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Assessment of a nucleation and growth model in CrB-structured alloys

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HELMHOLTZ
RESEARCH FOR GRAND CHALLENGES

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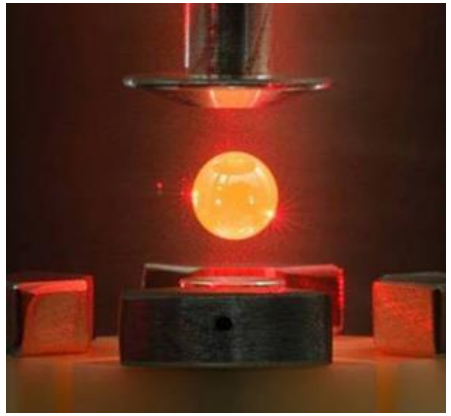
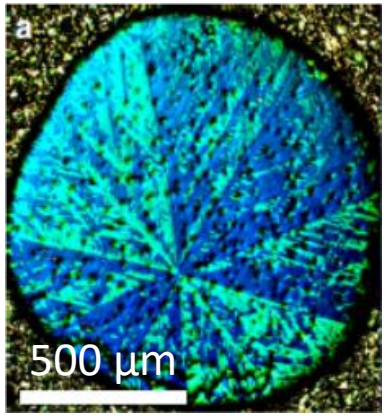
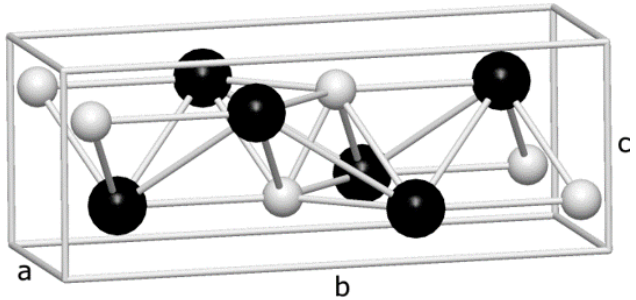
What are we doing?

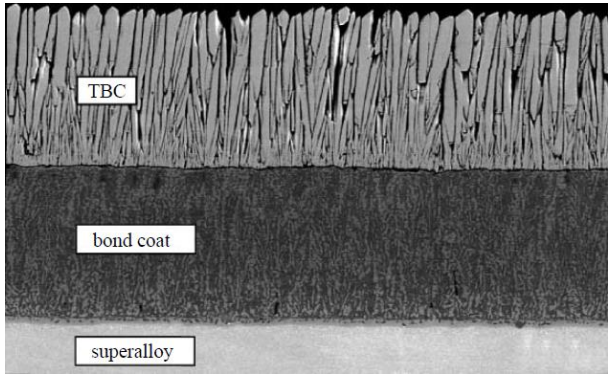
- Solidification from undercooled metallic melts
  - → contact free processing
  - → non-equilibrium conditions
  - → several 100 K below T_m
  - → microstructure analysis





- In **orthorhombic** systems
  - $\alpha = \beta = \gamma \mid a \neq b \neq c$
  - Weaker mechanical properties than cubic systems
  - Specialized technological uses
    - → Perovskite in photovoltaics
    - → YSZ coatings on gas turbines
    - → Tin based solder alloys



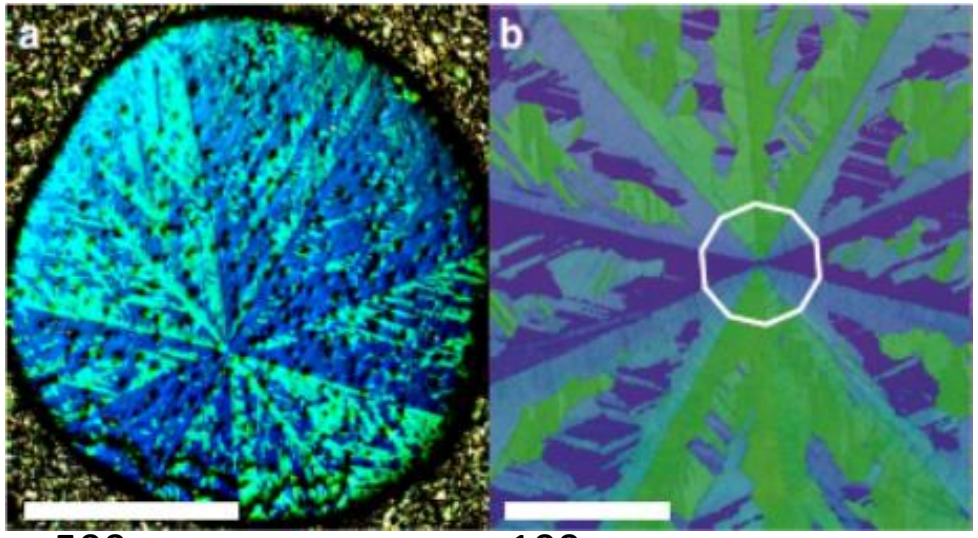


[1] C. Mercer et.al., Proc. R. Soc. A, 463 (2007) 1393-1408

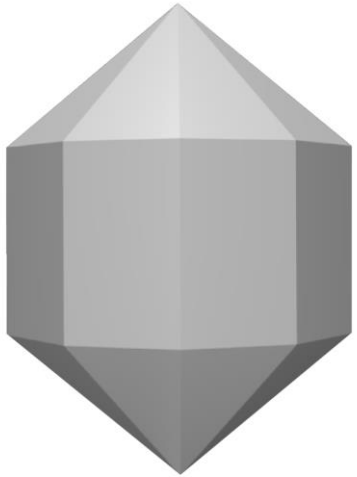
Motivation – n-fold twinned growth mechanism

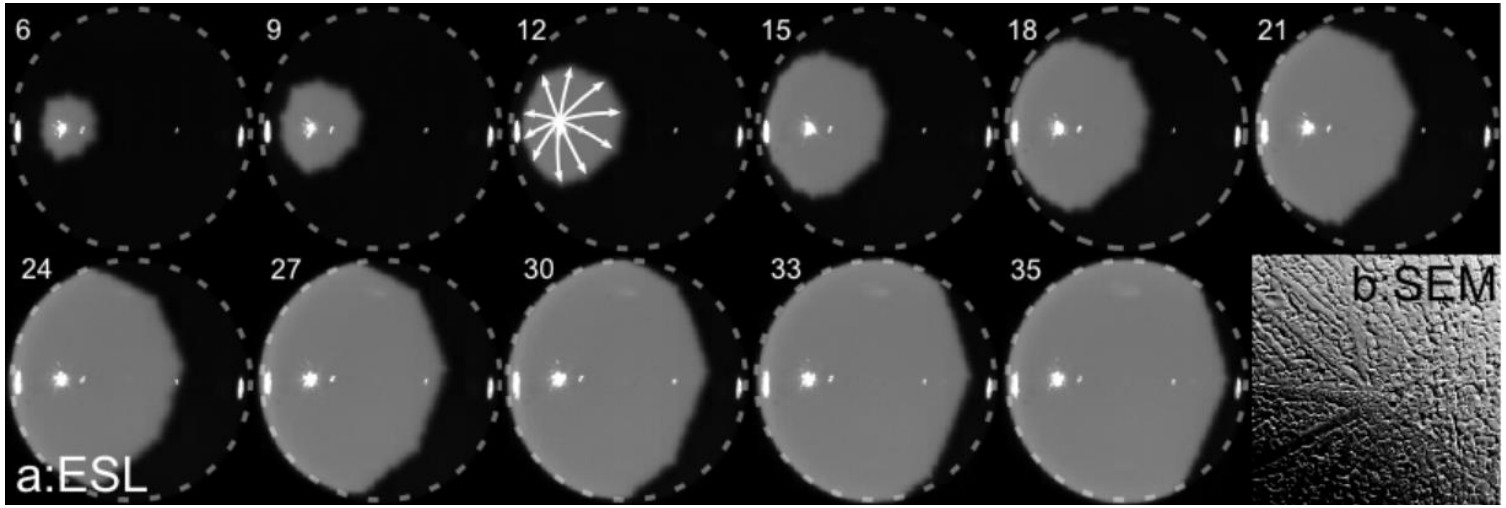
Solidification in the NiZr system [2,3]

- Star-like structure emerging from a single nucleus
- 10-fold symmetry
- Straight grain boundaries over the whole sample
- Result from high temperature solidification proven with high-speed camera images



500 µm 100 µm

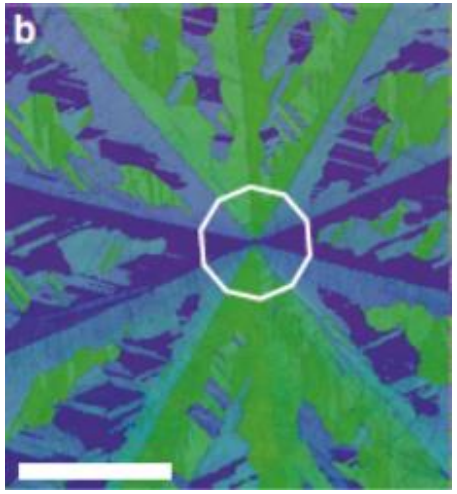




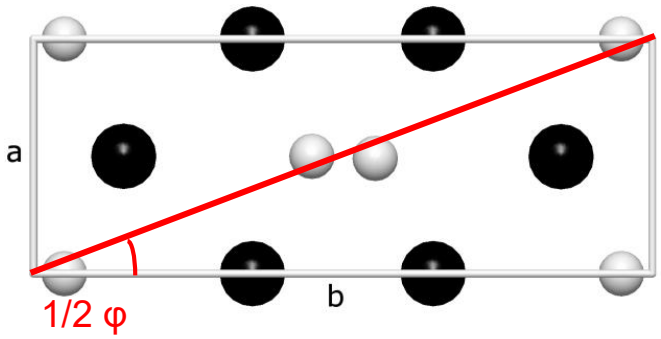
[2] Hornfeck, W., Kobold, R., Kolbe, M. *et al*. ***Nat Comm* 9,** 4054 (2018)
[3] R. Kobold, M. Kolbe, W. Hornfeck, D.M. Herlach, J. Chem. Phys. 148, 114502 (2018)

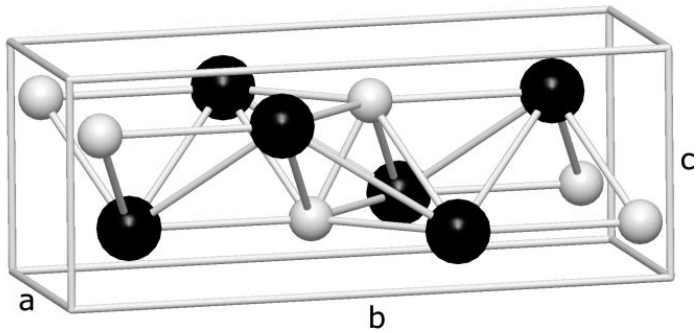
Motivation – n-fold twinned growth mechanism

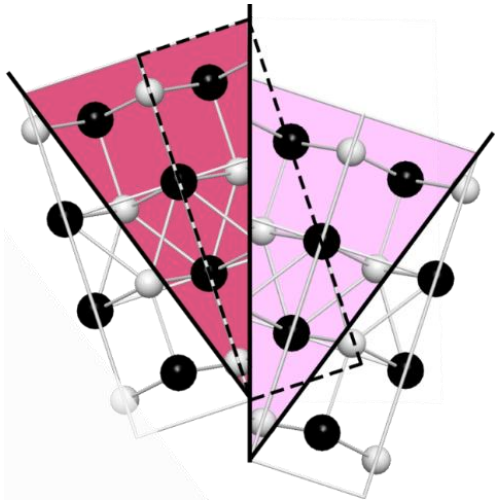
- Misorientation angle of 36° between grains
  - → measured with EBSD
  - → 10-fold symmetry
- Orthorhombic unit cell
  - → grain boundary through the diagonal of the unit cell



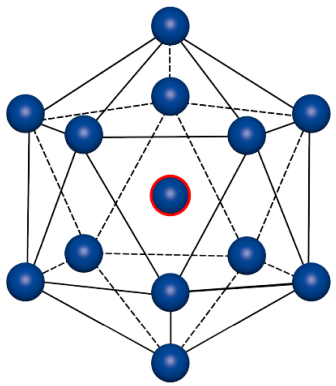
100 µm





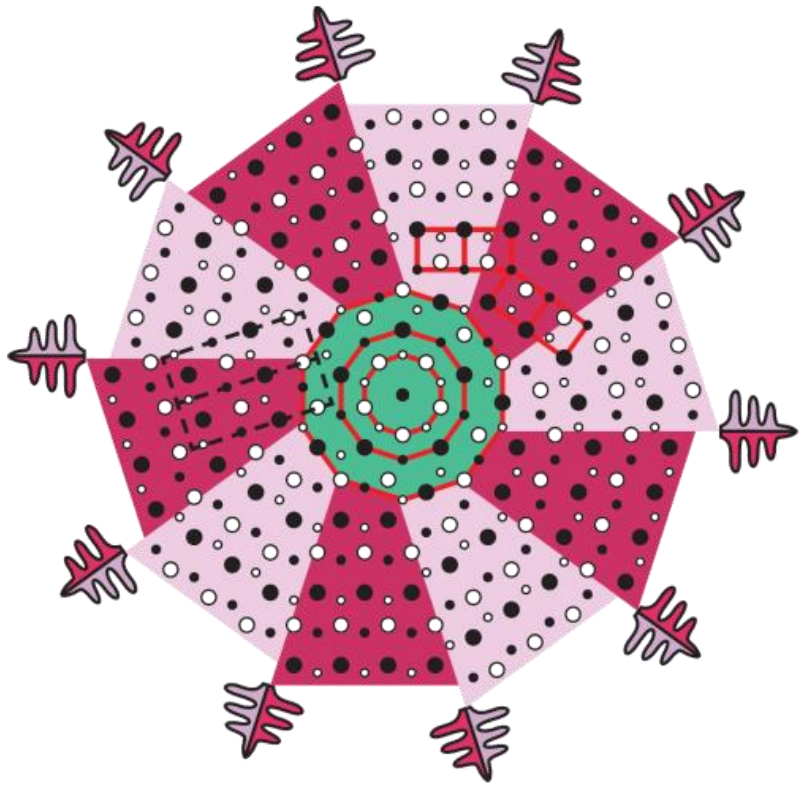


Motivation – n-fold twinned growth mechanism



Growth model in NiZr by Hornfeck-Kobold-Kolbe [2,3]

- Homogeneous nucleation at high undercoolings
  → due to high purity and contact-free levitation
- Nucleus of icosahedral short-range order with 5-fold symmetry, quasi-crystalline
- Further growth into multi-twinned orthorhombic structure (10-fold)
  B33 phase, CrB-structure
- Cell symmetry preserved across boundaries



[2] Hornfeck, W., Kobold, R., Kolbe, M. et al. **Nat Comm 9,** 4054 (2018)
[3] R. Kobold, M. Kolbe, W. Hornfeck, D.M. Herlach, J. Chem. Phys. 148, 114502 (2018)
[4] R. Kobold, W. W. Kuang, H. Wang, W. Hornfeck, M. Kolbe, D.M. Herlach, Philosophical Magazine Letters, 97:6, 249-256 (2017)

Motivation – universal nucleation and growth model?

Can this be replicated in other systems?

- Other symmetries can be calculated geometrically

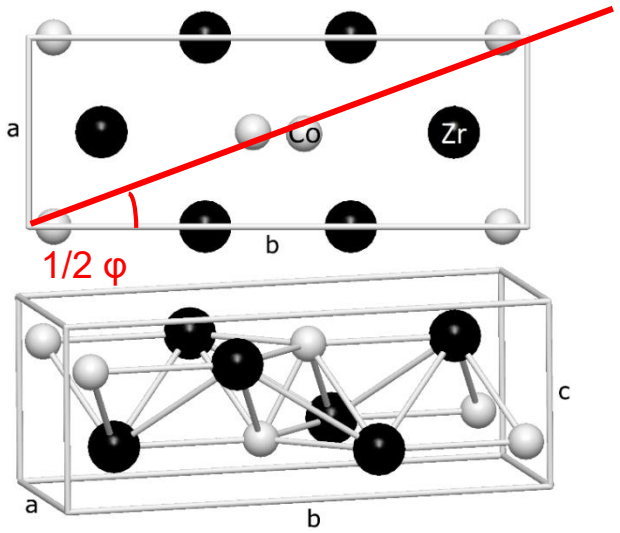
  → $\varphi = 2 \tan^{-1} (a/b)$

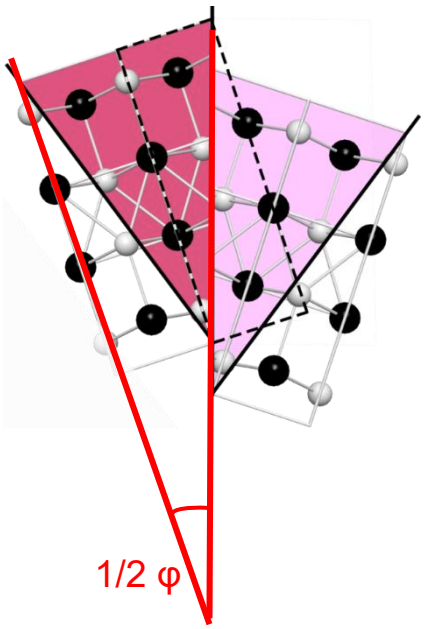
in NiZr: $\varphi = 36°$ → 10-fold symmetry

in NiGd: $\varphi = 40°$ → 9-fold symmetry

In NiB: $\varphi = 45°$ → 8-fold symmetry

etc…





- Exclusive in NiZr or present as a universal growth mechanism?

  → more than 130 CrB-structured binary alloys known
- Deep undercooling is needed to more likely get single nucleus
- Challenges? → most systems are highly oxidative

  → impurities/ oxides act as nucleation sites → heterogeneous nucleation/ low ΔT

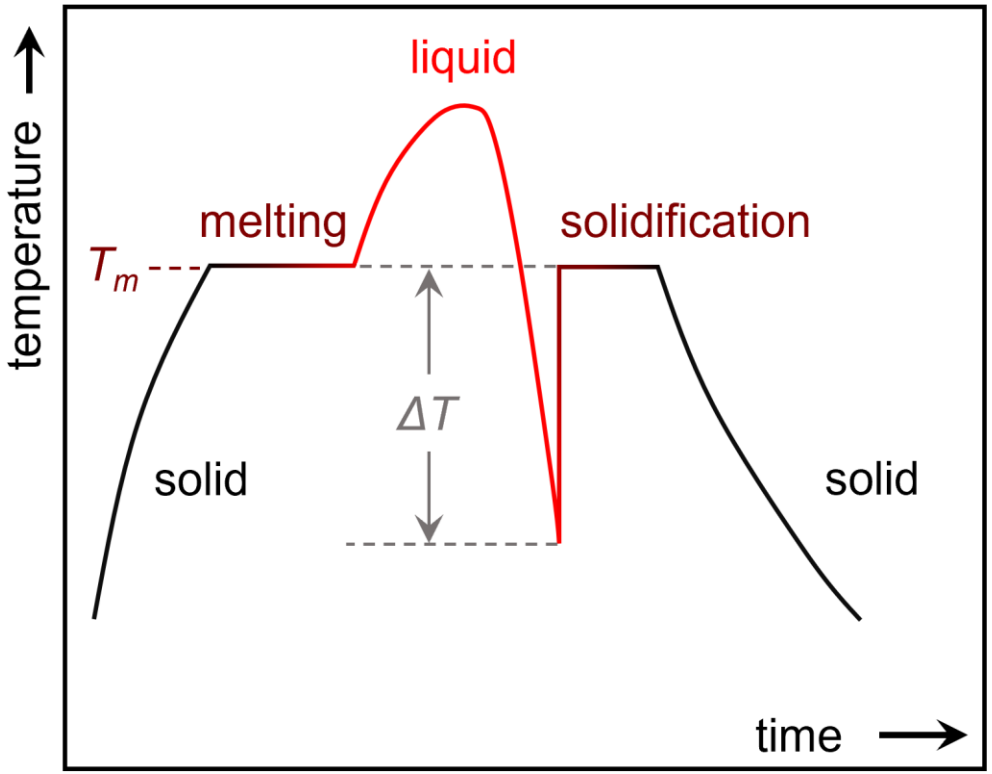
  → solid-phase transitions → change of microstructure

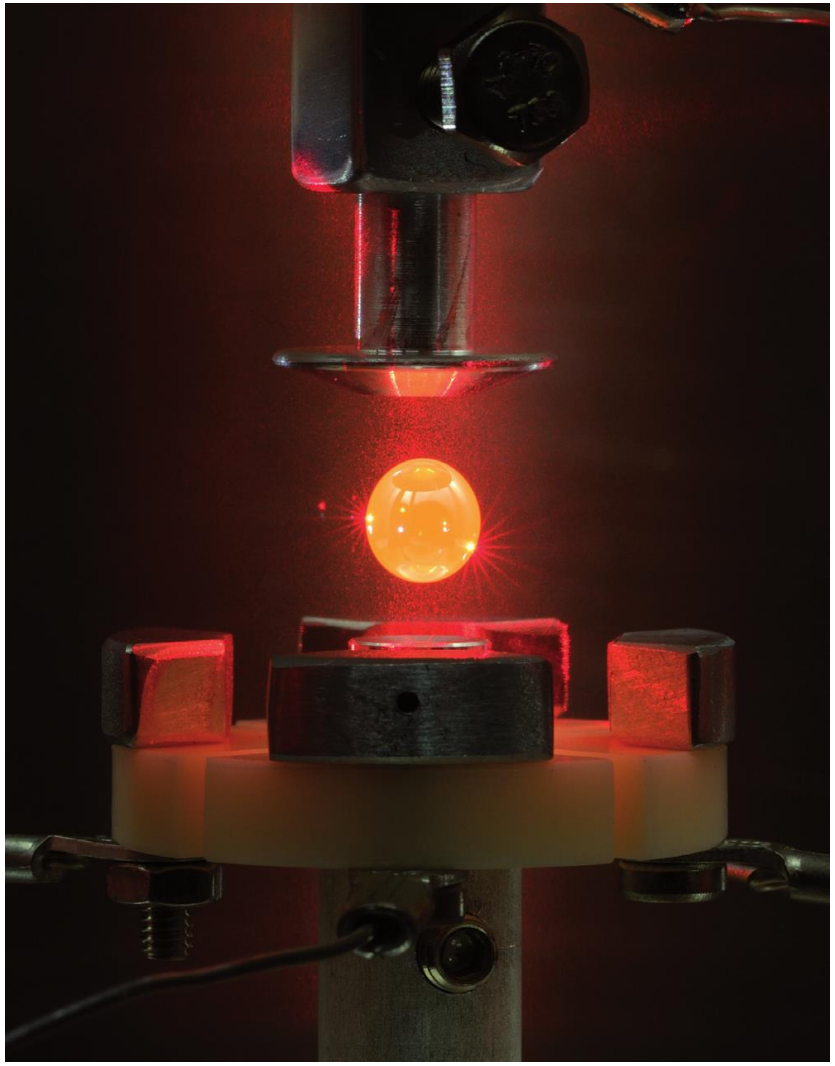
Electrostatic levitation

- UHV, <10^{-6} mbar
- processing without any mechanical contacts
- high purity elements

→ high ΔT

Recalescence: - latent heat is released
- elevated temperature observable with HSC



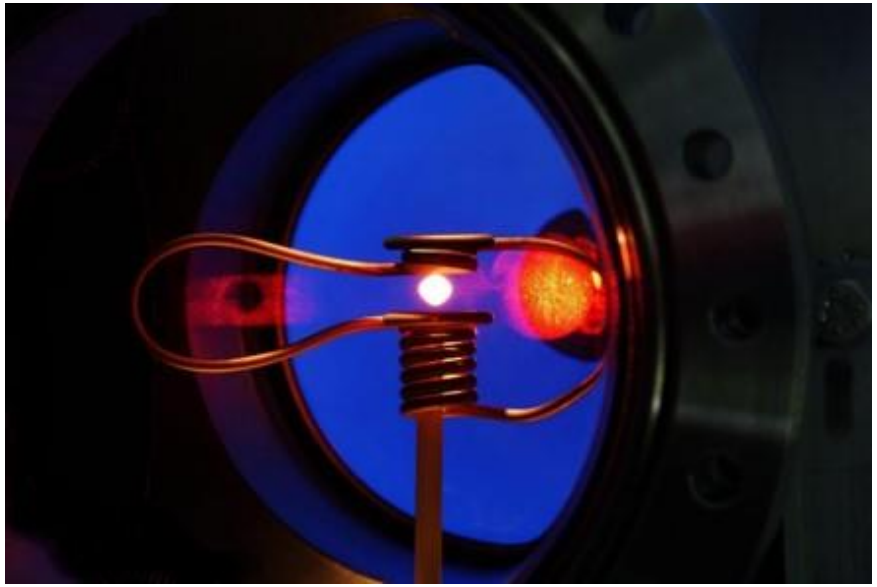


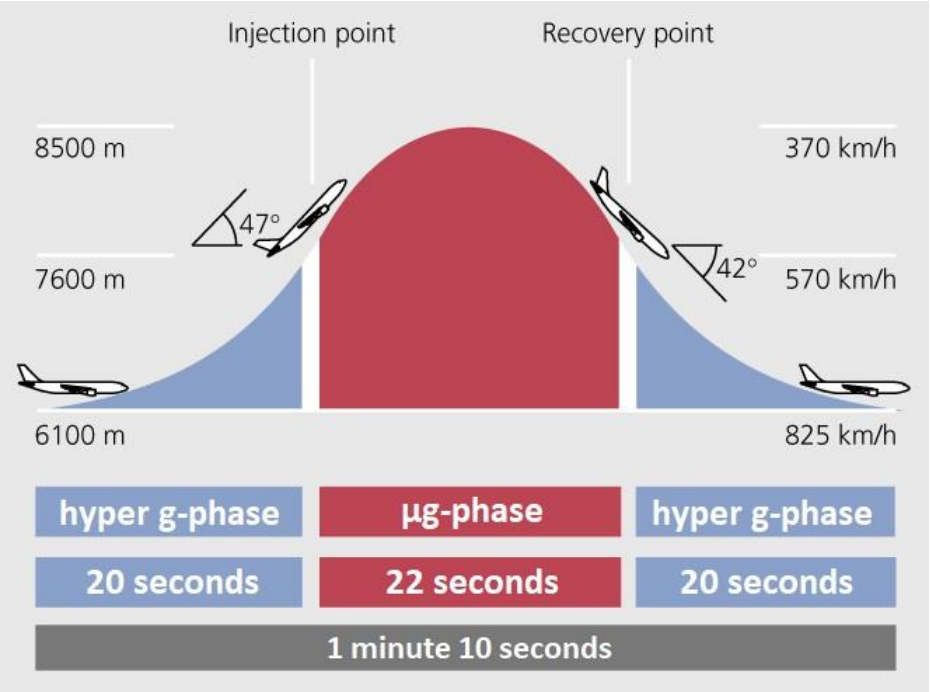
Electromagnetic levitation | parabolic flights

- 22 seconds of µ-gravity
- less convection and disturbances in melt – in contrast to ground EML

→ option for alloys that can't be levitated on ground → e.g. AuGd

→ also for highly oxidative systems or when impurities on surface are not solvable

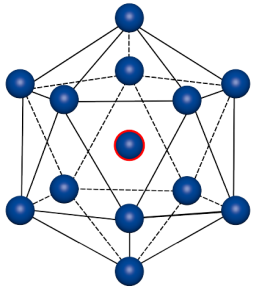


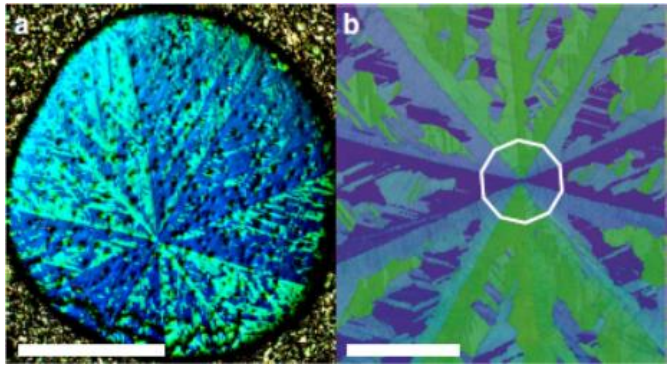


Assessment of universal growth model

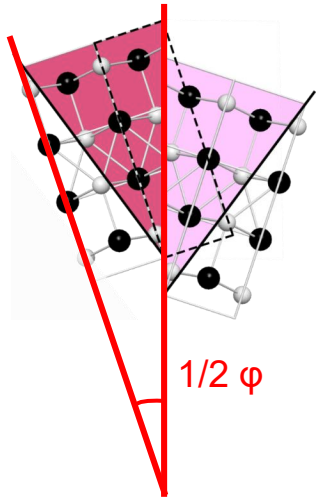
Crucial features needed, based on the NiZr prototype system, to observe this growth:

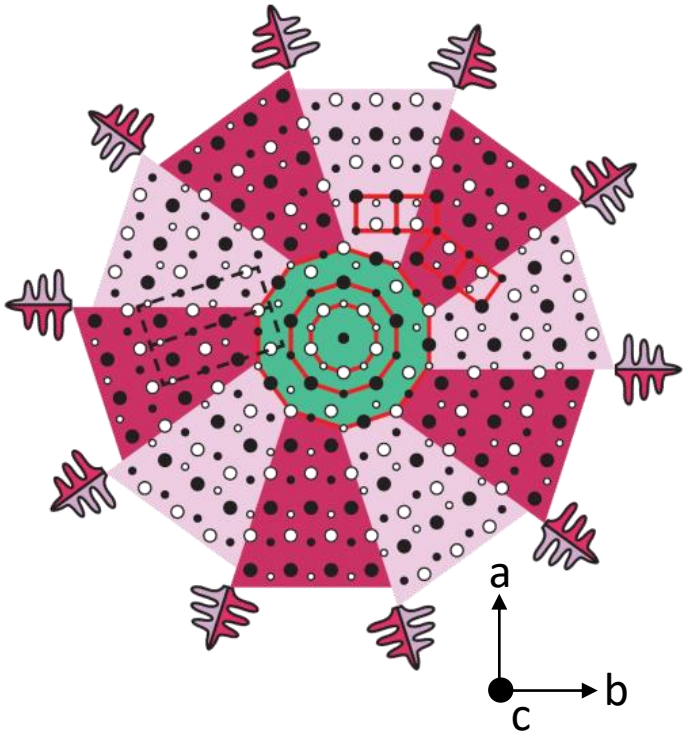
1. Deep undercooling
   → possibly homogeneous
   → singular nucleation event
2. Nucleus based on icosahedron
   → transition from QC to twinned microstructure
3. Solidification within CrB-structure (B33 phase)
   → lattice parameter ratio a/b
   → twinned dendrites
4. Orientation around common <001> direction (c)
5. Stable phase - for microstructure analysis





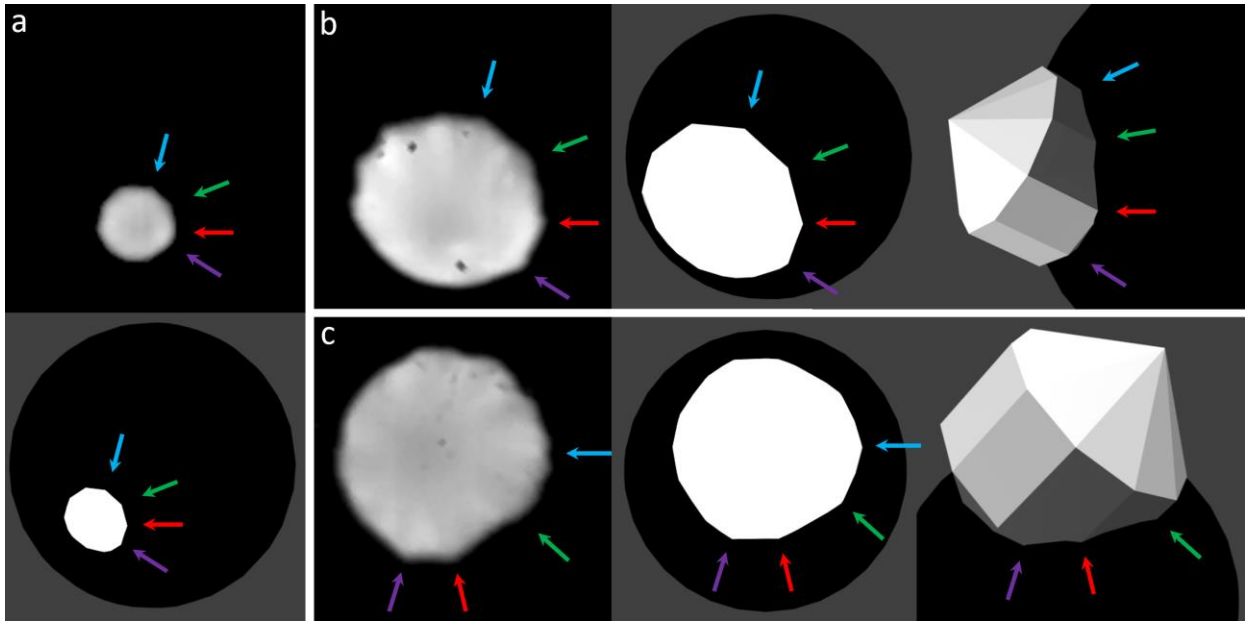
500 µm 100 µm

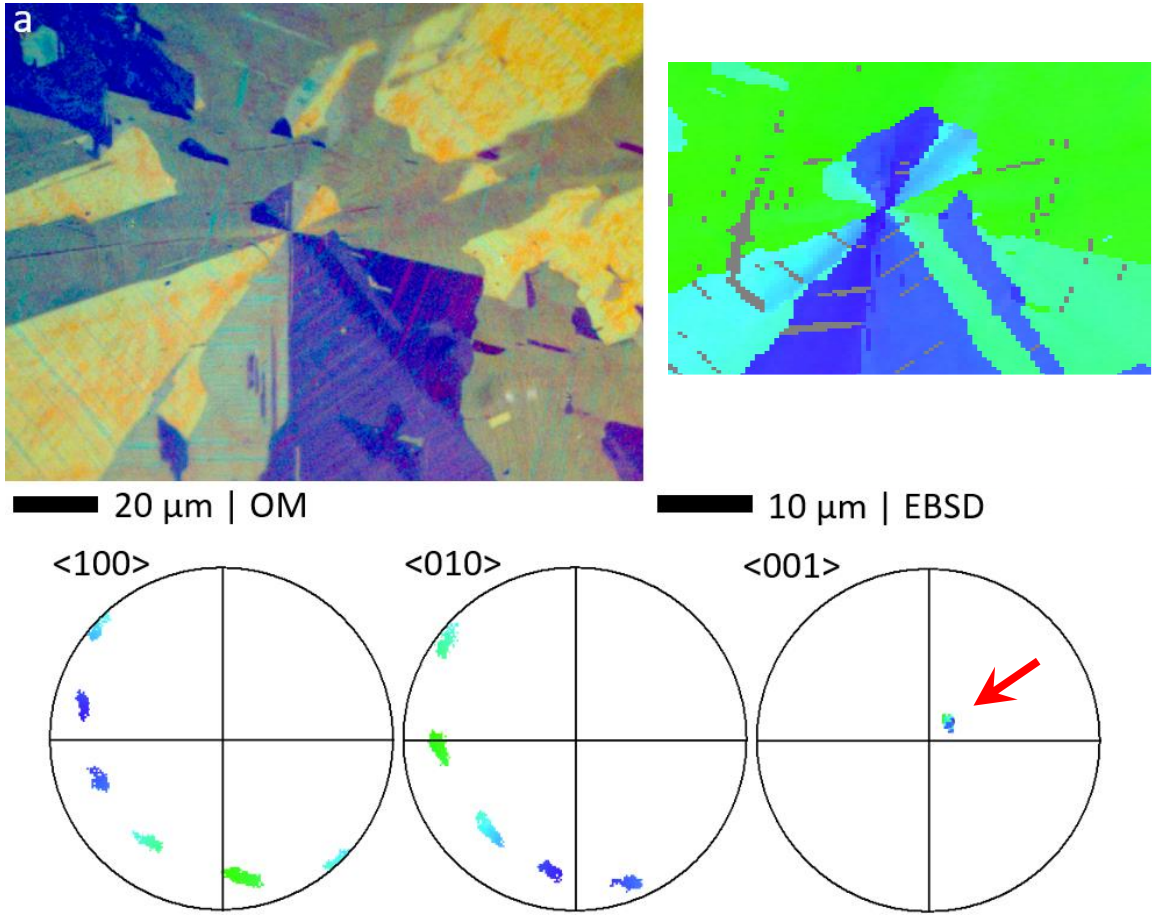




NiHf | 10-fold symmetry

- Undercoolings up to ΔT = 460 K
- same heat front as in NiZr
- ten-fold symmetric structures
- EBSD and pole figures show ten orientations around common <001> direction
- φ = 36° matches 10-fold expectation

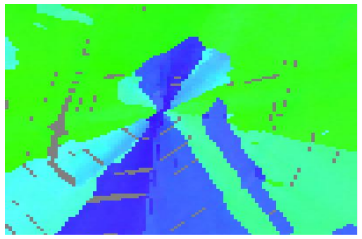




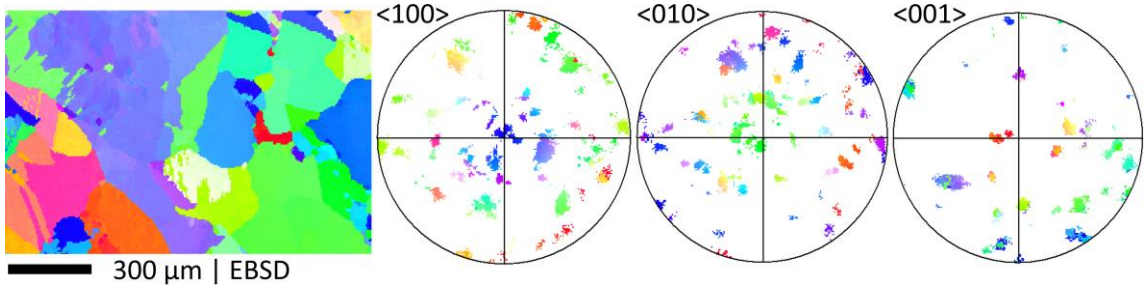
NiHf | solid-phase transition

- Solid-solid transition present
- high-temperature B2 phase, cubic

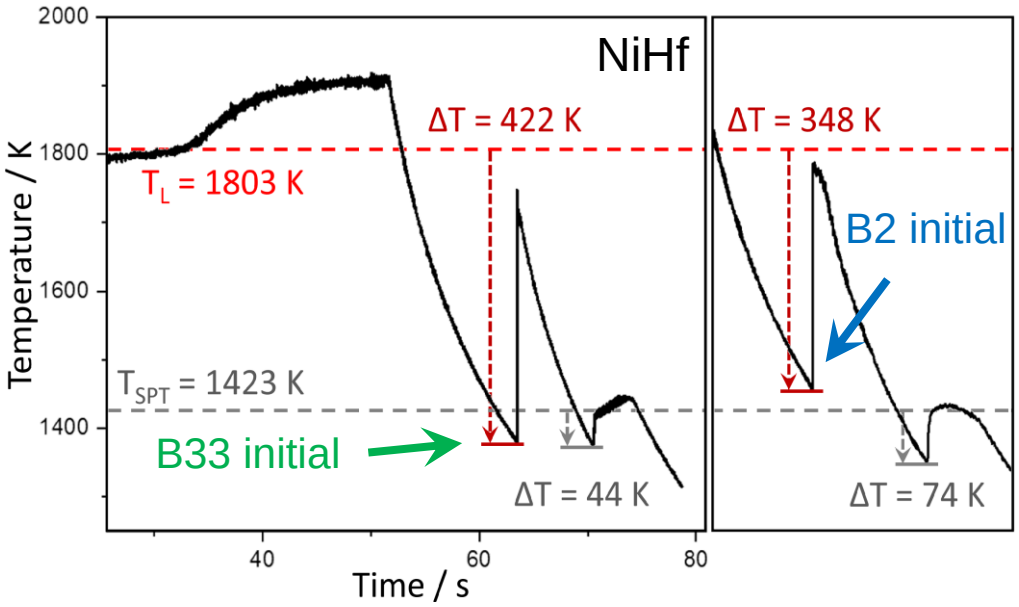
  → into B33, orthorhombic
- nucleation and growth model only present, when B33 is initial phase →



- otherwise, if B2 is initital:



- subject of current studies, will be presented in detail in future publications



hypercooling, if ΔT > 360 K

→ 100% solidified during recalescence

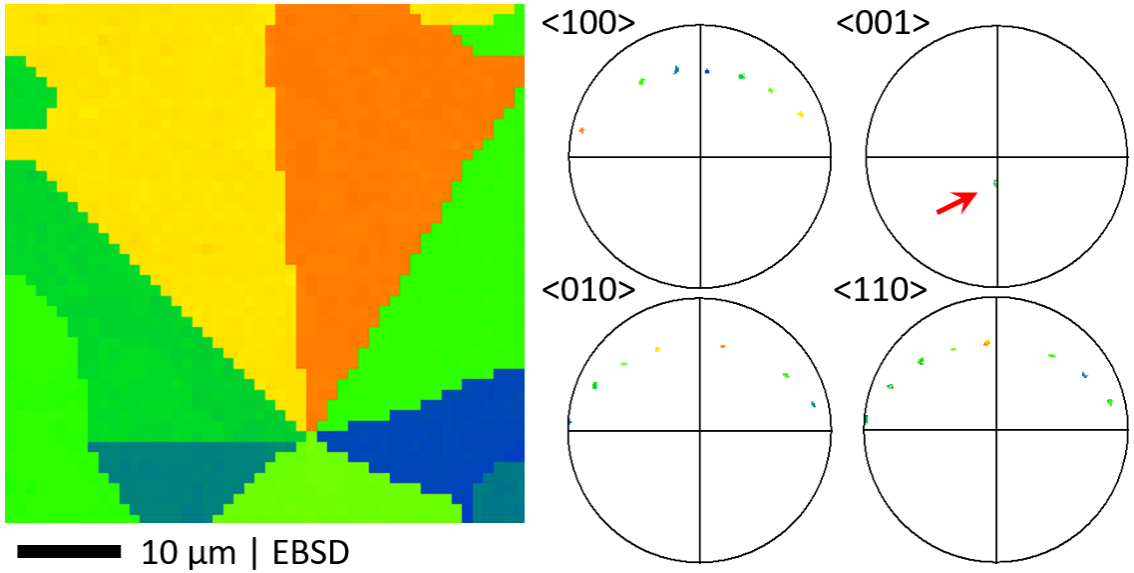
NiGd | *uneven* 9-fold symmetry

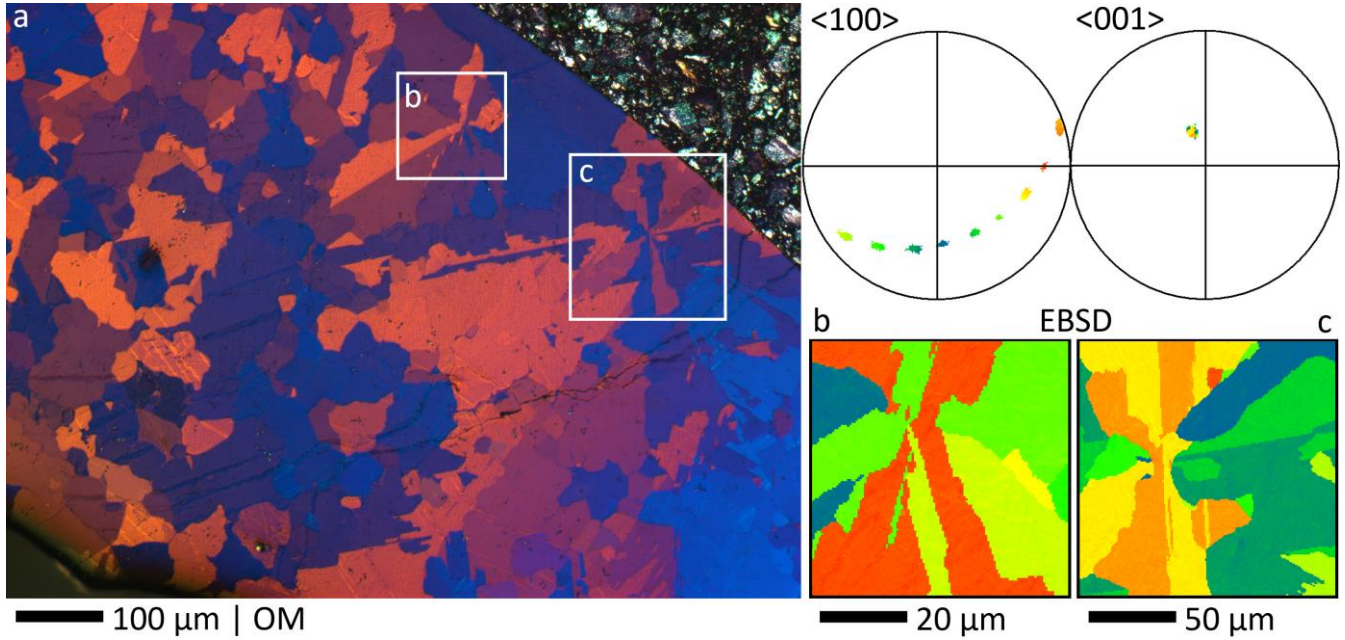
- First expected uneven symmetry
- φ = 40° matches expectations
- common <001> direction

- up to now only low undercoolings (ΔT up to 90 K)
- only incomplete or distorted structures present

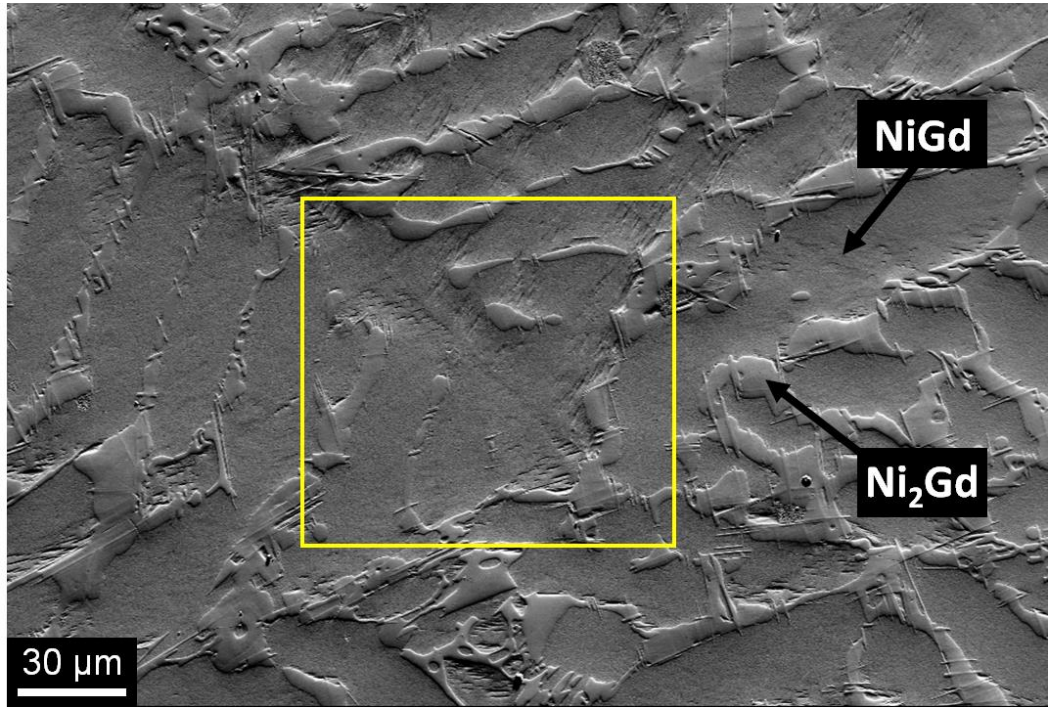
- Adaptation of model may be necessary
  - → heterogeneous growth front
  - → multiple symmetric structures
  - → same <001>

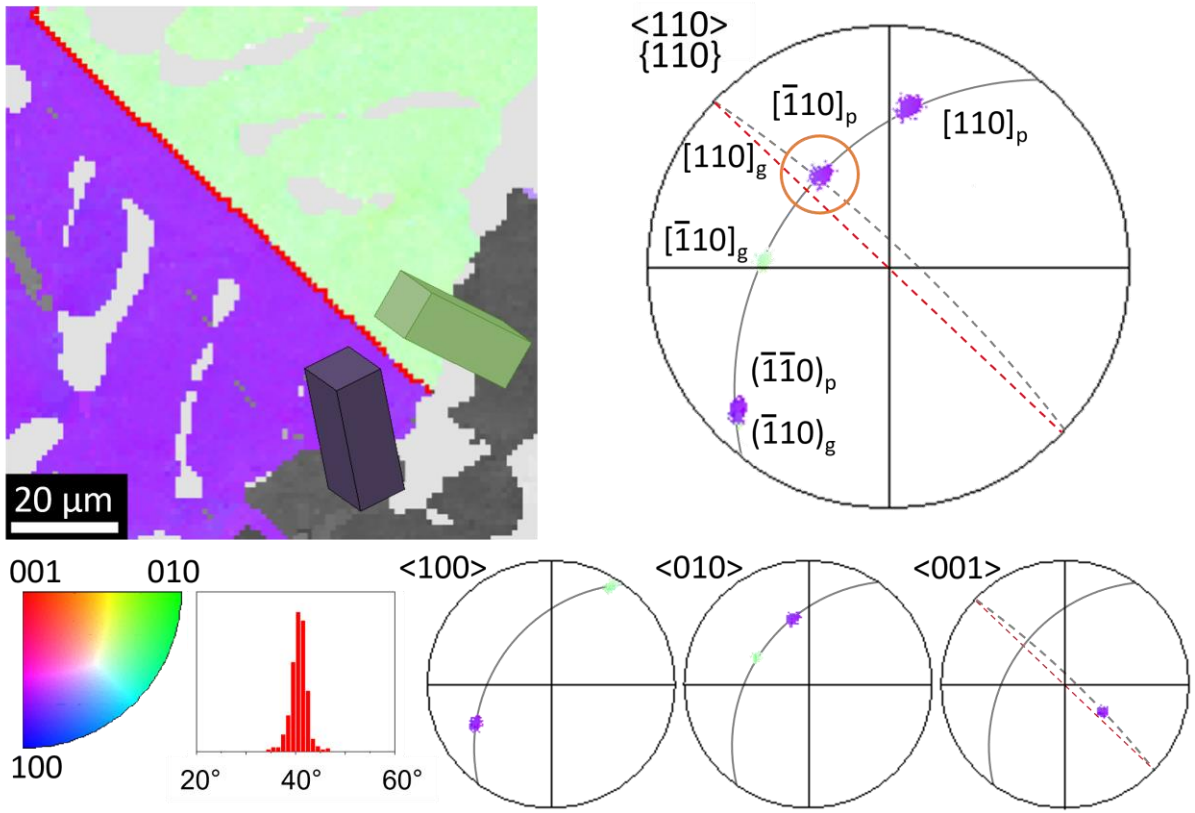
- Similarities to *iQC-mediated nucleation mechanism* by Rappaz et.al. in fcc-alloys





NiGd | *twinned dendrites*





- Twinned dendrites confirmed in NiGd
- both parts share a common {110}
- common <001> direction

[5] T. Niersbach, M. Kolbe, M. Becker and F. Kargl, *Twinned dendrites in CrB-structured intermetallic NiGd*. (2022) IOP Conf. Ser.: Mat. Sci. Eng. Accepted, June 2022.

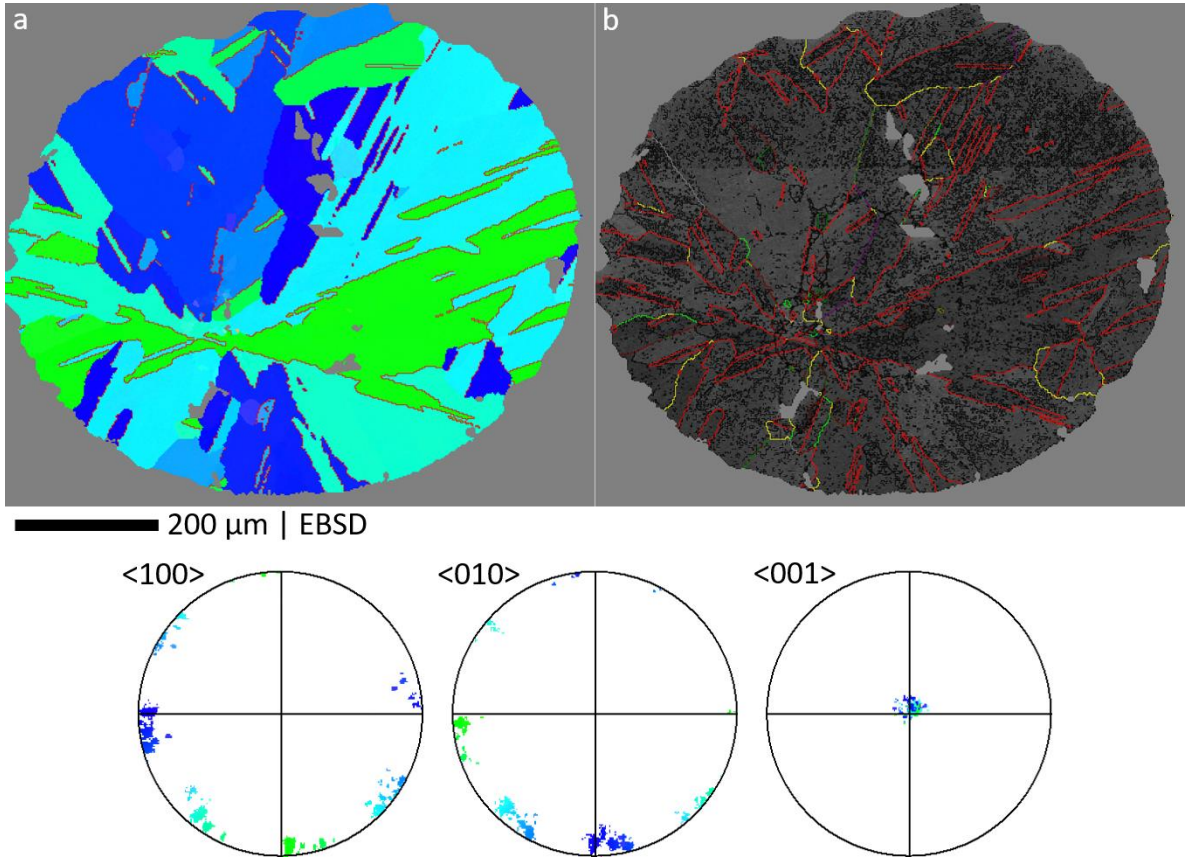
NiB | 8-fold symmetry

- φ = 45° matches expectations
- common <001> direction
- undercoolings up to 110 K

  → oxides/ impurities on surface
- One growth structure through whole cross-section

  → as present in NiZr
- Distorted grain boundaries

  → degrading symmetry across grain boundary

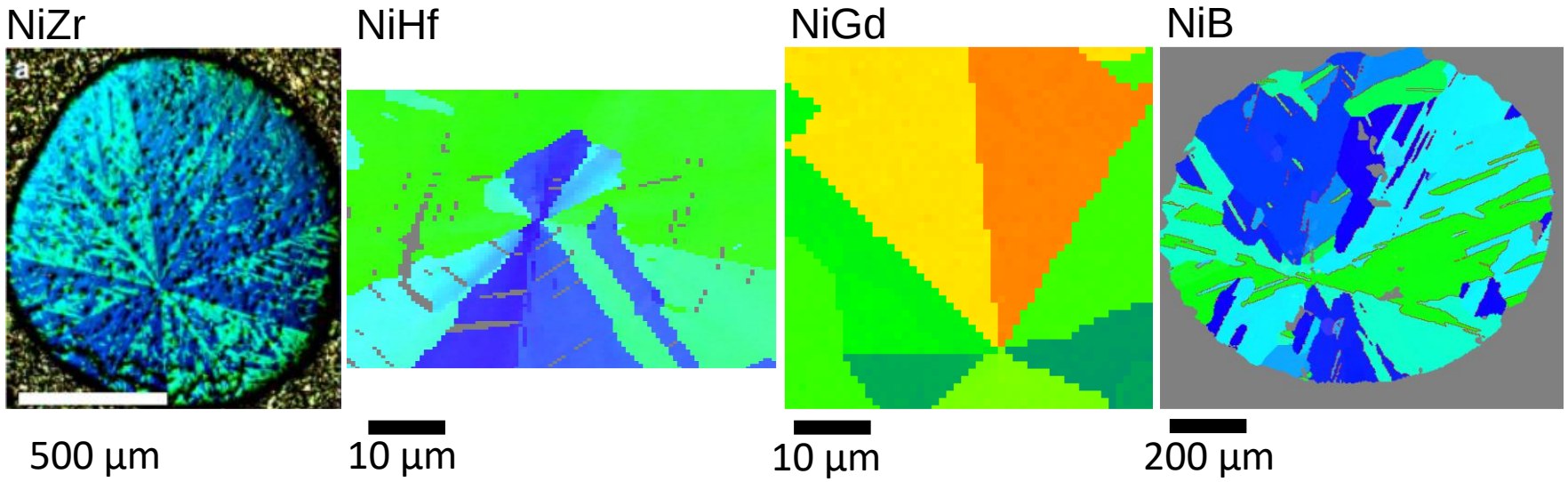


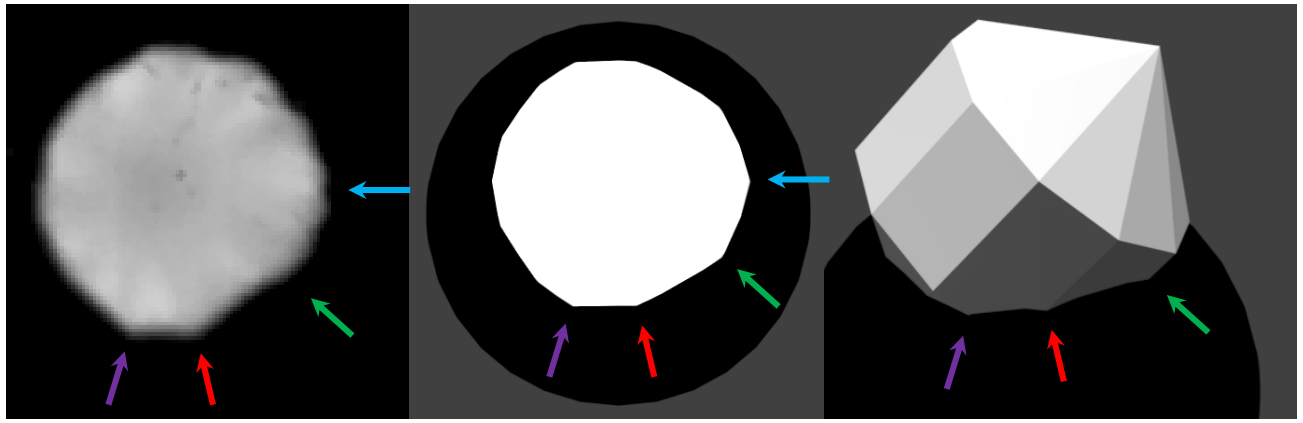
Discussion – Universal nucleation and growth model

Experimental measurements
Singular nucleation events

↓

In situ observations
n-fold solidification front





Discussion – Universal nucleation and growth model

Experimental measurements
Singular nucleation events

↓

In situ observations
n-fold solidification front

↓

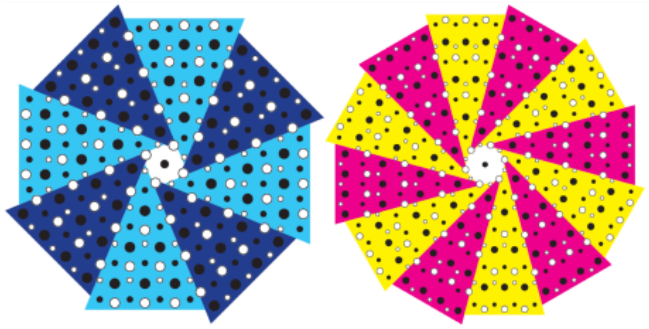
Analysis of microstructure
Checking crucial features

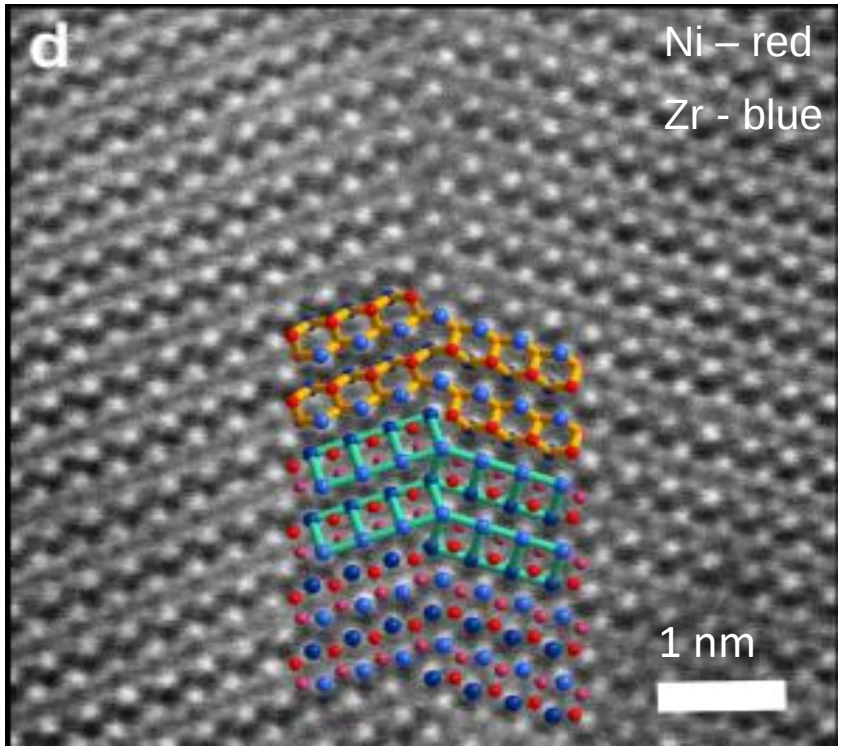
↓

Further validation
TEM, other variants
other orthorhombic phases

Crucial features

1. Solidification in B33 ✓
2. Angle φ ✓
3. Common <001> ✓
4. Deep undercoolings X
5. Icosahedral core ?
6. Stable grain boundaries





HAADF-STEM micrograph of coherent twin boundary in NiZr (⊥ [001])

[2] Hornfeck, W., Kobold, R., Kolbe, M. *et al.* ***Nat Comm* 9,** 4054 (2018)

thank you for your attention