Domain structures and twinning

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Basic definitions
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
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/)
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.
Antiphase domains

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

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

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

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)

$H_i =$ point group of the i-th domain state $D_i$

$\varphi_i =$ operation mapping $D_1 \rightarrow D_i$

$H_i = \varphi_i H_1 \varphi_i^{-1}$
Twin domains (cont.)

$G_1$ and $G_2$ are of the same type (same Hermann-Mauguin symbol) but are different groups because corresponding symmetry elements are differently oriented in space.

\[
\begin{align*}
\text{t}D_1 &= D_2 \\
D_1 &= t^{-1}D_2 \\
t(g_{1,i}D_1) &= g_{2,j}D_2 \\
tg_{1,i}t^{-1}D_2 &= g_{2,j}D_2 \\
g_{2,j} &= tg_{1,i}t^{-1}, \forall i,j \\
G_2 &= tG_1t^{-1}
\end{align*}
\]

conjugation (a similarity transformation)
How do domains form?

Genetic classification of domains
1 – Transformation domains

Origin: symmetry change under 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
2 – Mechanical domains

Origin: the application of an external force

In general, no precise symmetry relation between the original crystal and the resulting domain structure.
3 – Growth domains

**Origin:** the “randomness” (errors in crystal growth or coalescence of nano, micro or macrocrystals*)

No *a-priori* symmetry relation between the original crystal and the resulting domain structure.

* http://dx.doi.org/10.1127/0935-1221/2004/0016-0401
Classification of subgroups (reminder)

- G and \{1\} are the **trivial subgroups** of G.
- All the other subgroups are called **proper subgroups**.
- Let it be \( G \supset H \). If there is not group intermediate between H and G, then H is called a **maximal subgroup** of G.
- If G and H has all the translations in common, then H is called a **translationengleiche subgroup** (t-subgroup) of G.
- If G and H belong to the same geometric crystal class (have the same point group), then H is called a **klassengleiche subgroup** (k-subgroup) of G.
- Let H be a k-subgroup of G. If G and H belong to the same space-group type (they have the same Hermann-Mauguin symbol), then H is called an **isomorphic subgroup** (i-subgroup) of G.
Reduction of symmetry following a phase transition

Thermodynamic classification of phase transitions (Ehrenfest and Tisza)

First order, second order, lambda....

Buerger’s classification

- Reconstructive
- Displacive
- Order-disorder

Domain structure

- t-subgroup
- k-subgroup
- general subgroup

Orientation domains (twin)
Antiphase domains
Twin and antiphasic

Index: Number of (types of) domains  Cosets: Orientation and position of domains
SrTiO$_3$, perovskite structure type, space-group type $Pm\bar{3}m$

Low-temperature phase (below 105K): octahedra rotation produces lowering of symmetry

$$Pm\bar{3}m \rightarrow I4/mcm$$
$$c \rightarrow 2c$$
$$V \rightarrow 4V \text{ (V: volume of the unit cell)}$$

Following this phase transition:

- Determine the number of twin domain states
- Determine the number of antiphase domain states
- Determine the operation (coset representative) that maps each pair of domain state
Exercise (solution)

\( Pm\bar{3}m \to I4/mcm \)

- \( c \to 2c \)
- \( V \to 4V \)

\[
\begin{pmatrix}
    1 & 1 & 0 \\
    1 & 1 & 0 \\
    0 & 0 & 2
\end{pmatrix} = (a'_1 \ a'_2 \ c')
\]

Determinant 4. BUT \( P \to I \)

\[ i_L = 2 \]

\[ i = i_p \cdot i_L = 3 \cdot 2 = 6 \]

- 6 types of domain states. Taking one as reference:
  - 3 pairs are in twin relation (one trivial)
  - the other 3 are in antiphase relation
Exercise (solution)

Coset decomposition of $Pm\bar{3}m$ in terms of $I4/mcm$ $(a-b, a+b, 2c)$

\[ Pm\bar{3}m = I4/mcm \cup 3^{+}_{[111]} I4/mcm \cup 3^{-}_{[111]} I4/mcm \cup t(100)I4/mcm \cup t(010)I4/mcm \cup t(001)I4/mcm \]
Exercise (solution)

\[ Pm\bar{3}m = I4/mcm \cup 3^{+}_{[111]} I4/mcm \cup 3^{-}_{[111]} I4/mcm \cup t(100)I4/mcm \cup t(010)I4/mcm \cup t(001)I4/mcm \]

- \( D1 \rightarrow D2: 3^{+}_{[111]} \)
- \( D1 \rightarrow D3: 3^{-}_{[111]} \)
- \( D1 \rightarrow D4: t(100) \)
- \( D1 \rightarrow D5: t(010) \)
- \( D1 \rightarrow D6: t(001) \)

- \( D2 \rightarrow D3: (D1 \rightarrow D2)^{-1} \rightarrow D3: 3^{-}_{[111]} \cdot 3^{-}_{[111]} = 3^{+}_{[111]} \)
- \( D2 \rightarrow D4: (D1 \rightarrow D2)^{-1} \rightarrow D4: t(100) \cdot 3^{-}_{[111]} \)
- \( D4 \rightarrow D6: (D1 \rightarrow D4)^{-1} \rightarrow D6: t(001) \cdot t(\bar{1}00) = t(\bar{1}01) \)

etc. etc. etc.
“Seeing” domains
Fourier transform of the content of the crystal

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 ($\mathbf{r}^\ast$ is a vector spanning the reciprocal space)

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

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

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

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

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

atomic nature
atomic positions

zero outside reciprocal lattice nodes

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

\[ = \sum_{j=1}^{N} f_j(\mathbf{r}_{hkl}^*) \exp(2\pi i \mathbf{r}_{hkl}^* \cdot \mathbf{r}_j) \]

atomic nature
diffraction spot positions
atomic positions
The phase problem

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

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

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

Amplitude \hspace{2cm} 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

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

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

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

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

Translation of \( \rho(r) \) by a vector \( t \) in direct space is equivalent to modifying the Fourier transform by the phase factor \( \exp(2\pi i r^* \cdot t) \) 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**
(same lattice, lower point group, differing by orientation)

**Translationengleiche subgroup**
(same lattice, lower point group)

**Antiphase domains**
(sublattice, same point group, differing by position)

**Klassengleiche subgroup**
(sublattice, same point group)

Visible in the diffraction pattern, which shows the overlap of two (or more) lattices differently oriented.

Invisible in the diffraction pattern (effect on the phase)

Visible by electron microscopy
Twinning
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 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.
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).

One node out of $n$ restored by the twin operation: we say that the twin index is $n$ (3 in this example)
Definition of obliquity
Computation of the obliquity

\[ \omega = \cos^{-1} \frac{|hu + kv + lw|}{L^*(hkl)L(uvw)} \]

\[ L^*(hkl)L(uvw)\cos\omega = (hkl) \begin{pmatrix} a^* \\ b^* \\ c^* \end{pmatrix} \begin{pmatrix} u \\ v \\ w \end{pmatrix} = |hu + kv + lw| \]
Effect of the obliquity on the diffraction pattern

- **Split reflections**: Large obliquity
- **Partial overlap**: Small obliquity
- **Complete overlap**: Zero obliquity

Source: Andrea Thorn, Computing School 2011
How to find the direction \([uvw]\) quasi-perpendicular to \((hkl)\) necessary to compute the obliquity?

Easy! Find the irrational expression of \([hkl]^{*}\) in direct space.
Easy!

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

\[
(\begin{array}{c}
hkl \\
b^* \\
c^*
\end{array}) =
(\begin{array}{c}
uvw \\
b \\
c
\end{array})
\]

\[
(\begin{array}{c}
\mathbf{a}^* \\
\mathbf{b}^* \\
\mathbf{c}^*
\end{array}) = (\begin{array}{c}
\mathbf{a} \\
\mathbf{b} \\
\mathbf{c}
\end{array})
\]

\[
(\begin{array}{c}
hkl \\
b^* \\
c^*
\end{array}) \mathbf{G}^* \mathbf{G}
(\begin{array}{c}
\mathbf{a}^* \\
\mathbf{b}^* \\
\mathbf{c}^*
\end{array}) =
(\begin{array}{c}
vw \\
\mathbf{b} \\
\mathbf{c}
\end{array})
\]

\[
(\begin{array}{c}
\mathbf{a} \\
\mathbf{b} \\
\mathbf{c}
\end{array}) (\begin{array}{c}
\mathbf{a}^* \\
\mathbf{b}^* \\
\mathbf{c}^*
\end{array}) = (\begin{array}{c}
vw \\
\mathbf{b} \\
\mathbf{c}
\end{array})
\]

\[
\mathbf{v}_i \cdot \mathbf{v}_j^* = \delta_{ij}
\]
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... $$(uvw) G = (hkl)$$
Basis transformation (general)

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

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

\[
P = \begin{bmatrix}
  a & a'_a & a'_b & a'_c \\
  b & b'_a & b'_b & b'_c \\
  c & c'_a & c'_b & c'_c
\end{bmatrix}
\]

Check the determinant!
Basis transformation (twinning)

$$P = \begin{bmatrix} u_{\perp} & u_1 & u_2 \\ v_{\perp} & v_1 & v_2 \\ w_{\perp} & w_1 & w_2 \end{bmatrix}$$

Direction quasi-perpendicular to \((hkl)\)

\(hx + ky + lz = 0\): \((hkl)\) plane passing through the origin

\([uvw]\): direction passing through nodes 000, \(uvw\), \(2u2v2w\)…. 

\(hu + kv + lw = 0\): condition for the \([uvw]\) direction to be contained in the \((hkl)\) plane
Exercise

Celestine, SrSO$_4$, $Pbnm$ $a = 8.359\text{Å}$, $b = 5.352\text{Å}$, $c = 6.866\text{Å}$

Twinned on (210)
Find the directions quasi-perpendicular to (210) and CHOOSE ONE!

\[
\begin{pmatrix}
\frac{1}{a^2} & 0 & 0 \\
0 & \frac{1}{b^2} & 0 \\
0 & 0 & \frac{1}{c^2}
\end{pmatrix}
= \begin{pmatrix}
0.02862 & 0.03491 & 0
\end{pmatrix}
= \begin{pmatrix}
1 & 1.220 & 0
\end{pmatrix}
\]

$u$ $v$ $v/u$

1 1 1
1 2 2
2 3 1.5
3 4 1.333
4 5 1.25
Calculate the obliquity

\[ \omega = \cos^{-1}\left| hu + kv + lw \right| / L^* (hkl) L(uvw) = \cos^{-1} \sqrt{\left( hkl \right)^* G \left( hkl \right) \left(uvw\right)^* G} \]

<table>
<thead>
<tr>
<th>uvw</th>
<th>( \omega )</th>
</tr>
</thead>
<tbody>
<tr>
<td>110</td>
<td>5.36°</td>
</tr>
<tr>
<td>120</td>
<td>( \times ) 14.03°</td>
</tr>
<tr>
<td>230</td>
<td>5.86°</td>
</tr>
<tr>
<td>340</td>
<td>2.50°</td>
</tr>
<tr>
<td>450</td>
<td>0.69°</td>
</tr>
</tbody>
</table>
Exercise: results

<table>
<thead>
<tr>
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<th>ω</th>
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<tr>
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</tr>
<tr>
<td>230</td>
<td>5.86°</td>
</tr>
<tr>
<td>340</td>
<td>2.50°</td>
</tr>
<tr>
<td>450</td>
<td>0.69°</td>
</tr>
</tbody>
</table>
Summary

<table>
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<th>$uvw$</th>
<th>$\omega$</th>
<th>$n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>110</td>
<td>5.36º</td>
<td>3</td>
</tr>
<tr>
<td>230</td>
<td>5.86º</td>
<td>7</td>
</tr>
<tr>
<td>340</td>
<td>2.50º</td>
<td>5</td>
</tr>
<tr>
<td>450</td>
<td>0.69º</td>
<td>13</td>
</tr>
</tbody>
</table>

Smaller index, larger obliquity
Smaller obliquity, larger index

Which one would you choose? **Both!**
(210) twin in celestine is a hybrid twin

How many lattice nodes in the cell of $L_T$?

10

How many of these belong to the red or blue sublattice?

5

Global lattice restoration due to twinning?

$\frac{10}{5} = 2.0$

Effective twin index
Cell parameters of the twin lattice

\[
(a \ b \ c) \mathbf{P} = (a' \ b' \ c')
\]

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

But check the determinant!

\[
\mathbf{P} = \begin{vmatrix} u_{1,hkl} & u_{2,hkl} & u \perp \\ v_{1,hkl} & v_{2,hkl} & v \perp \\ w_{1,hkl} & w_{2,hkl} & w \perp \end{vmatrix}
\]

\[
\begin{bmatrix} u_{1,hkl} & v_{1,hkl} & w_{1,hkl} \end{bmatrix} \text{ and } \begin{bmatrix} u_{2,hkl} & v_{2,hkl} & w_{2,hkl} \end{bmatrix}
\]

are contained in (hkl)

(choose the shortest!)

\[
\begin{bmatrix} u \perp & v \perp & w \perp \end{bmatrix}
\]

is the direction quasi-perpendicular to (hkl)
Cell parameters of the (210) twin in celestine based on (210)/[340] cell

\[
[u_{1,hkl},v_{1,hkl},w_{1,hkl}] = [001]
\]

\[
[u_{2,hkl},v_{2,hkl},w_{2,hkl}] [120]
\]

\[
[u_{\perp} v_{\perp} w_{\perp}] = [340]
\]

\[
\mathbf{P} = \begin{pmatrix}
0 & 1 & 3 \\
0 & 2 & 4 \\
1 & 0 & 0
\end{pmatrix}
\]

\[|\mathbf{P}| = 10 > 0\]

N.B. \( n = 5 \) but \(|\mathbf{P}| = 10 \). Why?
Cell parameters of the (210) twin in celestine

\[
\begin{pmatrix}
0 & 0 & 1 & a^2 & 0 & 0 & 0 & 1 & 3 \\
1 & 2 & 0 & 0 & b^2 & 0 & 0 & 2 & 4 \\
3 & 4 & 0 & 0 & 0 & c^2 & 1 & 0 & 0
\end{pmatrix}
\]

\[
P^t GP = \begin{pmatrix}
0 & 0 & c^2 & 0 & 1 & 3 \\
a^2 & -2b^2 & 0 & 0 & 2 & 4 \\
3a^2 & 4b^2 & 0 & 1 & 0 & 0
\end{pmatrix} = \begin{pmatrix}
c^2 & 0 & 0 \\
0 & a^2 + 4b^2 & 3a^2 - 8b^2 \\
0 & 3a^2 - 8b^2 & 9a^2 + 16b^2
\end{pmatrix}
\]

\[a_T = c_i = 6.866 \, \text{Å} \quad b_T = 13.581 \, \text{Å} \quad c_T = 32.972 \, \text{Å} \]

\[\alpha_T = \cos^{-1} \frac{3a^2 - 8b^2}{b_T c_T} = \cos^{-1} \frac{-19.533}{13.581 \cdot 32.972} = \]

\[= \cos^{-1} (-0.0436) = 92.50^\circ\]
Twin lattice and pseudo-symmetry of (210) twin in celestine

\[ a_T = 6.866 \text{ Å}; b_T = 13.581 \text{ Å}; \]
\[ c_T = 32.972 \text{ Å}; \alpha_T = 92.50^\circ \]

mA, ψ-oA (easily transformed to mC, ψ-oC)

In twinning, the pseudo-symmetry is often more important than the true symmetry
Now that you know how to do it, let a software do it for you....

http://www.crystallography.fr/lab/geminography/
• Twin Lattice Symmetry (TLS): the restoration of the lattice of the individual (total or partial) is perfect.

• Twin Lattice Quasi-Symmetry (TLS): the restoration of the lattice of the individual (total or partial) is imperfect.

• TLQS only occurs when $\omega \neq 0$ if the twin operation is twofold.

• When the twin operation is a (direct or inverse) rotation of order higher than 2, TLQS may occur also for $\omega = 0$. 
Zero-obliquity TLQS twinning

\[ b \approx c \]

\[ \delta \]

twin misfit

90°