Domain-structure analysis in structural phase transitions

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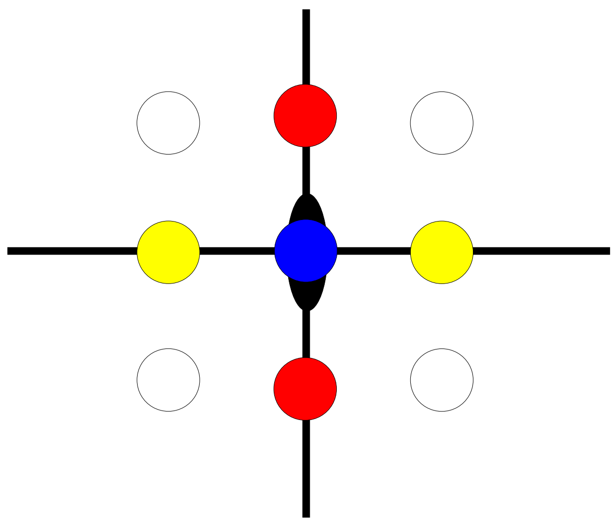
Classification of subgroups

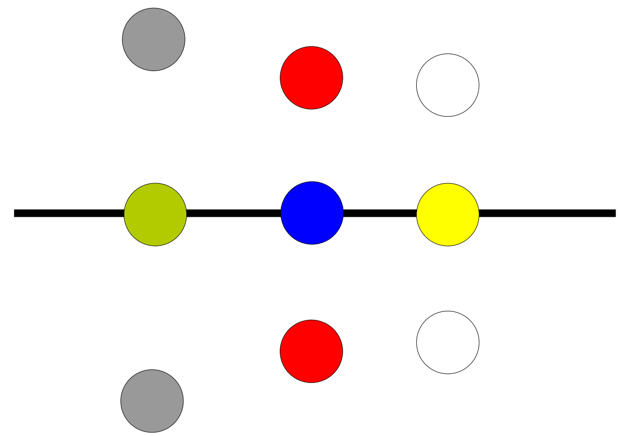
- G itself and {1|000} are the two **trivial subgroups** of G。
- All the other subgroups of G are called **proper subgroups**.
- If H is a proper subgroup of G (G ⊃ H) such that there is no intermediate group between G and H, then H is called a **maximal subgroup** of G.
- If G and H have the same translation subgroup, *i.e*. the same lattice (warning: not just the same ***type*** of lattice!), then H is called a **t-subgroup** (**translationengleiche subgroup**) of G.
- If G and H have the same type of point group (i.e. they belong to the same geometric crystal class), then is called a **k-subgroup** (**klassengleiche subgroup**) of G.
- If H is a k-subgroup of G and is of the same type as G (same Hermann-Mauguin symbol), then H is called an **i-subgroup** （**isomorphic subgroup**） of G.

Effect of the symmetry reduction of Wyckoff positions

G



H ⊂ G



	Multiplicity	Site-symmetry group (s.s.g)
	4	1
	2	*m..*
	2	*.m.*
	1	*mm2*

Splitting

Reduction of s.s.g

		Multiplicity	Site-symmetry group (s.s.g)
		2	1
		1	*m..*
		2	1
		1	*m..*

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Symmetry reduction following a phase transition

Thermodynamic classification of phase transitions (Ehrenfest and Tisza)

First order, second order, lambda...

Mechanistic classification of phase transitions (Buerger)

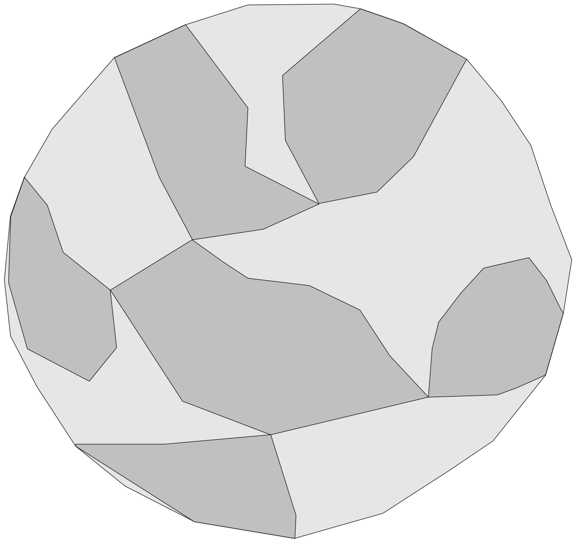
- Reconstructive phase transition (quenchable) (Order-disorder phase transition) → First order
- Displacive phase transition (unquenchable) → First or second order

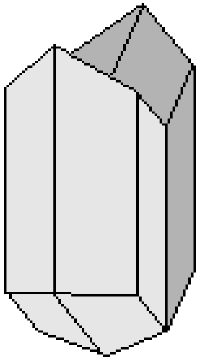
→ Domain structure
- t-subgroup → Orientation domains (twins)
- k-subgroup → Antiphase domains
- general subgroup → Twins AND antiphase domains

Index of subgroup: number of domain states

Cosets: Orientation (twin) and position (antiphase) of the domains

Domains vs. domain states





Two twinned individuals

Two **domain states** (variants)
dark grey: 6 **domains**
light grey: 5 **domains**

Example

$SrTiO_3$ peroskite structure type, space-group type $Pm\bar{3}m$

At low T (below 105 K) the relative rotation of the octahedra results in a phase transition

$$Pm\bar{3}m \rightarrow I4/mcm$$

$$c \rightarrow 2c$$

V → 4V (V is the volume of the unit cell)

Determine the consequences of this phase transition, namely:

The number of domain states

The classification of the domain states (twin, antiphase)

The (representative) operation mapping two domain states

Example (solution)

$Pm\bar{3}m \rightarrow I4/mcm$

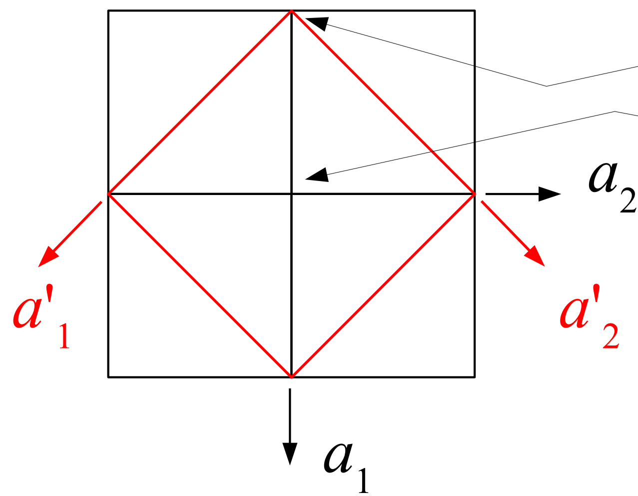
$c \rightarrow 2c$

$\mathrm{V} \rightarrow 4\mathrm{V}$

$z = 0,1,2,3,4\cdots \rightarrow 0,0.5,1,1.5,2\cdots$

0,0.5,1,1.5,2···

0,0.5,1,1.5,2···



$$(\mathbf{a}_1 \quad \mathbf{a}_2 \quad \mathbf{c})\begin{pmatrix} 1 & 1 & 0 \\ \bar{1} & 1 & 0 \\ 0 & 0 & 2 \end{pmatrix} = (\mathbf{a'}_1 \quad \mathbf{a'}_2 \quad \mathbf{c'})$$

Determinant: 4. BUT $P \rightarrow I$

$$\mathrm{i}_\mathrm{L} = 2$$

$$\mathrm{i}_\mathrm{P} = |m\bar{3}m|/|4/mmm| = 48/16 = 3$$

$$\mathrm{i} = \mathrm{i}_\mathrm{P} \cdot \mathrm{i}_\mathrm{L} = 3 \cdot 2 = 6$$

6 domain states

- 3 orientation domain states.
  Representative operation: $3^{+}_{[111]}$ and $3^{-}_{[111]}$
- For each of the three, 2 antiphase domain states.
  Representative operation: t(½½0)

Effect of translation of Fourier Transform

$\rho_T(\mathbf{r}) = \rho(\mathbf{r}-\mathbf{t})$ $\mathbf{t}$ = translation vector $F_T(\mathbf{r}^*) = \mathcal{T}^{-1}[\rho_T(\mathbf{r})]$

$$F_T(\mathbf{r}^*) = \int \rho(\mathbf{r}-\mathbf{t}) \exp(2\pi i \mathbf{r}^* \cdot \mathbf{r}) dV_{\mathbf{r}} =$$

$$= \exp(2\pi i \mathbf{r}^* \cdot \mathbf{t}) \int \rho(\mathbf{r}-\mathbf{t}) \exp(2\pi i \mathbf{r}^* \cdot \mathbf{r} - \mathbf{t}) dV_{\mathbf{r}} =$$

$$= F(\mathbf{r}^*) \exp(2\pi i \mathbf{r}^* \cdot \mathbf{t})$$

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

Diffraction pattern of a domain structure

$$F_T(\mathbf{r}^*) = F(\mathbf{r}^*)\exp(2\pi i\mathbf{r}^*\cdot\mathbf{t})$$

$I(hkl) \propto |F(hkl)|^2$

G group of the parent phase

↓

H group of the daughter phase

translationengleiche subgroup
(same lattice, lower point group)

Twin domains
(differing by orientation)

Visible in the diffraction pattern, which appears as the overlap of the diffraction pattern of each domain state.

klassengleiche subgroup
(sublattice, same point group)

Antiphase domains
(differing by position)

Invisible in the diffraction pattern
(effect on the ***phase***)
Visible by electron microscopy.

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Superlattice vs. sublattice

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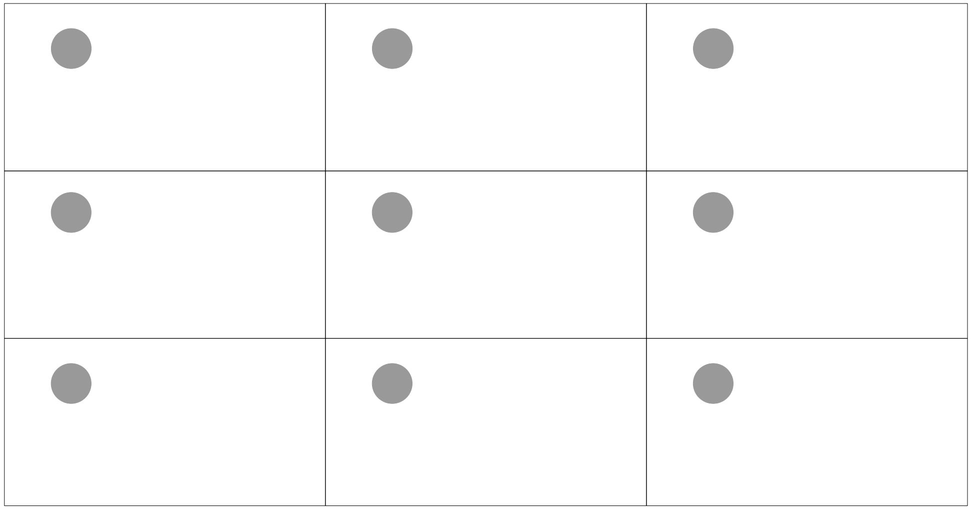


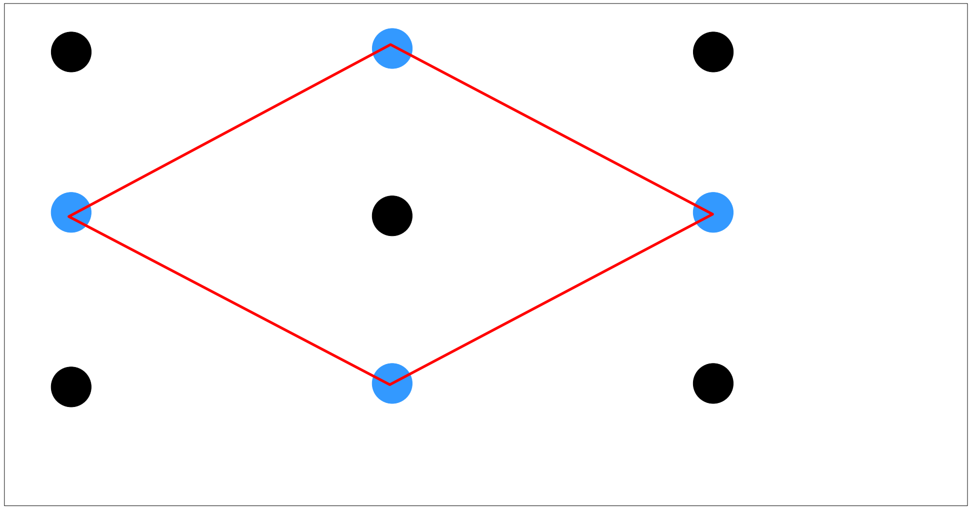
Basic structure (aristotype)
Space-group G
Translation subgroup T(G)

supercell

T(H) is a subgroup of T(G)
→ **sub**lattice

subcell

T(G) is a supergroup of T(H)
→ **super**lattice



Derivative structure (hettotype)
$H \subset G$
$T(H) \subset T(G)$