c^* \end{array} \right) \left( \begin{array}{ccc} a^* & b^* & c^* \end{array} \right) P^* = P^* t G^* P^* 
\]

\[
v_i \cdot v^*_j = \delta_{ij} \quad \rightarrow \quad G^* = G^{-1}
\]

\[
G'^* = G'^{-1} = (P^t G P)^{-1} = P^{-1} G^{-1} P^{-1} = P^{-1} G^* P^{-1, t}
\]

\[
P^* = P^{-1, t}
\]
Twin lattice metric tensor

\[(a\ b\ c)P = (a'\ b'\ c')\]

\[G' = \begin{pmatrix} a' \\ b' \\ c' \end{pmatrix} (a'\ b'\ c') = P^t \begin{pmatrix} a \\ b \\ c \end{pmatrix} (a\ b\ c)P = P^tGP\]

\[P = \begin{pmatrix} u_{1,hkl} & u_{2,hkl} & u_{\perp} \\ v_{1,hkl} & v_{2,hkl} & v_{\perp} \\ w_{1,hkl} & w_{2,hkl} & w_{\perp} \end{pmatrix}\]

\[[u_{1,hkl} v_{1,hkl} w_{1,hkl}] and [u_{2,hkl} v_{2,hkl} w_{2,hkl}] are contained in (hkl) (choose the shortest!)\]

\[[u_{\perp} v_{\perp} w_{\perp}] is the direction quasi-perpendicular to (hkl)\]
Plane of the family \((hkl)\) which passes through the origin:

\[hx + ky + lz = 0\]

Lattice row \([uvw]\): it passes through the origin and the lattice node \(uvw\).

For the lattice node \(uvw\) to be contained in the plane \((hkl)\) the equation of the plane that passes through the origin must be satisfied for \(x = u, y = v\) et \(z = w\):

\[hu + kv + lw = 0\]
How to find the direction $[uvw]$ quasi-perpendicular to $(hkl)$?

Easy! Find the irrational expression of $[hkl]^*$ in direct space

How?
Easy!

Find \(u, v, w\) (in general non-integer) satisfying:

\[
\begin{pmatrix}
a^* \\
b^* \\
c^*
\end{pmatrix} =
\begin{pmatrix}
a \\
b \\
c
\end{pmatrix}
\begin{pmatrix}
hkI \\
b^* \\
c^*
\end{pmatrix} =
\begin{pmatrix}
a^* \\
b* \\
c^*
\end{pmatrix} =
\begin{pmatrix}
a \\
b \\
c
\end{pmatrix}
\]

\[
\begin{pmatrix}
a^* \\
b^* \\
c^*
\end{pmatrix} =
\begin{pmatrix}
a \\
b \\
c
\end{pmatrix}
\begin{pmatrix}
hkI \cdot G^* \cdot G \\
b^* \\
c^*
\end{pmatrix} =
\begin{pmatrix}
a \\
b \\
c
\end{pmatrix}
\]

\[
\begin{pmatrix}
a \\
b \\
c
\end{pmatrix}
\begin{pmatrix}
ahkI \cdot G^* \\
abc \\
c^*
\end{pmatrix} =
\begin{pmatrix}
a \\
b \\
c
\end{pmatrix}
\]

\[
\begin{pmatrix}
v_i \\
v_j \\
v_k
\end{pmatrix} \cdot \begin{pmatrix}
v_i^* \\
v_j^* \\
v_k^*
\end{pmatrix} = \delta_{ij}
\]
Easy!

Find \( u, v, w \) (in general non-integer) satisfying:

\[
(hkl) G^* \begin{pmatrix}
a \\
b \\
c \\
\end{pmatrix} 3 = (uvw) \begin{pmatrix}
a \\
b \\
c \\
\end{pmatrix}
\]

\[
[hkl] G^* = [uvw]
\]

and of course... \((uvw) G = (hkl)\)
Example: Hausmannite, $\text{Mn}_3\text{O}_4$

\[ a = b = 5.7574, \, c = 9.4239 \, \text{Å}, \, \alpha = \beta = \gamma = 90^\circ \]

Bravais-lattice type: \(I\)

Twin plane: (112)

Directions in the plane: \(1u + 1v + 2w = 0\)

Solutions:

\[[1\bar{1}0]\]

\[[11\bar{1}]\] Lattice nodes on this direction

\(000, \, \frac{1}{2}\frac{1}{2}\frac{1}{2}, \, 11\bar{1}, \, \text{etc.}\)
Example: Hausmannite, $\text{Mn}_3\text{O}_4$

\[ a = b = 5.7574, \ c = 9.4239 \ \text{Å}, \ \alpha = \beta = \gamma = 90^\circ \]

Bravais-lattice type: $I$

Twin plane: $(112)$

Direction (quasi)-perpendicular to the plane:

\[ [hkl]^* G^* = [uvw] \]

\[
G = \begin{pmatrix}
a^2 & 0 & 0 \\
0 & a^2 & 0 \\
0 & 0 & c^2
\end{pmatrix}
\]

\[
G^* = \begin{pmatrix}
\frac{1}{a^2} & 0 & 0 \\
0 & \frac{1}{a^2} & 0 \\
0 & 0 & \frac{1}{c^2}
\end{pmatrix}
\]

\[ [112]^* G^* = [a^2 a^2 2c^2] = [0.030168 0.030168 0.02252] \]

\[ = [1.34 1.34 1] \sim [443] \]
Example: Hausmannite, $\text{Mn}_3\text{O}_4$

$$a = b = 5.7574 \text{ Å, } c = 9.4239 \text{ Å, } \alpha = \beta = \gamma = 90^\circ$$ Bravais-lattice type: $I$

Twin plane: (112)

Cell parameters of the twin lattice

$$\textbf{G}' = \textbf{P}'\textbf{G}\textbf{P}$$

$$\textbf{P} = \begin{pmatrix} 4 & 1 & \frac{1}{2} \\ 4 & -1 & \frac{1}{2} \\ 3 & 0 & \frac{1}{2} \end{pmatrix}$$

Determinant = 7 > 0

$$\textbf{G}' = \begin{pmatrix} 4 & 4 & 3 \\ 1 & -1 & 0 \\ \frac{1}{2} & \frac{1}{2} & -\frac{1}{2} \end{pmatrix} \begin{pmatrix} a^2 & 0 & 0 \\ 0 & a^2 & 0 \\ 0 & 0 & c^2 \end{pmatrix} \begin{pmatrix} 4 & 1 & \frac{1}{2} \end{pmatrix} = \begin{pmatrix} 32a^2 + 9c^2 & 0 & 4a^2 - 3c^2/2 \\ 0 & 2a^2 & 0 \\ 4a^2 - 3c^2/2 & 0 & a^2/2 + c^2/4 \end{pmatrix}$$

$$a_T = (32a^2 + 9c^2)^{\frac{1}{2}} = 43.128 \text{ Å}$$

$$b_T = a(2)^{\frac{1}{2}} = 8.142 \text{ Å}$$

$$c_T = (a^2/2 + c^2/4)^{\frac{1}{2}} = 6.227 \text{ Å}$$

$$\beta_T = \cos^{-1}[(4a^2 - 3c^2/2)/(a_Tc_T)] = 90.13^\circ$$
Chromatic symmetry
The idea of “colour change”

Identity  Reflection  Anti-identity  Anti-reflection
Operations mapping a domain state onto itself are “achromatic” (colour-preserving) operations.

Operations mapping a domain state onto another domain state are “chromatic” (colour-changing) operations.

- White → white, black → black: achromatic operations
- White ↔ black: chromatic operations

Symmetry of the domain structure: dichromatic group
Chromatic operations and domain structures

Symmetry of the domain structure: quadrichromatic group

- Antiphase domains: chromatic translations
- Twin domains: chromatic (proper or improper) rotations
- General domains: both types of chromatic operations
Symmetry of a twin

- H*: intersection group of the point groups of the individuals
- **Dichromatic** crystallographic point groups: Shubnikov groups $K^{(2)}$
- **Polychromatic invariant** extension of crystallographic point groups: Koptsik groups $K^{(p>2)}$
- **Polychromatic non-invariant** extension of crystallographic point groups: Van der Waerden-Burckhardt groups $K_{WB}^{(p>2)}$
Exercise

(120) twinning in melilite, $H = \overline{42}m$

$H_1$ $H_2$

$H^* = 4$

$K = \overline{42}'m'$

$K \approx H$
Example of dichromatic (Shubnikov) $K^{(2)}$ groups

$H^* = 2$

$K^{(2)} = 2/m'$

$H^* = 2$

$K^{(2)} = 2'22'$
Three $K^{(2)}$ groups corresponding to the same holohedral achromatic group

$H^* = 422$

$H^* = \overline{4}2m$

$H^* = 4/m$

$K^{(2)} = 4/m'2/m'2/m'$

$K^{(2)} = 4/m'2/m'2'/m$

$K^{(2)} = 4/m2'/m'2'/m'$
Obtain the possible $K^{(2)}$ from the given $H^*$

$H^* = 3m1$

$K^{(2)} = \bar{3}'2'/m$

$K^{(2)} = \bar{6}'m2'$

$K^{(2)} = 6'mm'$
(210) twinning in hauynye, $H = \overline{4}3m$

Twinning by reticular merohedry

What is the twin index?

$K \subset H$

$H_1$

$H_2$

$H^* = 4$

$K = \overline{4}2'm'$

$K \subset H$
Example of Koptsik $K^{(p)}$ groups

$H^* = \overline{1}$

$K^{(3)} = \overline{3}^{(3)}$

$H^* = 222$

$K^{(3)} = (23^{(3)})^{(3)}$
Example of Koptsik $K^{(p)}$ groups

$K^{(2)} = 2/m'$

$K^{(2)} = 32'1 \rightarrow K^{(4)} = (6^{(2)} 2^{(2)} 2^{(2)})^{(4)}$
Example of Koptsik $K^{(p)}$ groups

$H^* = 2$

$K^{(2)} = 2/m'$

$K^{(4)} = \left( \frac{2^{(2)}}{m^{(2)}} \frac{2^{(2)}}{m^{(2)}} \frac{2^{(2)}}{m^{(2)}} \right)^{(4)}$

$H^* = 3$

$K^{(2)} = 32'1$

$K^{(4)} = (6^{(2)}2^{(2)}2^{(2)})^{(4)}$

$K^{(8)} = \left( \frac{6^{(2)}}{m^{(2)}} \frac{2^{(2)}}{m^{(2)}} \frac{2^{(2)}}{m^{(2)}} \right)^{(8)}$
Example of Van der Waerden-Burckhardt $K_{WB}^{(p)}$

$H^* = m^2 m$

$K' = \left( \frac{2'}{m}, \frac{2}{m'}, \frac{2'}{m} \right)$

$K_{WB}^{(4)} = \left( \frac{4^{(4)}}{m}, \frac{2^{(2,2)}}{m^{(2,2)}}, \frac{2^{(2)}}{m^{(2)}} \right)^{(4)}$