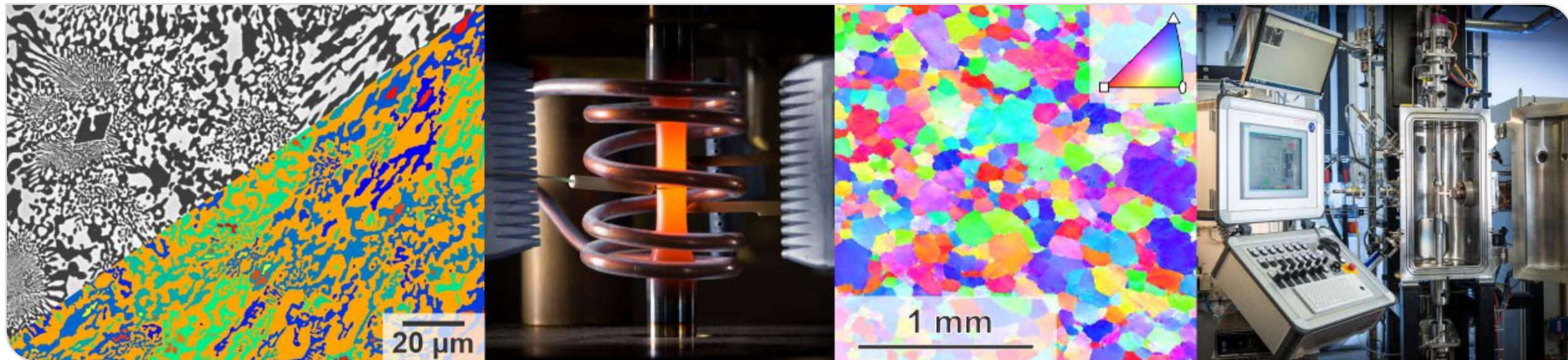


Phase Transformations in Materials

Lecture for “Mechanical Engineering” and “Materials Science and Engineering”
Dr.-Ing. Alexander Kauffmann (Bldg. 10.91, R. 375)
Dr. Sandipan Sen (Bldg. 10.91, R. 311)

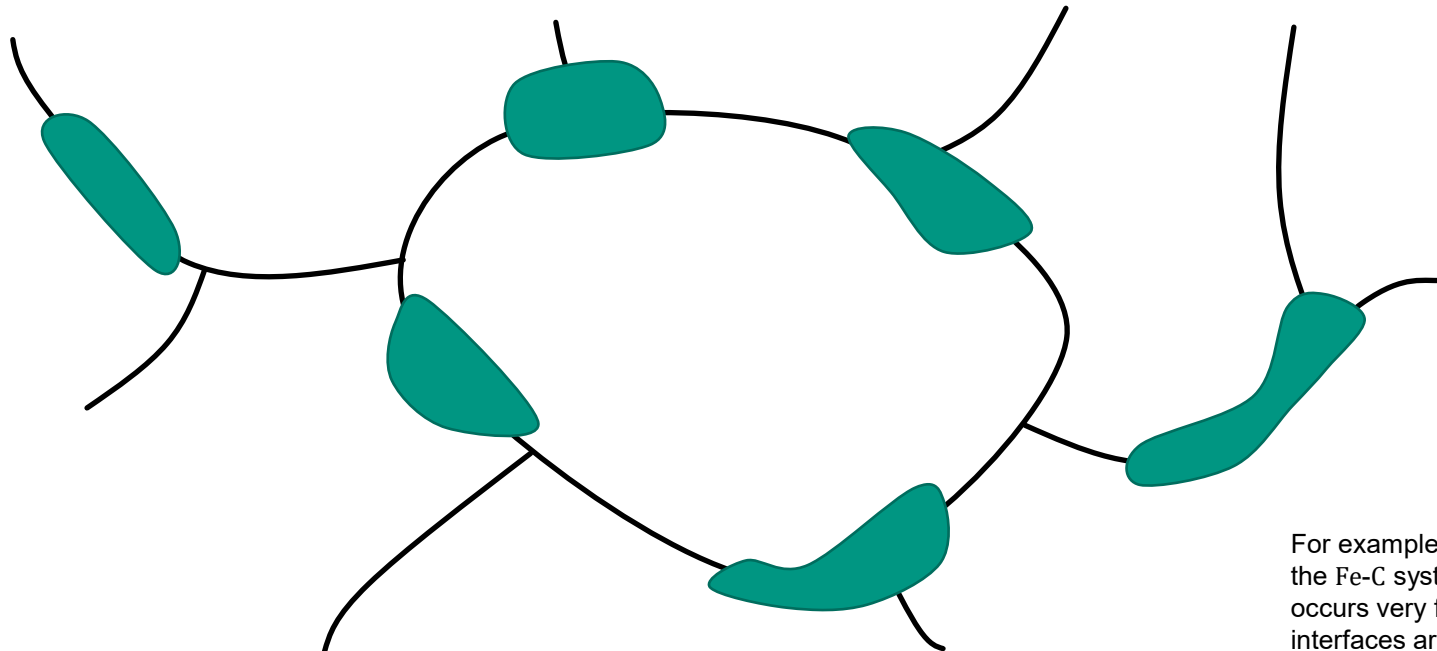
Version 24-01-30



- Solid State Transformations in Multi-Component Systems
 - Precipitation
 - Special Role of Boundaries
 - Allotriomorphs, Intragranular Precipitates and Widmannstätten Microstructure
 - Discontinuous Precipitation
 - Eutectoid Reactions
 - Ordering

Precipitation: Role of Boundaries

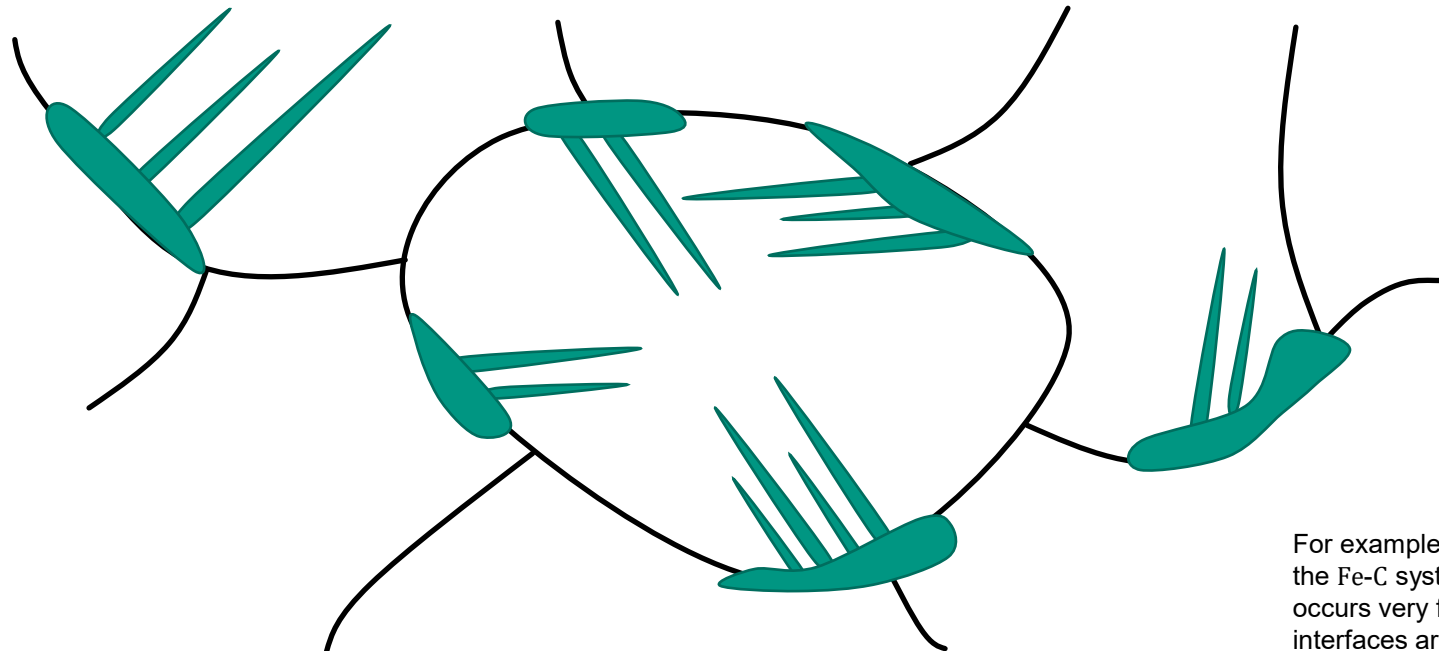
- When metastable, coherent or semi-coherent interfaces are absent, precipitation predominantly occurs via heterogeneous nucleation at grains boundaries.
- For low super cooling and sufficient nucleation sites, the precipitates form in block shape or with facets as seen in the previous slides. These blocks are called allotriomorphs:



For example pro-eutectoid α in γ in the Fe-C system. Since C diffusion occurs very fast, the growth rates of interfaces are decisive.

Precipitation: Role of Boundaries

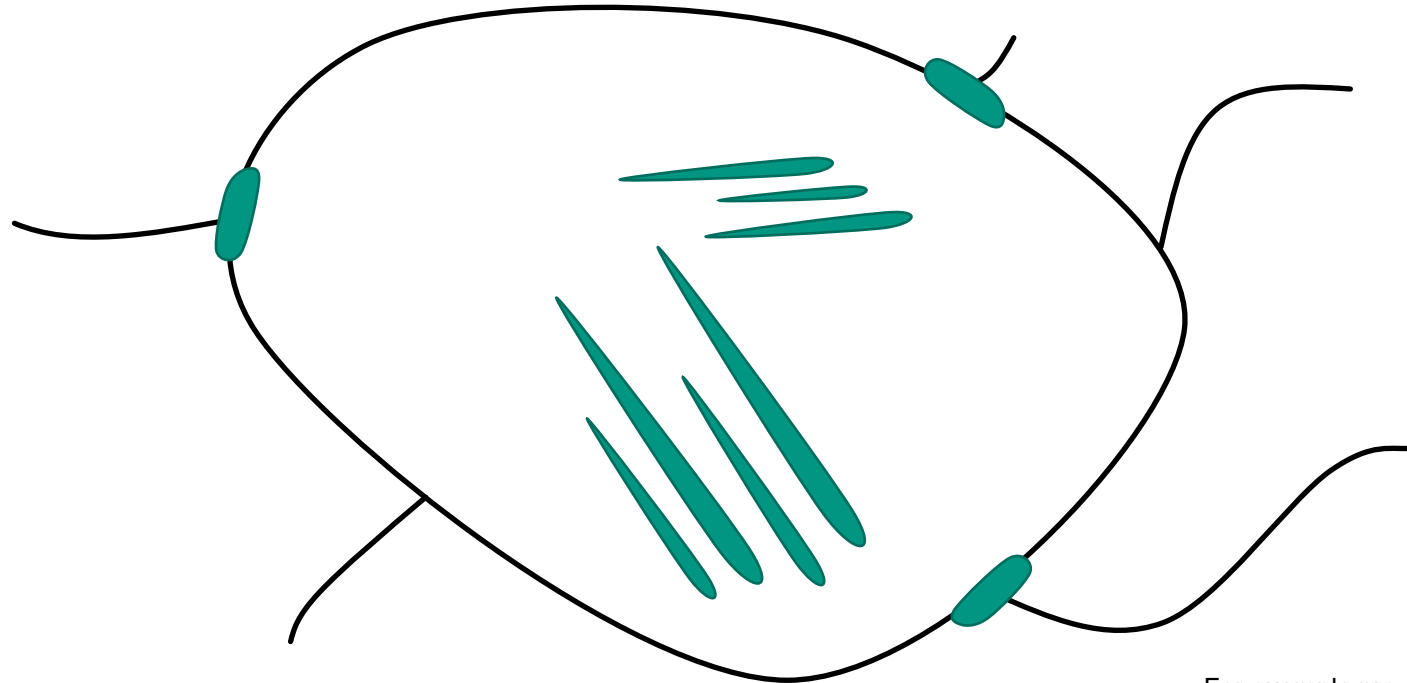
- For greater super cooling and less nucleation sites, the morphology changes to Widmannstätten-like microstructures. Different ratios of the mobility of coherent/semi-coherent and incoherent interface might change, e.g. incoherent interfaces at the tip of the needles is much higher under these circumstances. Further, the minimum tip radius decreases rapidly with increasing super cooling:



For example pro-eutectoid α in γ in the Fe-C system. Since C diffusion occurs very fast, the growth rates of interfaces are decisive.

Precipitation: Role of Boundaries

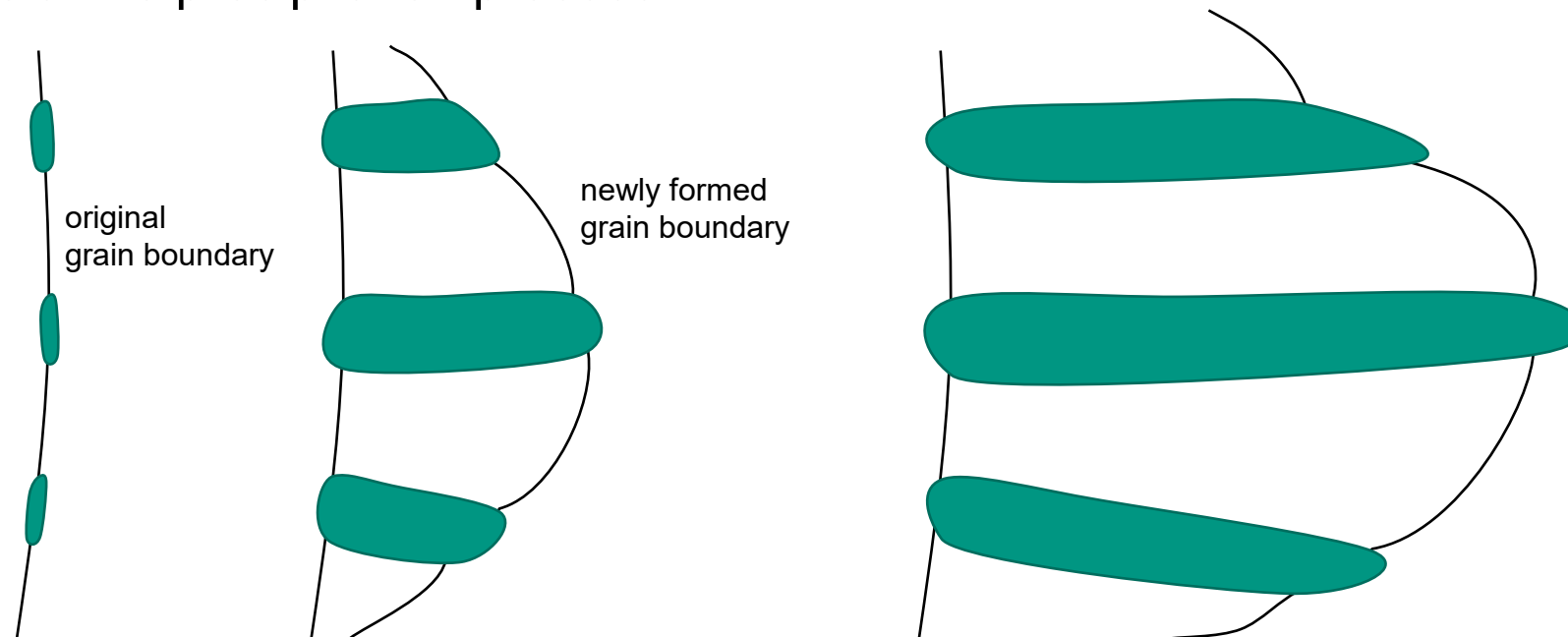
- For even greater super cooling and less nucleation sites by grain coarsening (in conjunction with longer distances to equilibrate composition), intragranular precipitation might occur:



For example pro-eutectoid α in γ in the Fe-C system. Since C diffusion occurs very fast, the growth rates of interfaces are decisive.

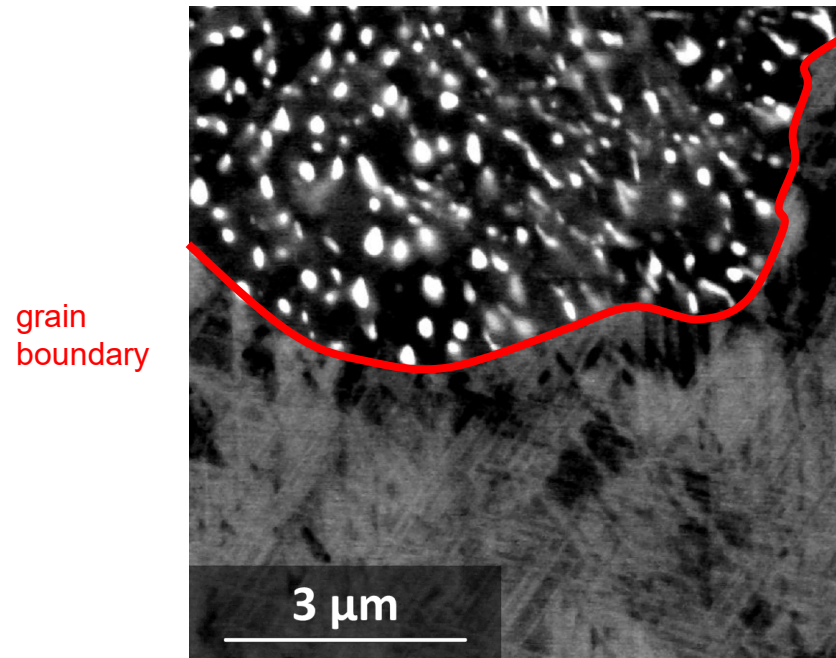
Precipitation: Role of Boundaries

- A special mode of precipitation is the occurrence of cellular precipitation. In literature, it is often referred to as “discontinuous” precipitation (as opposed to “continuous” intragranular precipitates). In this sense, discontinuous does not refer to the thermodynamic aspects as discussed in the lecture! Cellular precipitation is a recrystallization process, in which the moving boundaries assist the precipitation process:

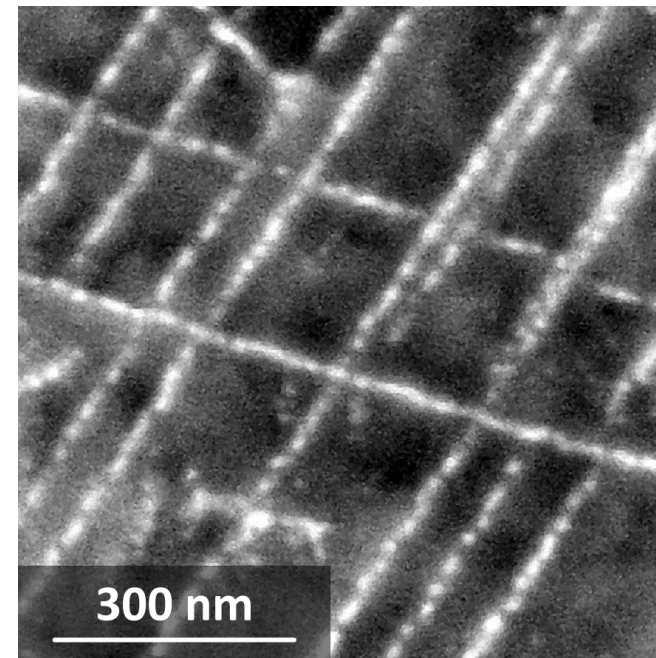


Precipitation: Role of Boundaries

coarse “discontinuous”
precipitated cells



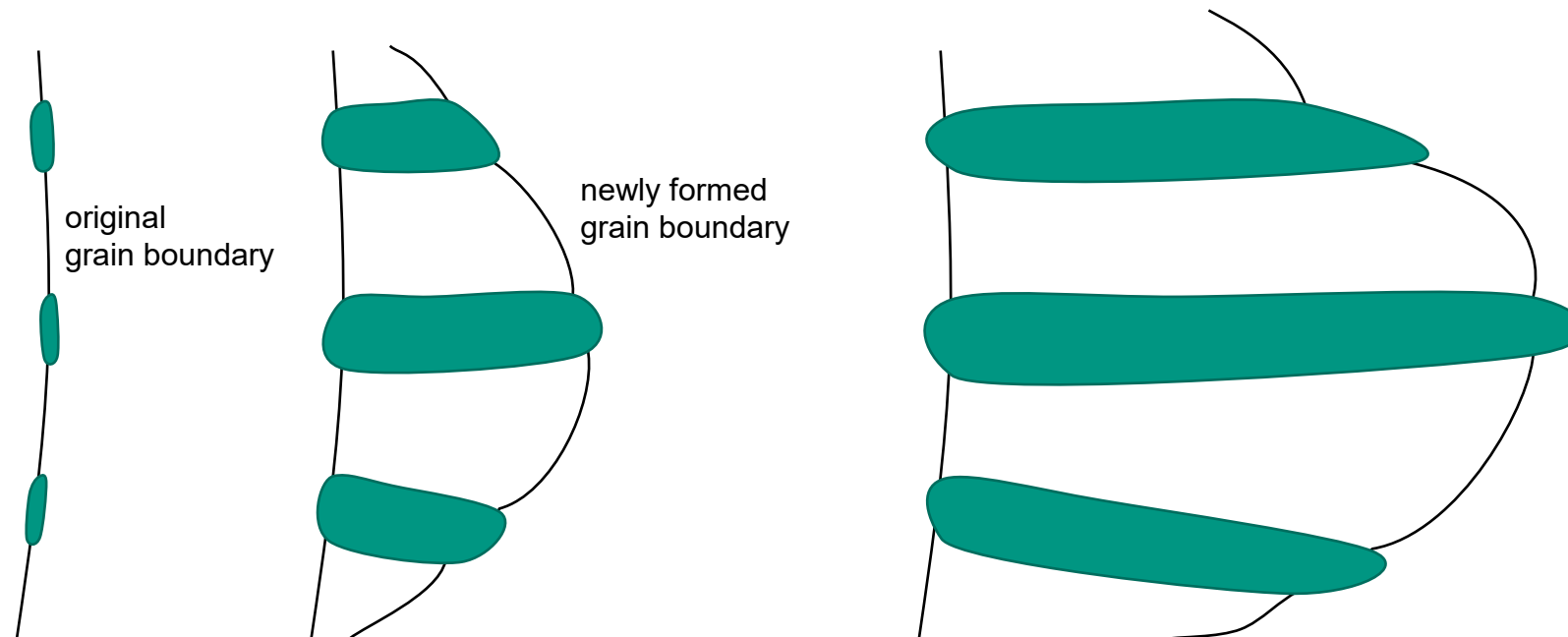
fine “continuous”
precipitates



Comparison of backscattered electron contrast micrographs of cellular and homogenous precipitates in a Cu-Ag-Zr alloy. Dark: Cu-rich solid solution, bright: Ag-rich precipitates. The faint lines in the left micrograph are continuous precipitates. Note the different lengths scales!

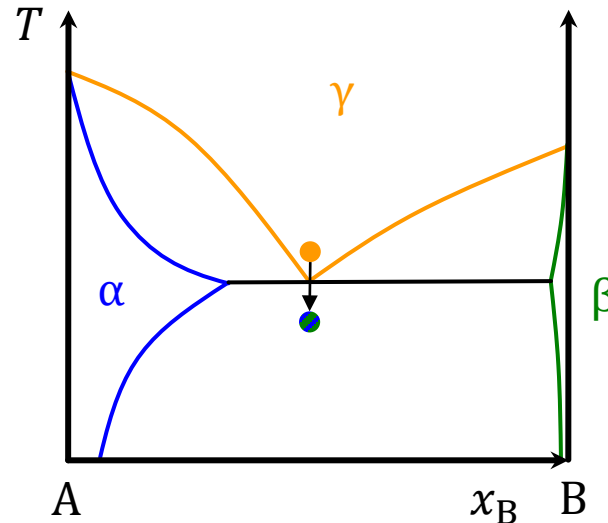
Precipitation: Role of Boundaries

- Cellular precipitation frequently occurs and is usually not wanted due to coarse dimensions of the precipitates and inhomogeneous distribution. The reasons for why cellular precipitation occurs are different for different alloys and not fully understood. Diffusion along the newly formed boundary or through the bulk in the super saturated solution ahead of the tips seem to be decisive.



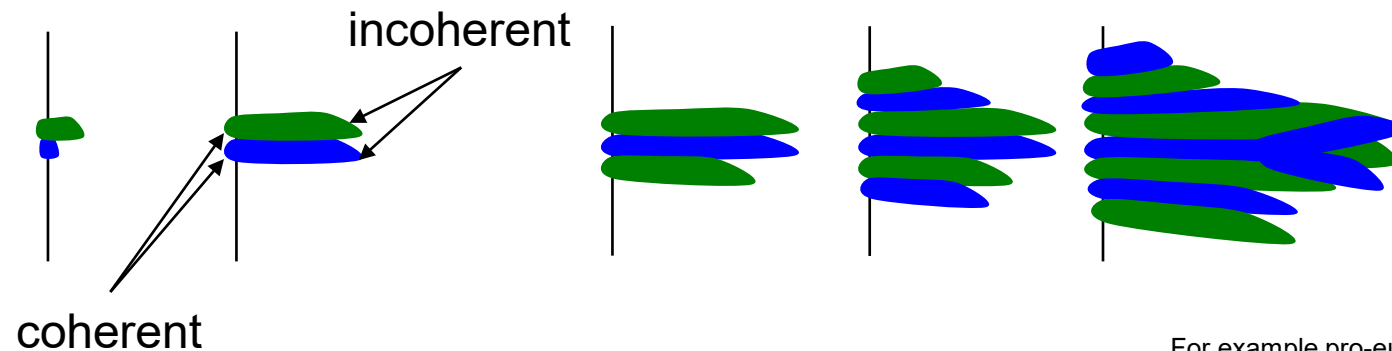
Eutectoid Reaction

- As previously pointed out, all the considerations on the origin and development of eutectic microstructures can be transferred to eutectoid reactions.
- Since the mobility of boundaries is of high importance in solid state transformations, orientation relationship between the growing phase, with the parent phase and potential pro-eutectoid initial phases might alter the conditions.



Eutectoid Reaction

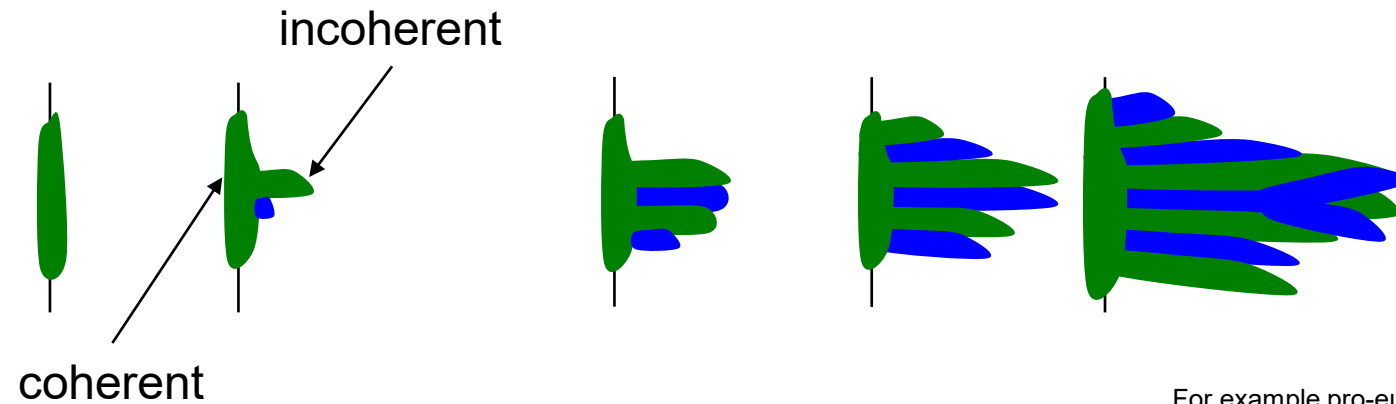
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For example pro-eutectoid $\alpha + \text{Fe}_3\text{C}$ from γ in the Fe-C system. Since C diffusion occurs very fast, the growth rates of interfaces are decisive. Nucleation of Fe_3C takes place first and results preceding nucleation of α .

Eutectoid Reaction

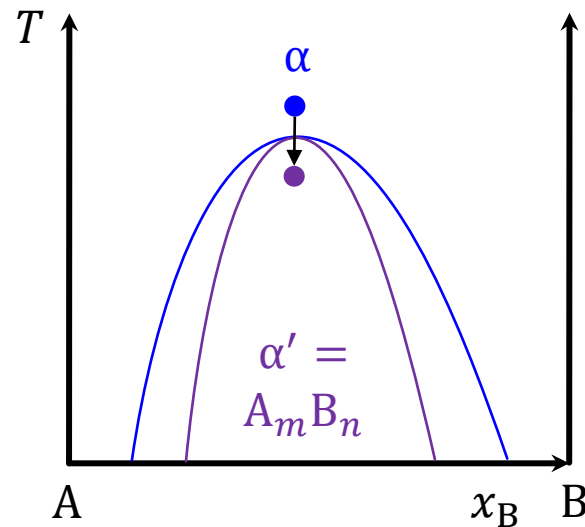
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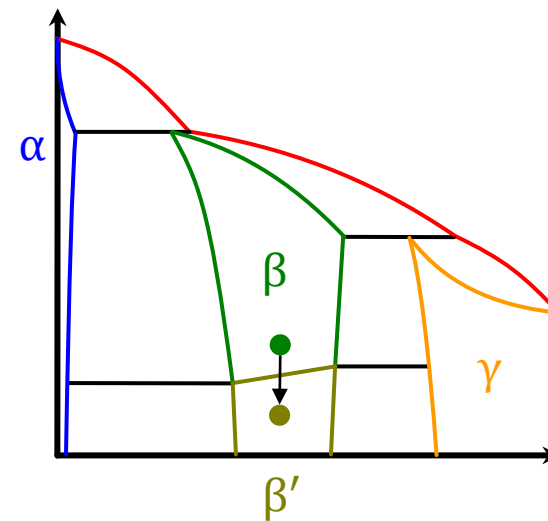
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Ordering

- Disordered phases might undergo crystallographic ordering below certain temperatures. Since only rearrangement of atoms within unit cells are required to obtain the different site occupations, no long-range diffusion is required. The reaction can be discontinuous (1st order) by thermal activation due to domain growth or continuous (2nd order, see Ch. 3e).



1st order with
two-phase region



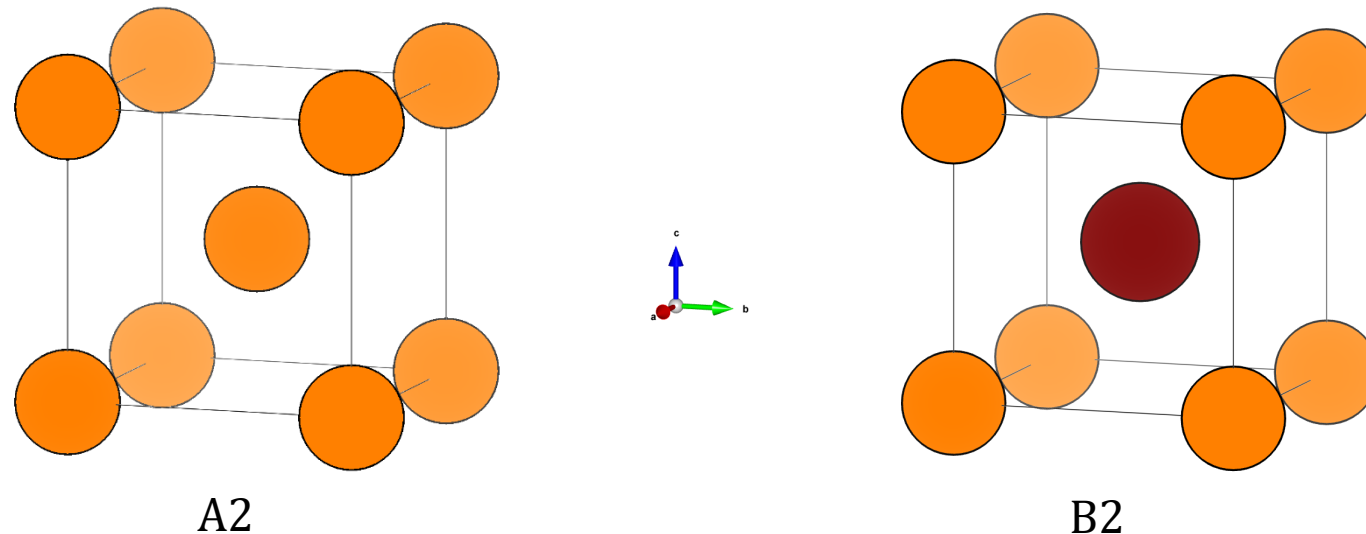
2nd order

Note that apart from variation in site occupation, slight modifications of the crystal structure (symmetry, dimensions) might be obtain as well. In contrast to pure elements (allotropic transf.), the transition from one crystal structure to another in alloys is usually referred to as polymorphic transformation.

Ordering

- Most crystal structures of intermetallic compounds exhibit strong similarity to disordered metals. Hence, the structures can easily be described by the symmetry breaking and the introduction of order:

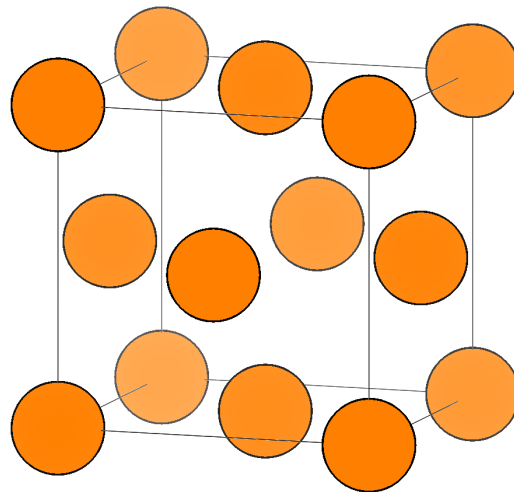
for example Fe und FeAl



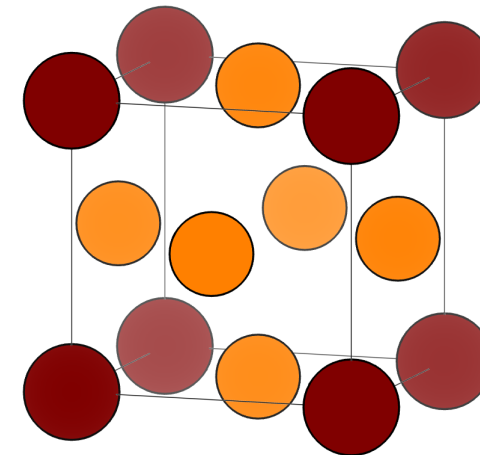
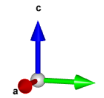
Ordering

- Most crystal structures of intermetallic compounds exhibit strong similarity to disordered metals. Hence, the structures can easily be described by the symmetry breaking and the introduction of order:

for example Ni und Ni₃Al



A1

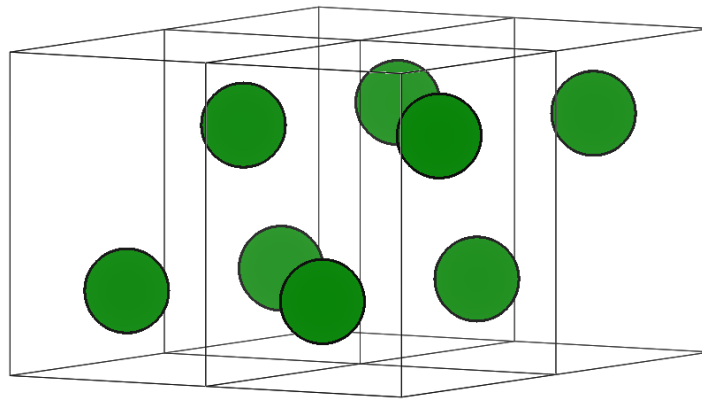


L1₂

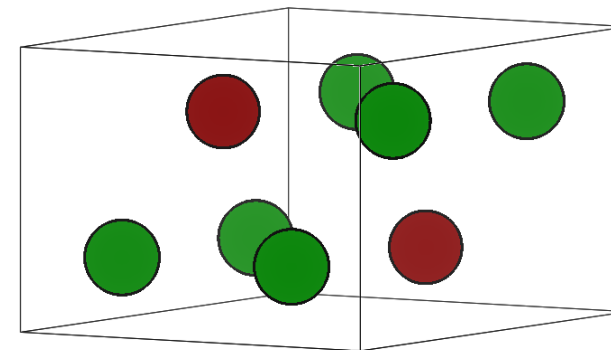
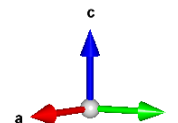
Ordering

- Most crystal structures of intermetallic compounds exhibit strong similarity to disordered metals. Hence, the structures can easily be described by the symmetry breaking and the introduction of order:

for example Ti und Ti_3Al



A3

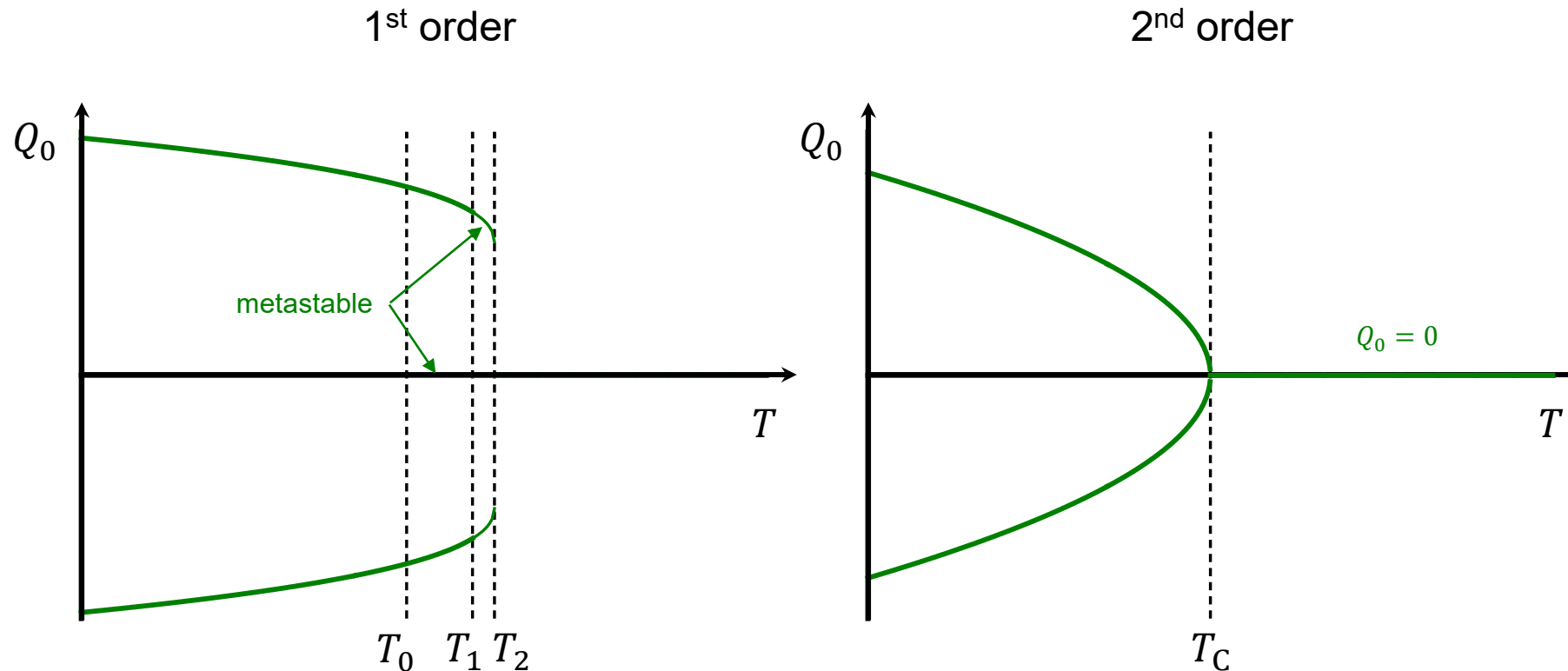


D0₁₉

Note that the A3 unit cell is rotated of 180° for better visibility of the relationship.

Order Parameter

- As we have seen in Ch. 3e, the order parameter needs to be defined and depending on its temperature dependence the different transformation behaviors are obtained:



Order Parameter

- Crystallographic order can be described by site occupation using values of $Q = 1$ for perfect order and $Q = 0$ for the random solid solution.

- For example:

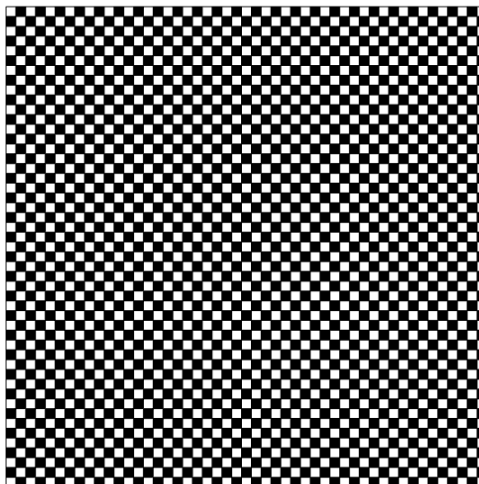
$$Q = \frac{r_{1,A} - x_A}{1 - x_A} = \frac{r_{2,B} - x_B}{1 - x_B}$$

- with $r_{1,A}$ or $r_{2,B}$ being the probability to obtain A or B on the correct (in the ordered state) lattice site 1 or 2, respectively.

Order Parameter

- Crystallographic order can be described by site occupation using values of $Q = 1$ for perfect order and $Q = 0$ for the random solid solution:

fully ordered



$$\begin{aligned}
 x_A &= 0.50, x_B = 0.50 \\
 r_{1,A} &= 1.00, r_{2,B} = 1.00 \\
 Q &= 1
 \end{aligned}$$



$$\begin{aligned}
 x_A &\approx 0.50, x_B \approx 0.50 \\
 r_{1,A} &= 0.76, r_{2,B} = 0.76 \\
 Q &= 0.52
 \end{aligned}$$

random



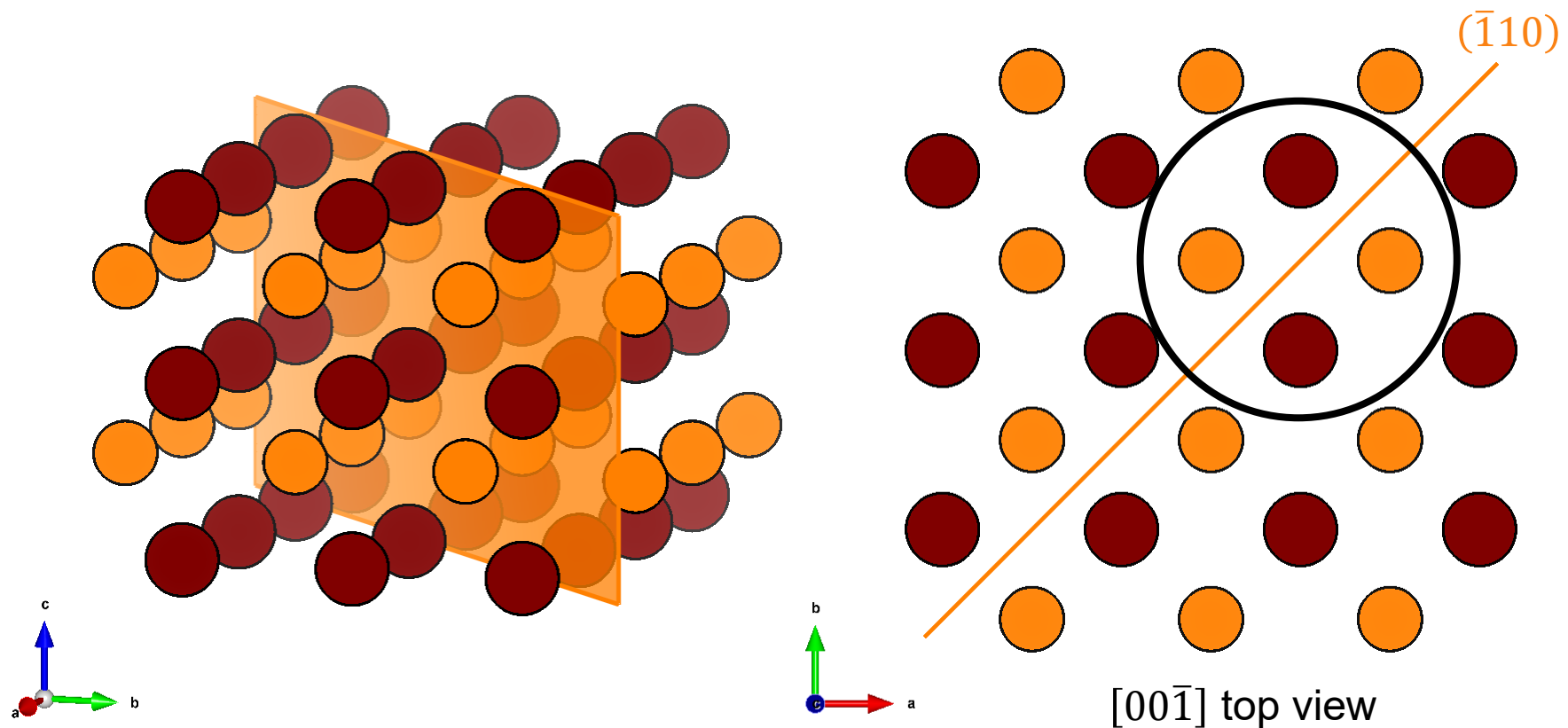
$$\begin{aligned}
 x_A &\approx 0.50, x_B \approx 0.50 \\
 r_{1,A} &= 0.50, r_{2,B} = 0.50 \\
 Q &= 0
 \end{aligned}$$

Ordering

- The progress of ordering can be different:
 - Gradual development of short- to long-range order (most likely for the 2nd order transformation or for large super cooling)
 - Or by nucleation and growth of ordered domains (note that the degree of order within the domains still increases with decreasing temperature, irrespective of 1st or 2nd order transformation)
- For the nucleation and growth, the coherent, ordered regions are called domains.
- When the domains come in contact with a translation vector between the two domains, an anti-phase domain boundary is formed.
- The energy of the boundary depend on its habit plane and planar number density of undesired bonds in the boundary. Note that $\varepsilon < 0$ with U_{AB} is more negative than $\frac{1}{2}(U_{AA} + U_{BB})$ as seen in Ch. 4c.
- These kind of defects might also be generated in ordered structures when other defects are considered, for example during the dissociation of dislocations.

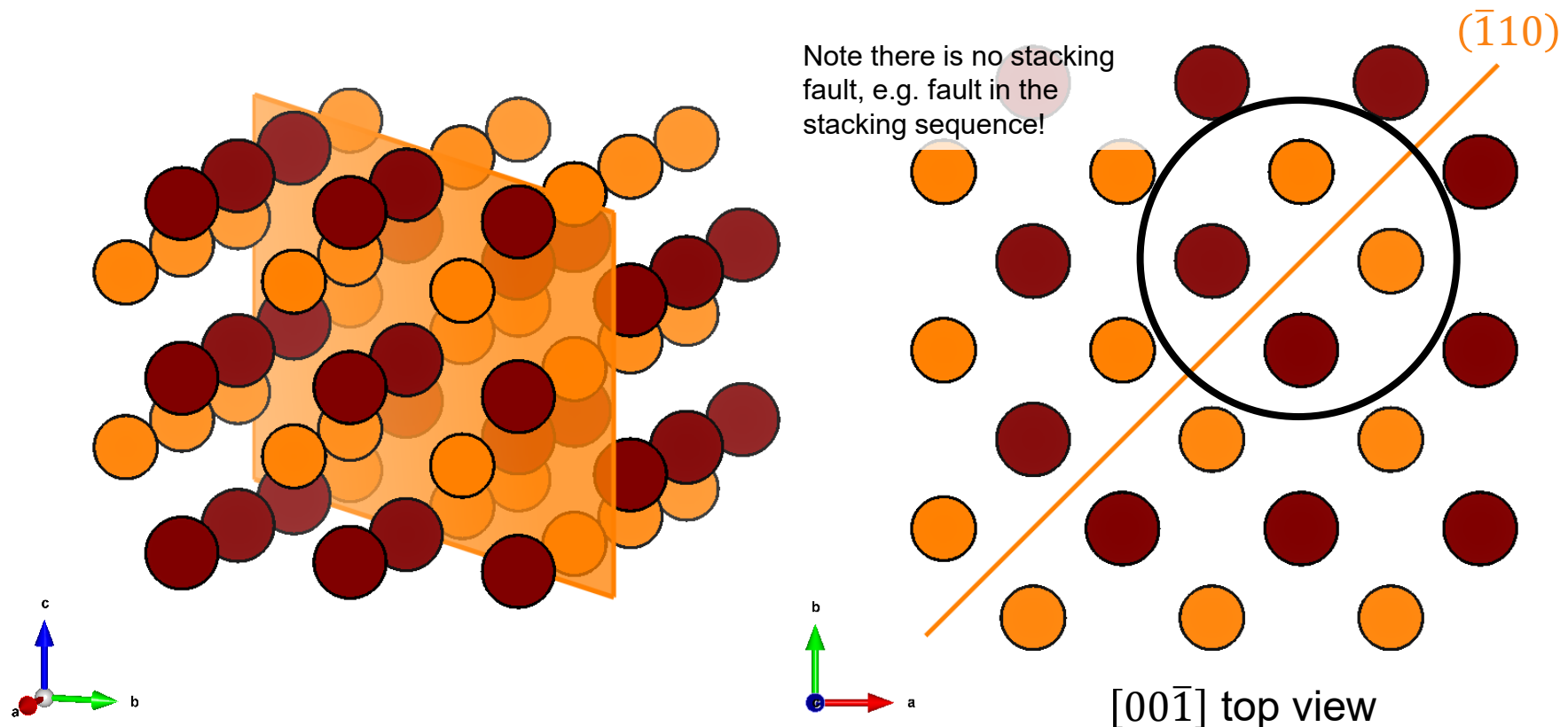
Anti-phase domain boundaries in B2

- Perfect B2 lattice, **all NN bonds are of A-B type!**



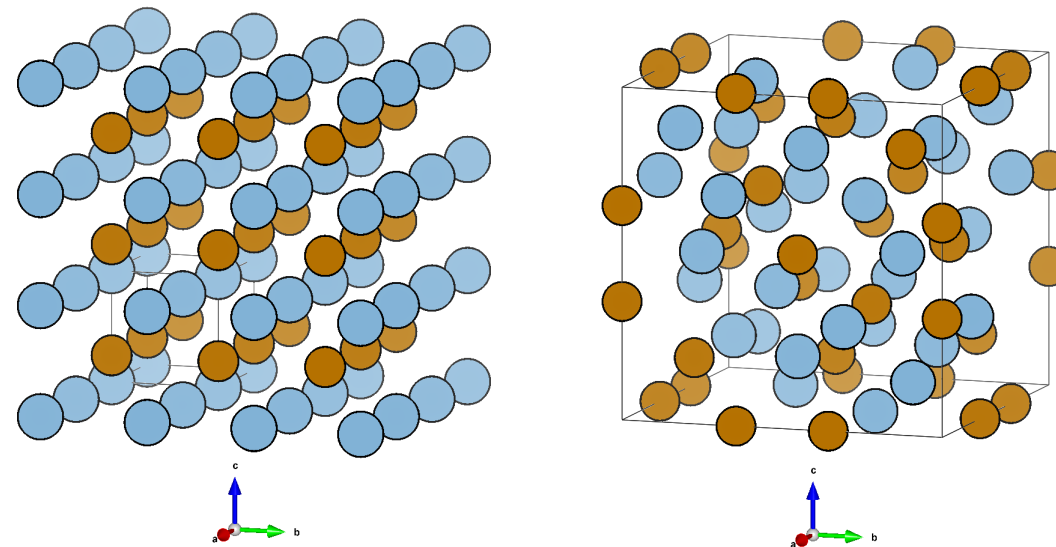
Anti-phase domain boundaries in B2

- Introduction of an antiphase boundary by $\frac{1}{2}[111]$ displacement within $(\bar{1}10)$. **The energy of the defect is determined by the excess energy of B-B and A-A bonds.**



Consequences

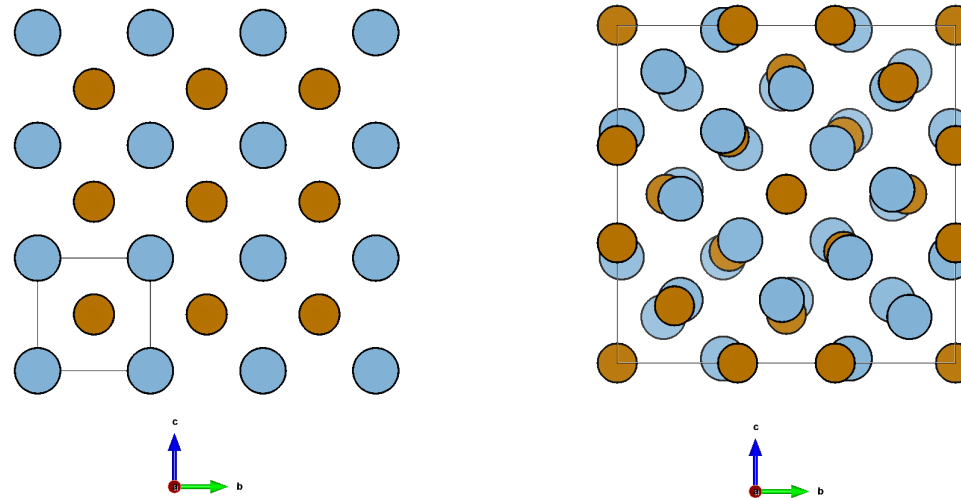
- Order is just an example, for the analogy treatment. Additionally, the atoms can be displaced from the ideal positions in the disordered structures.



FeAl (B2) and Fe₅Al₈ (D8₂)

Consequences

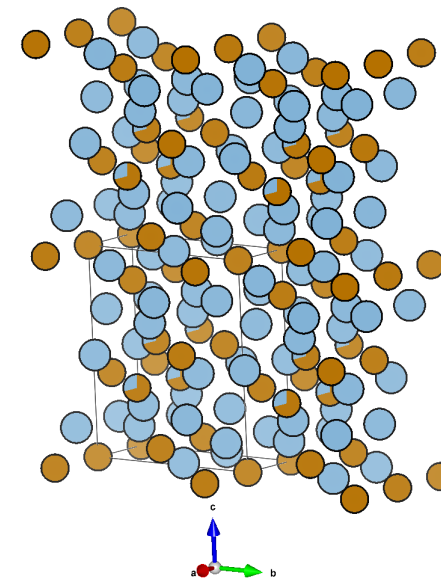
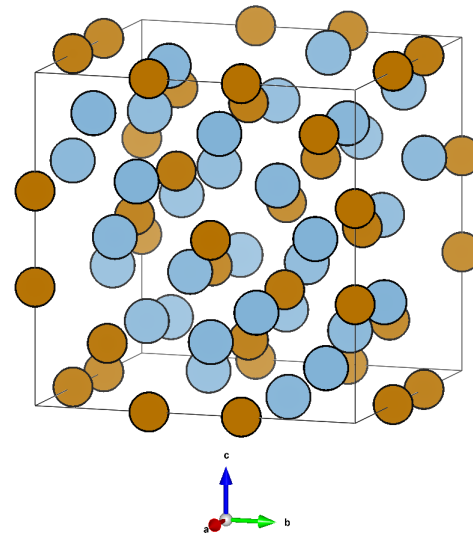
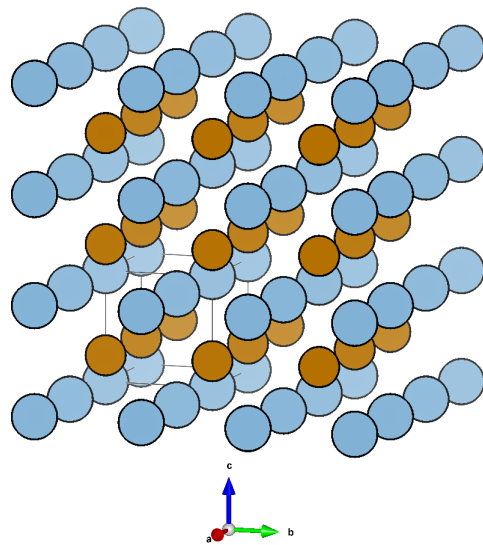
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Cu_5Zn_8 is a 3 FeAl (B2) and Fe_3Al_5 (D19.2) with additional displacements of the atoms.

Consequences

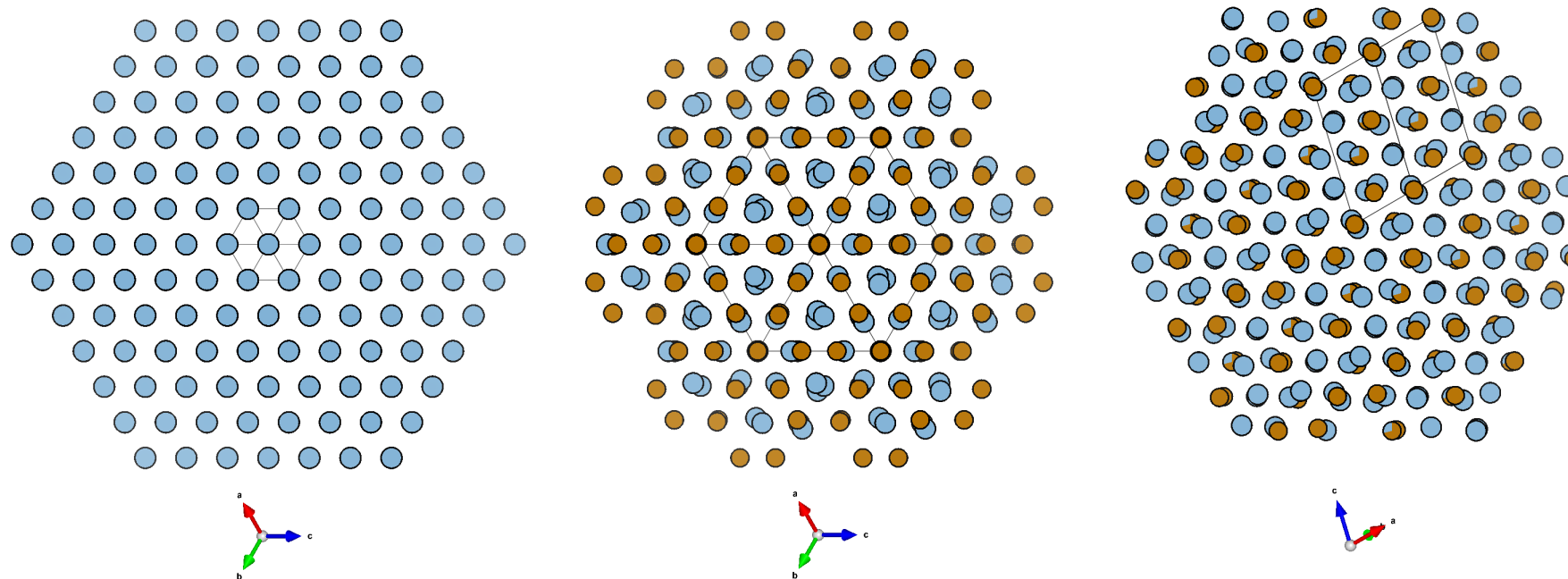
- Order is just an example, for the analogy treatment. Additionally, the atoms can be displaced from the ideal positions in the disordered structures.



FeAl (B2) and Fe₅Al₈ (D8₂) and triclinic FeAl₂

Consequences

- Order is just an example, for the analogy treatment. Additionally, the atoms can be displaced from the ideal positions in the disordered structures.



Even in very complex phases, it is a matter of view point!