Crucible-free Crystal Pulling of Germanium

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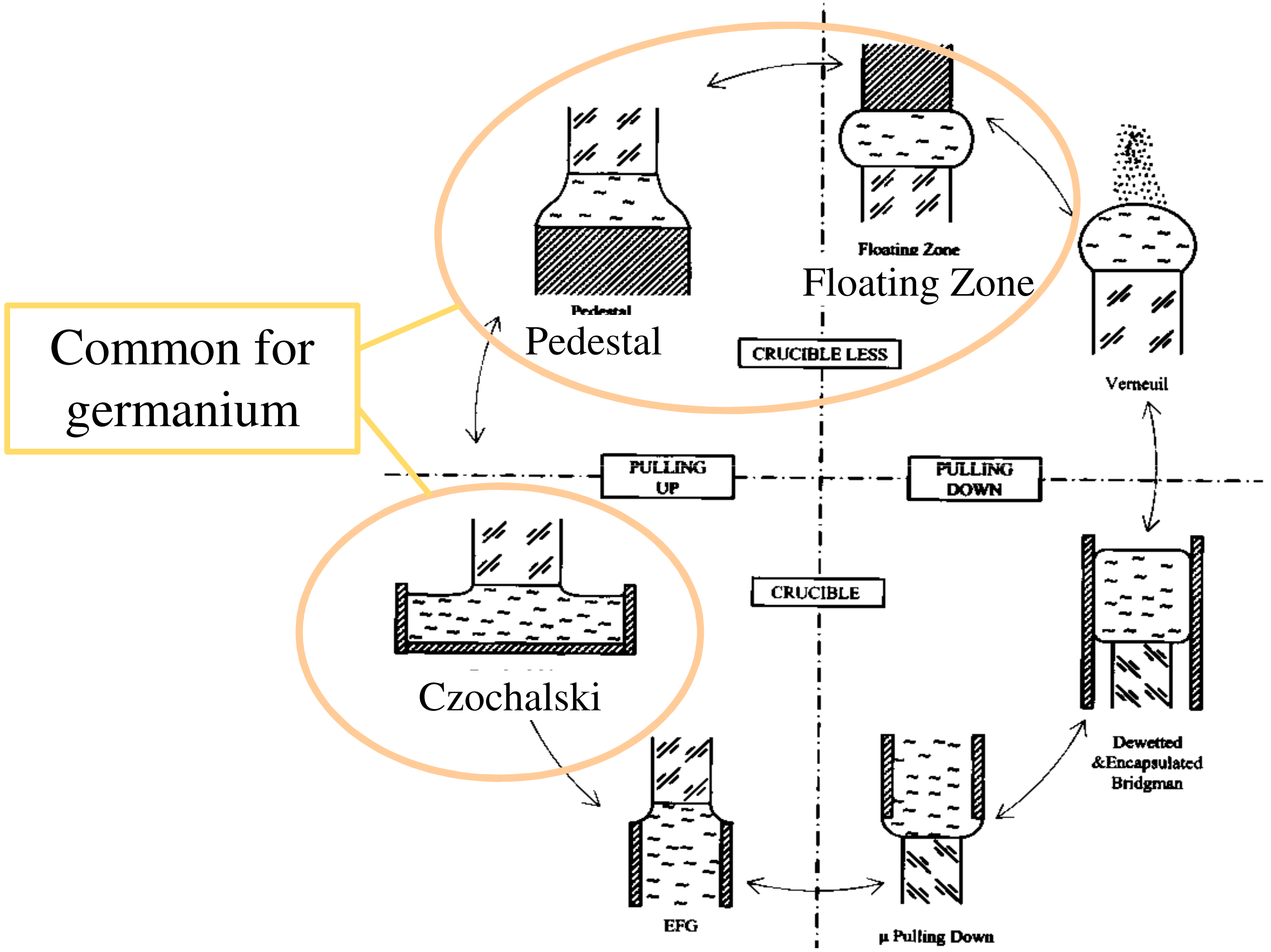
Crystal Growth Processes



"Crystal Growth Processes Based on Capillarity", Thierry Duffar, Wiley 2010

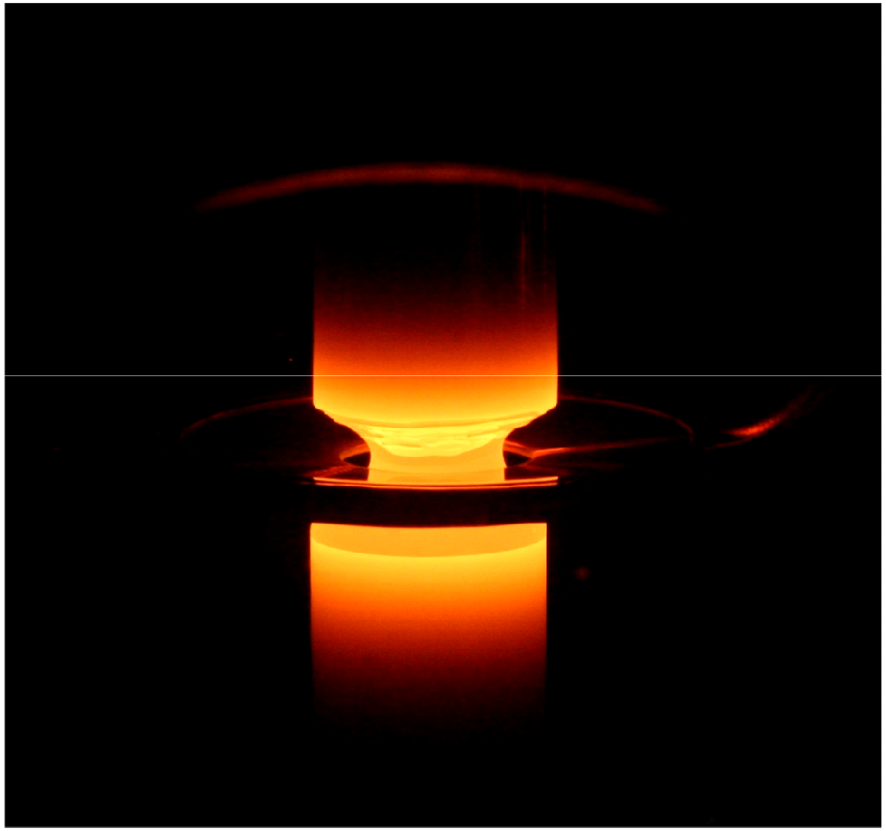
Motivation

- Features of crucible-free crystal growth:
  - Contactless (no additional impurities from crucible etc.)
  - Purification (depending on solubility of impurities)
  - low melt volume, low heat input, higher pull speed

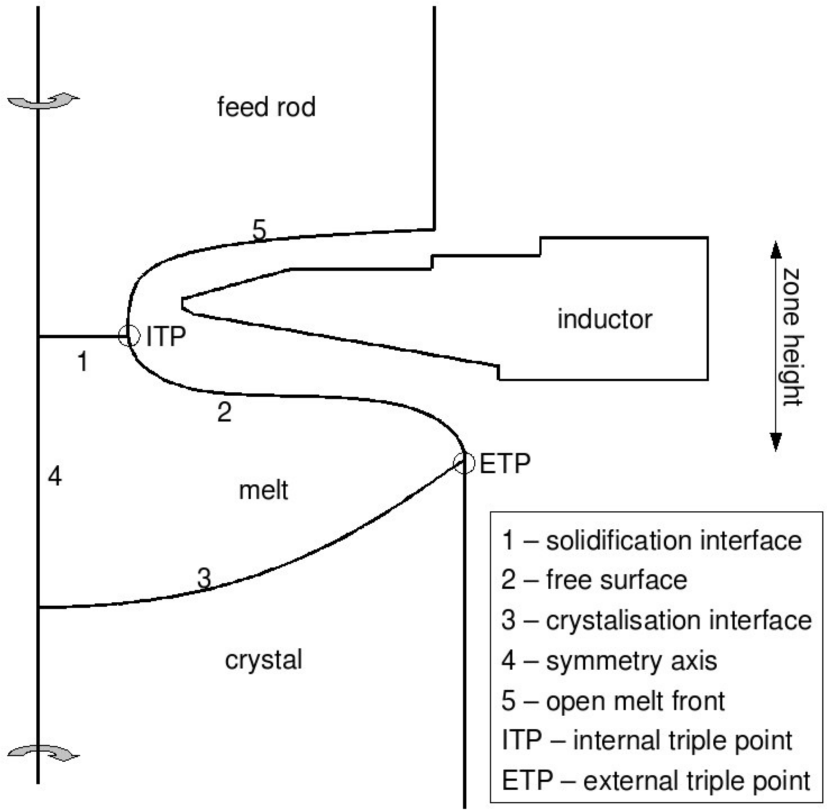
- Esteblished methods for silicon:
  - Floating zone
  - Pedestal

→ as for silicon, higher purity for germanium can be expected

Floating Zone Crystal Growth



1“ silicon process

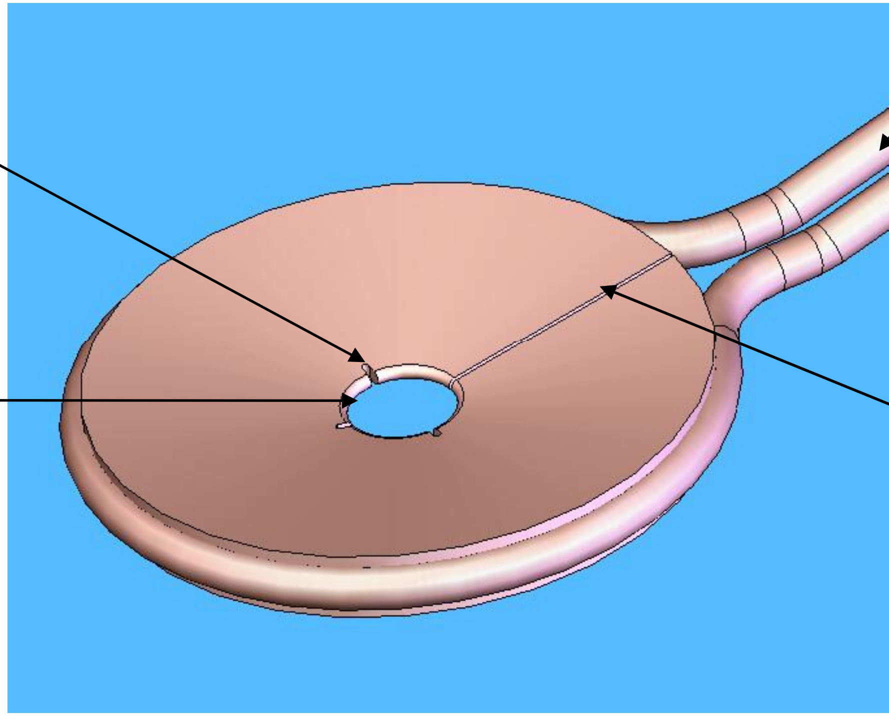


2.5D scheme

Induction Coil Design

Current supplies/cooling water

Side slits

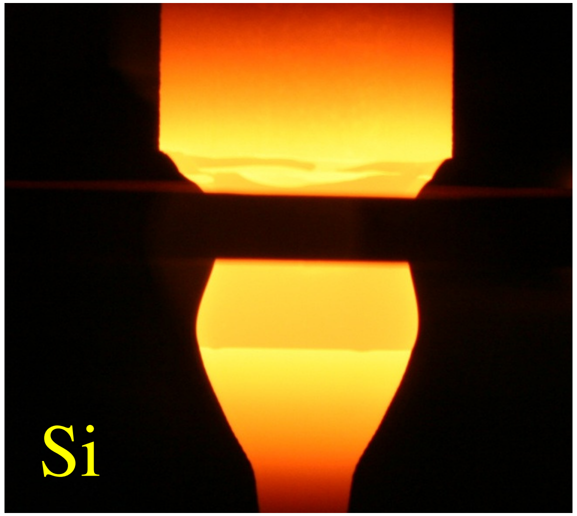


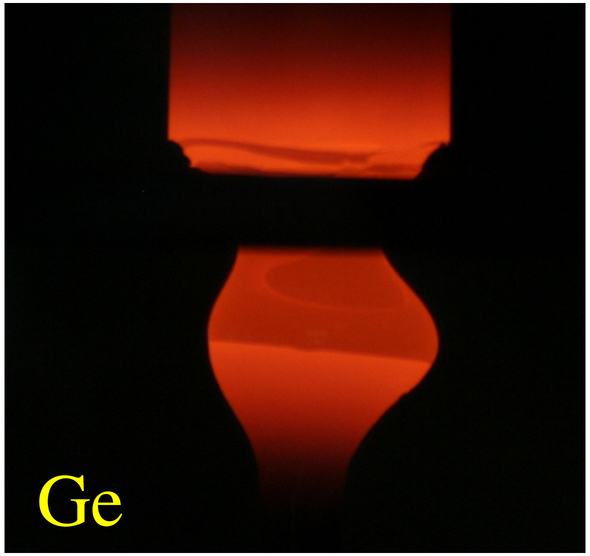
Hole
(Ø10-22mm)

Main slit
(1.5-0.3mm)

"Heart" of the process

Silicon Process Applied for Germanium (Ø≈20mm)





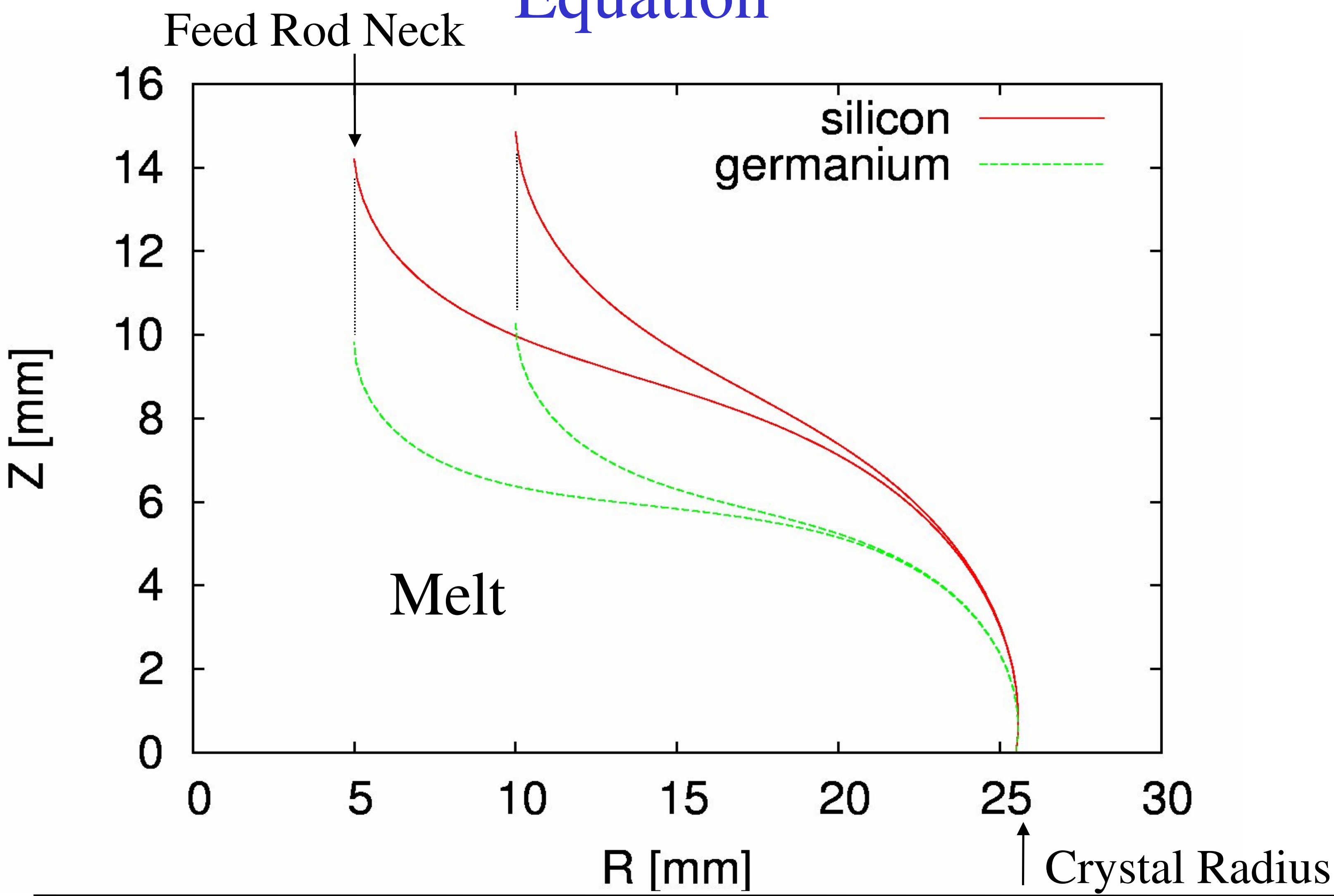
- Stable at least until 26mm
- flat induction coil with 22mm hole (top surface 3°)

- Sloped phase boundary starting at Ø≈16mm
- Screw-like growth until spill out
- Tried for different pull speeds 2 and 3mm/min with same result

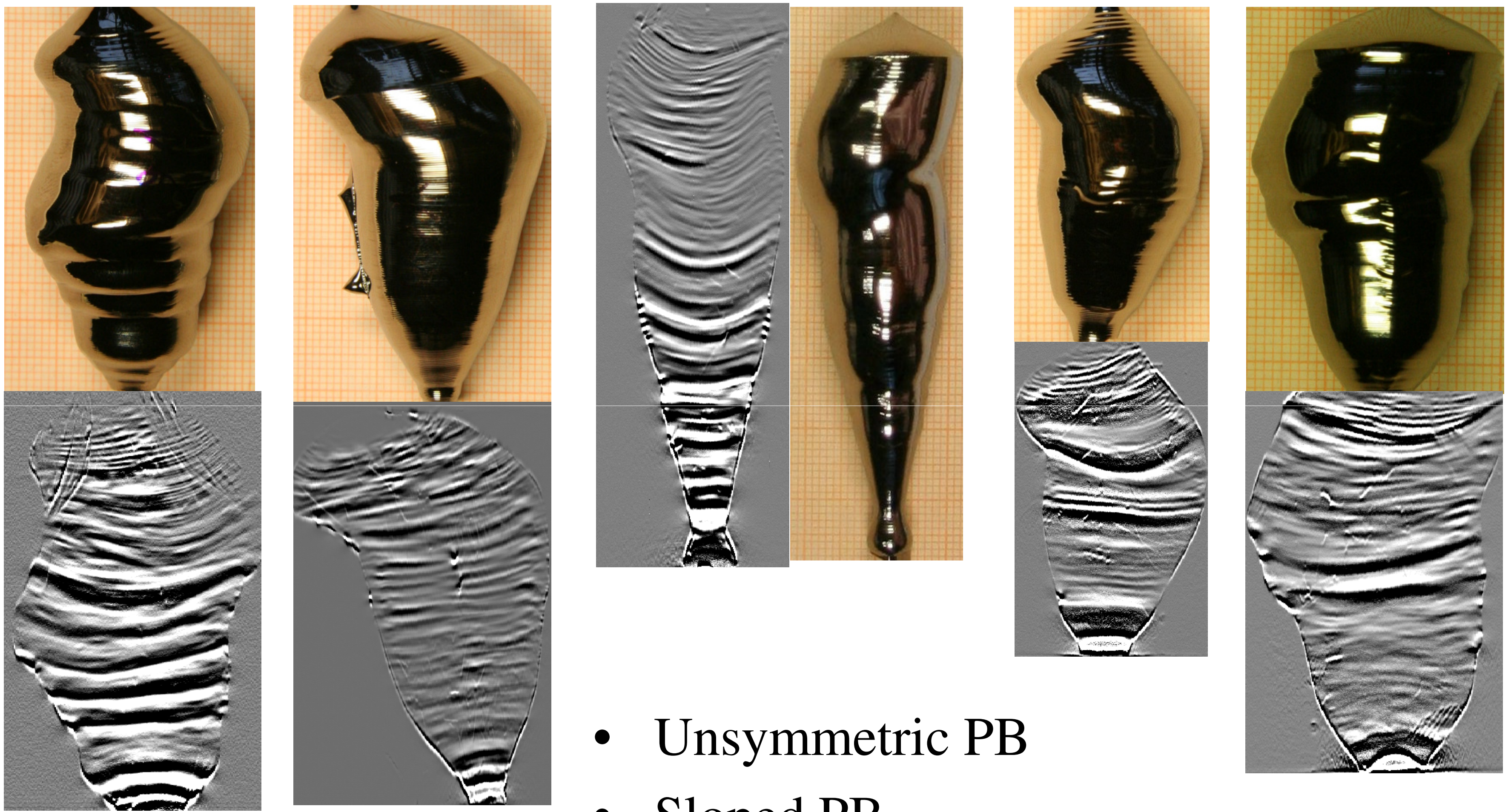
Key Parameters for Stabilization

- Induction coil design
  - Scaling down the FZ silicon process to a small hole (10mm)
  - Reducing main slit to 0.3mm → symmetric heating
  - Change of lower angle
- Increased feed rod diameter 20 → 30mm
- Gas cooling (increase heat losses)
  - Blowing argon of about 5-10 l/min with both 1 and 4 nozzles
  - Increased argon pressure of 3bar
  - Helium as inert gas
- Measures against spikes at the feed rod (because of Helium)
  - Additional heating with ring lamp (10% of 1.5KW)
  - Increased frequency from 2.6 → 3.6 MHz
  - Mixtures of helium and argon

Melt Surface Calculation – Laplace Young Equation



Striations - Phase Boundary (PB)



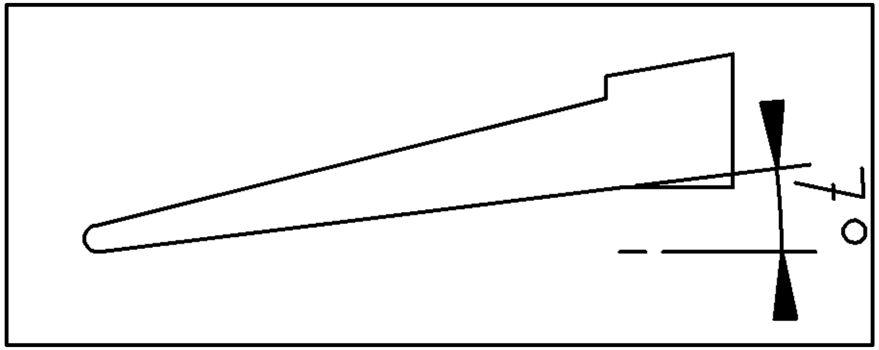
- Unsymmetric PB
- Sloped PB
- Bulges during experiments

Germanium Crystal Ø≈20mm

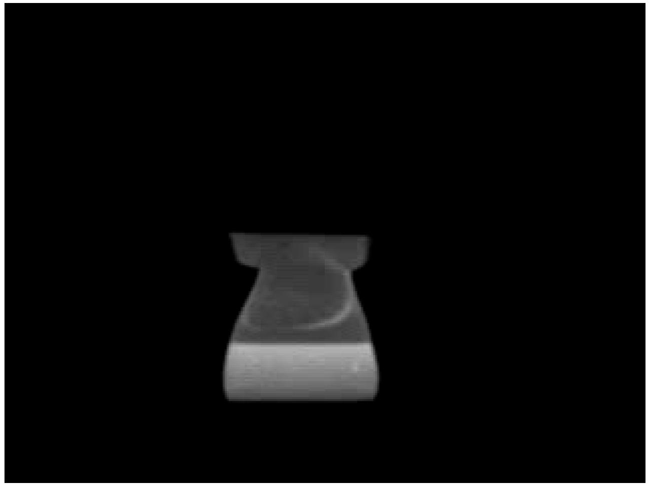
- Two different seeds 9/5mm
- Coil shape:

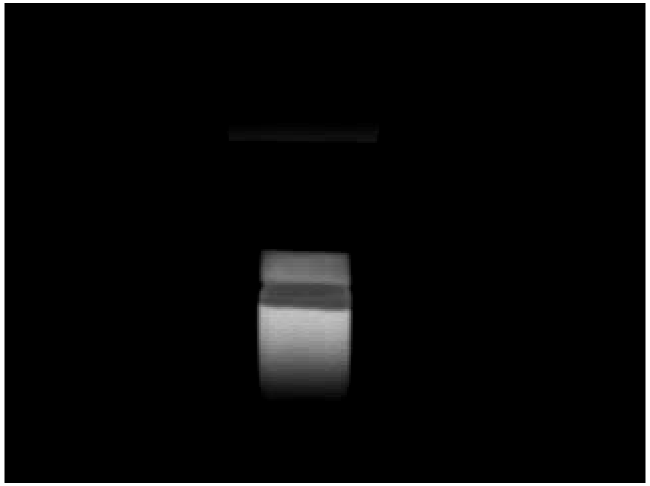
hole 17.5mm

angle 7° →



- Pull speed 3.5 (left) / 2.5 mm/min (right)





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- Increased feed rod diameter 20 → 30mm
- Gas cooling (increase heat losses)
  - Blowing argon of about 5-10 l/min with both 1 and 4 nozzles
  - Increased argon pressure of 3bar
  - Helium as inert gas(hydrogen could not be used by safety reasons)
- Measures against spikes at the melting front (because of Helium)
  - Additional heating with ring lamp (10% of 1.5KW)
  - Increased frequency from 2.6 → 3.6 MHz
  - Mixtures of helium and argon

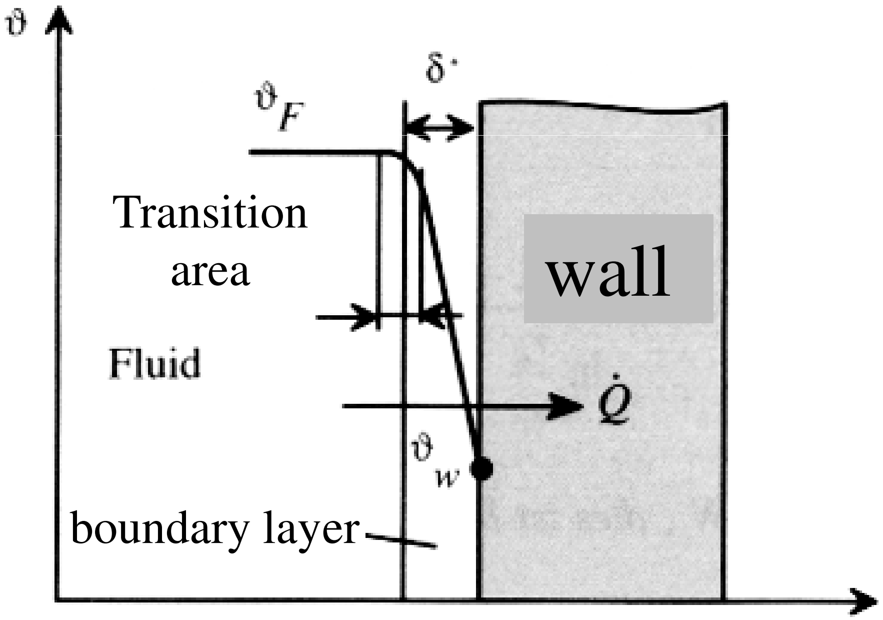
Cooling with Inert Gas: Helium

Heat transfer coeff.

$$\alpha = \frac{\lambda}{\delta} = \frac{Nu \cdot \lambda}{L}$$

Mean Nußelt number for a vertical cylinder

$$Nu_m = \left[0{,}825 + 0{,}387 \left(Ra \cdot f\left(Pr\right) \right)^{\frac{1}{6}} \right]^2 + 0{,}87 \frac{L}{d}$$



Quelle: Windisch - „Thermodynamik“

$$f\left(Pr\right) = \left[1 + \left(\frac{0{,}492}{Pr} \right)^{\frac{9}{16}} \right]^{-\frac{8}{27}}$$

Grashof number

$$Gr = \frac{L^3 g \Delta \Delta T}{\nu^2}$$

Rayleigh number

$$Ra = Gr \cdot Pr$$

Prandtl number

$$Pr = \frac{\nu \cdot c_p}{\lambda}$$

Cylinder height

$$L$$

Comparison for a 10cm Long Cylinder

(Air Liquide, 400K, 1bar)	**Argon**	**Helium**	**Hydrogen**
Viscosity [kg/ms]	2.85E-5	2.29E-5	1.13E-5
Density [kg/m3]	1.2	1.49E-1	6.17E-2
Heat capacity [J/kgK]	5.97E+2	5.19E+3	1.45E+4
Heat conductivity [W/mK]	2.58E-2	2.06E-1	2.60E-1
Prandtl number	0.66	0.58	0.63
Grashof (γ=1/350K,ΔT=50K)	1.78E+6	5.92E+4	4.22E+4
Nußelt number	28.4	13.1	12.6
α [W/m²K]	7.3	27.0	32.8
Gain	1	**3.7**	**4.5**

Heat Radiation

	T_m [K]	emissivity	heat radiation [kW/m²]	Si/Ge
Ge	1210	0,5	61	
Si	1685	0,5	229	3,76

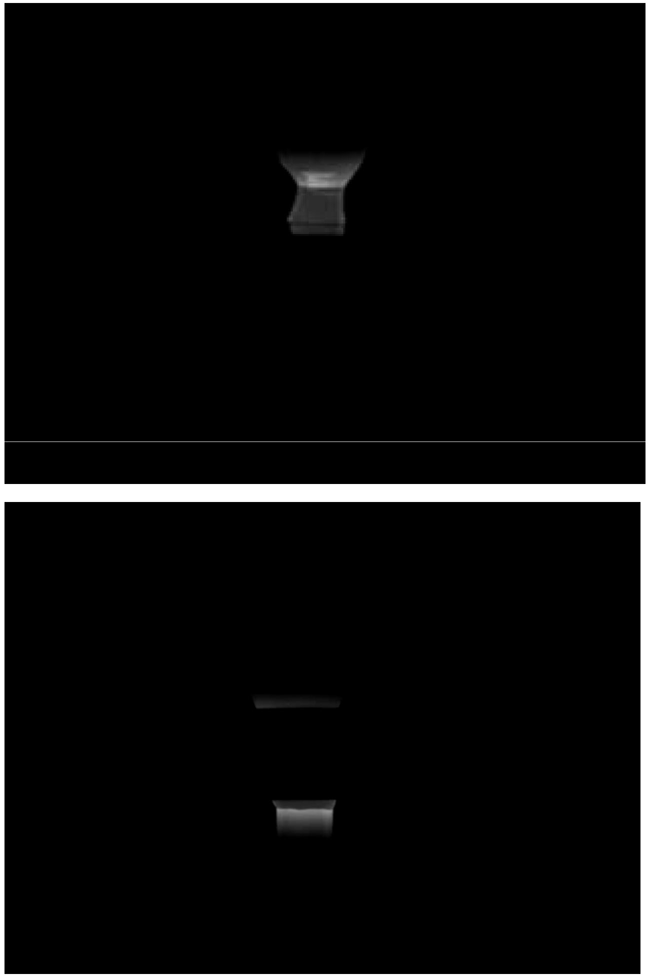
- For comparison :

  gas-cooling around the phase boundary

$$\Delta T \approx 900\mathrm{K} \rightarrow q_{He} \approx 25\mathrm{kW} / m^2$$

Crystal Growth in Helium

- until 21mm no visible screw (before: starting at 16mm)
- Reduced lateral buckling
- Spikes touch induction coil
- Slow feed rod rotation (10/0.8 min^{-1}) with two pull speeds (3.0/2.0 mm/min) → no influence on spikes



(fast motion)

Key Parameters for Stabilization

- Induction coil design
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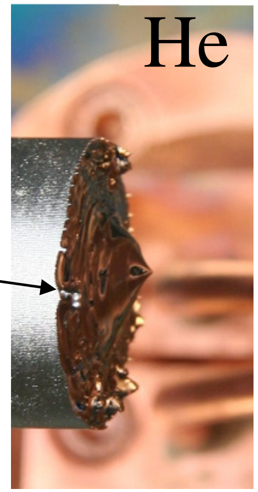
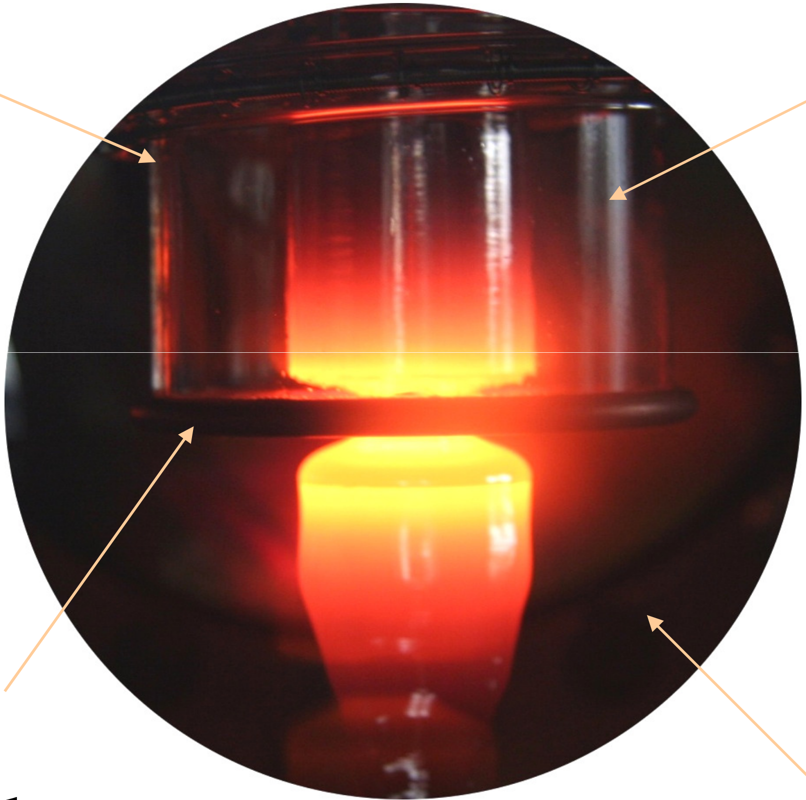


Different Gases around Feed Rod / Crystal

Argon inlet

Quartz cylinder

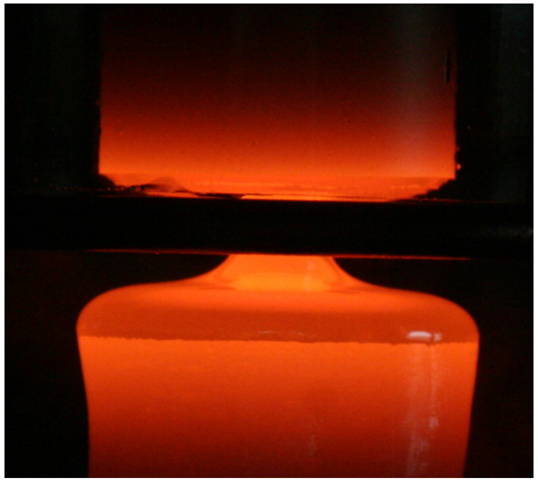


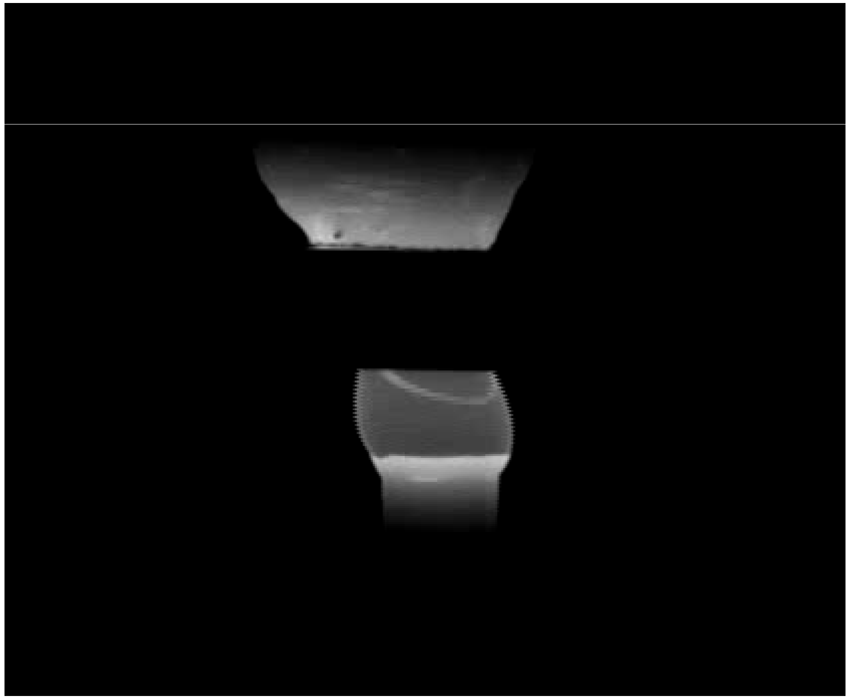
Induction coil

Helium in chamber

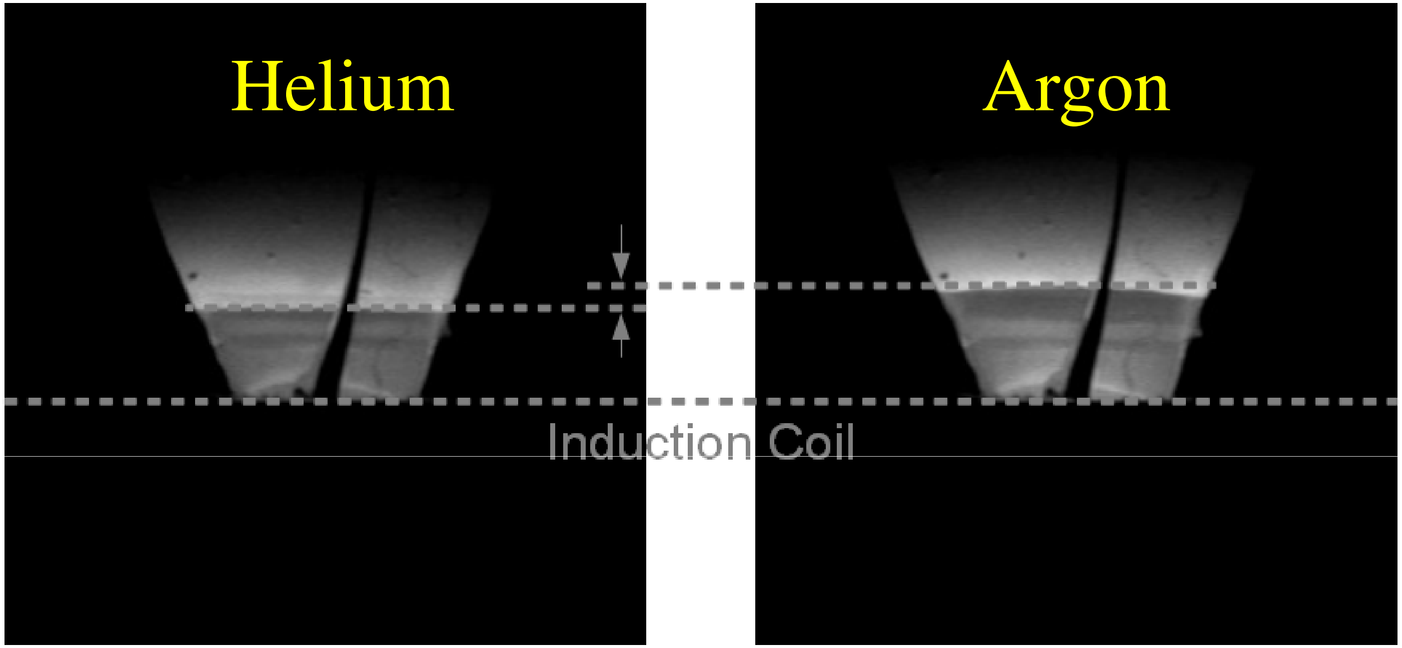
Different Gases around Feed Rod / Crystal

- Spikes come and go reproducibly depending on the gas around the feed rod
- By changing the argon flow, diameter is changing as well (more argon → more melt)
- Diameter up to 35mm





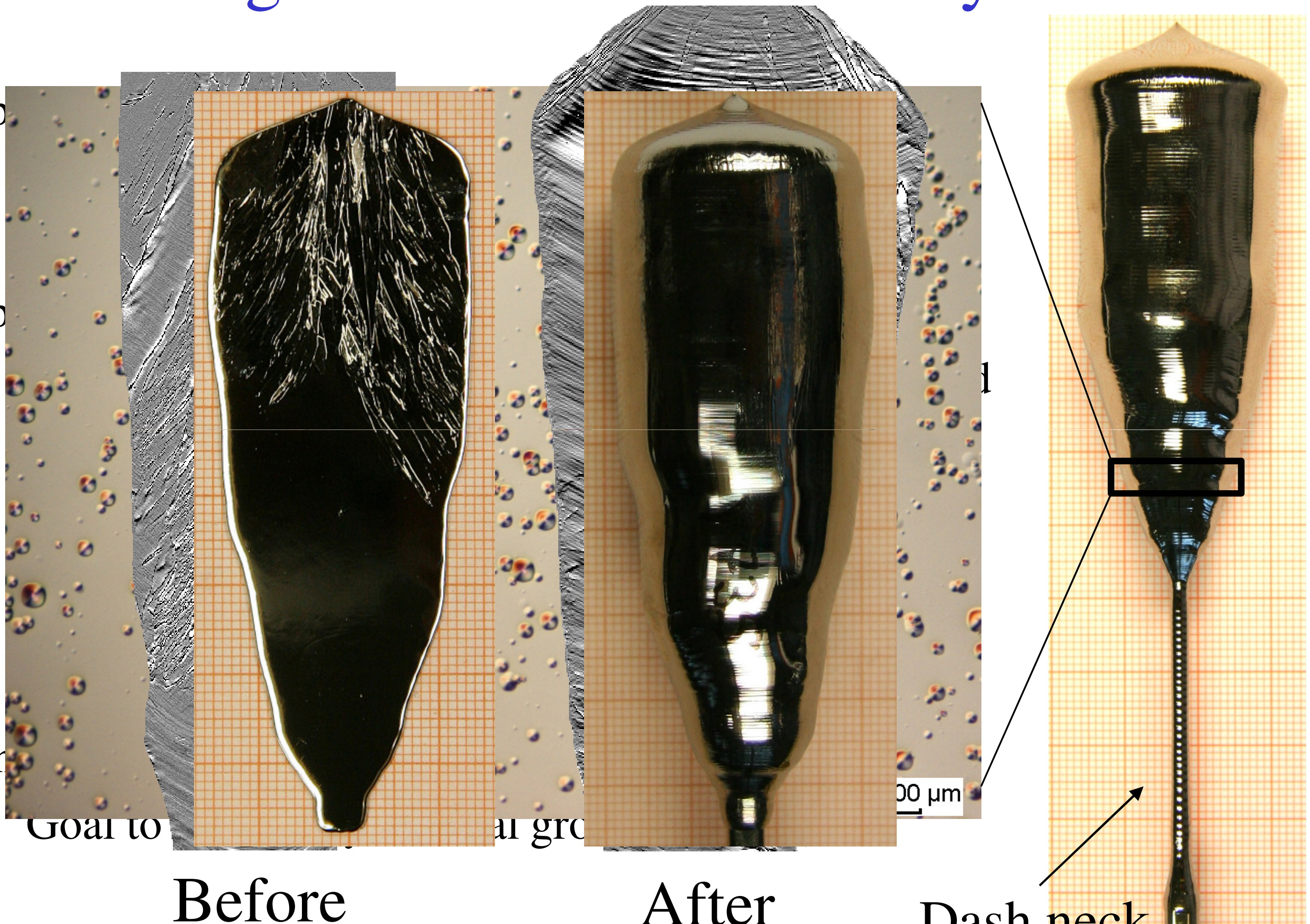
Change of Gas during Drop Forming



- Reversible change of drop volume (same power and position)
- Short reaction times - around 30sec for 30mm feed rod
- Melting off the spikes with increased argon flow rate (mixture between gases) - Spikes can be "blown away" during crystal growth

Working on Dislocation-free Crystals

- Op
  –
- Op
  –
  –
  –
- Si
  – Goal to … al gro



Before

After

Dash neck

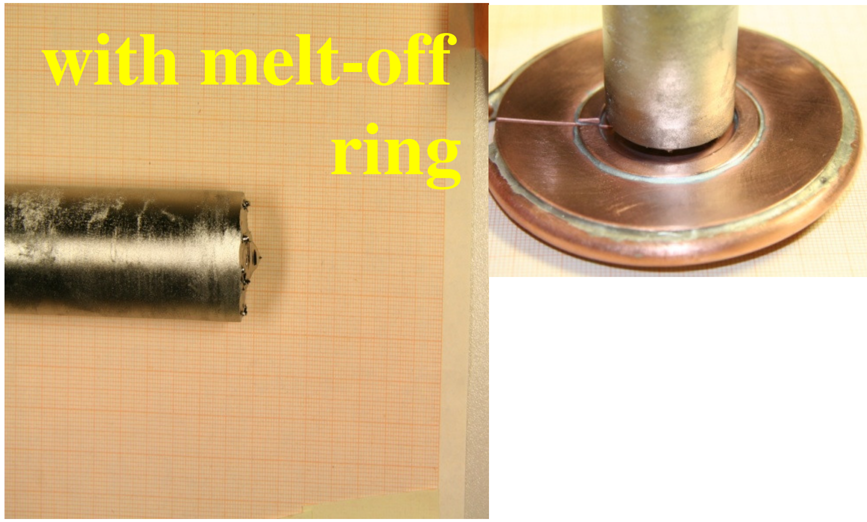
Conclusion

- Floating Zone for Germanium
  - Different setup compared to Si for stabilizing the growth
    - Gas cooling is important to compensate the lower radiative cooling
  - Two-gas setup to get rid of spikes

- Future
  - More tuning of parameters to get dislocation-free material
  - Investigation of increased purification
  - Gas cooling around crystal → reduce helium content

Thank you for your attention!

Measures against Noses



Melt-off ring uses the edge effect for power concentration

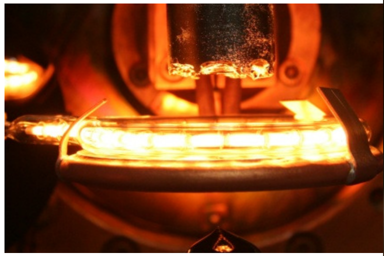
– Effect too small

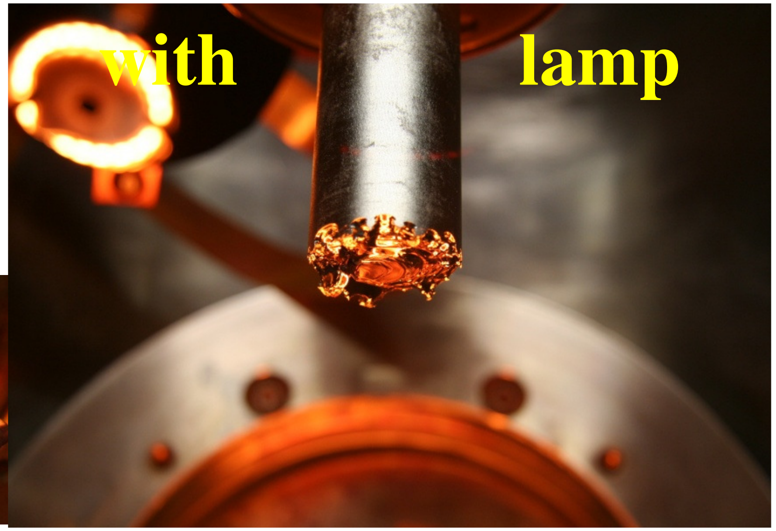
Combined optical heating

– Too much heating of feed rod

→ heat build-up

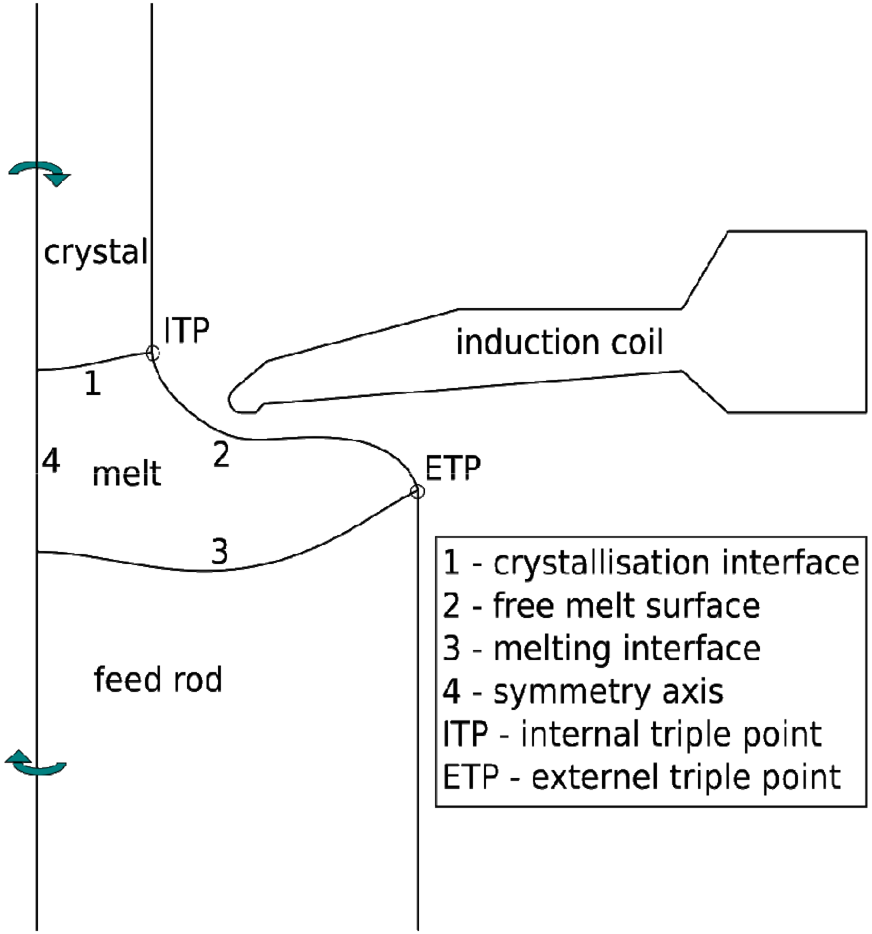
(reduction of gradients)





Pedestal Crystal Growth

0.5“ silicon process

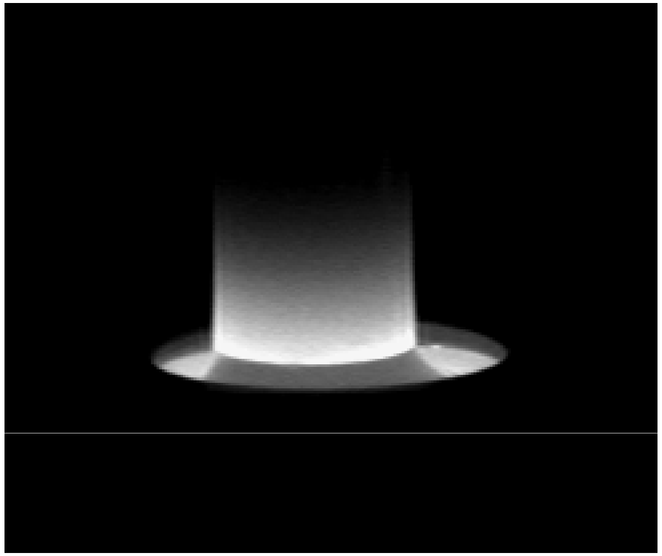


2.5D scheme

Melt Frozen in the Center

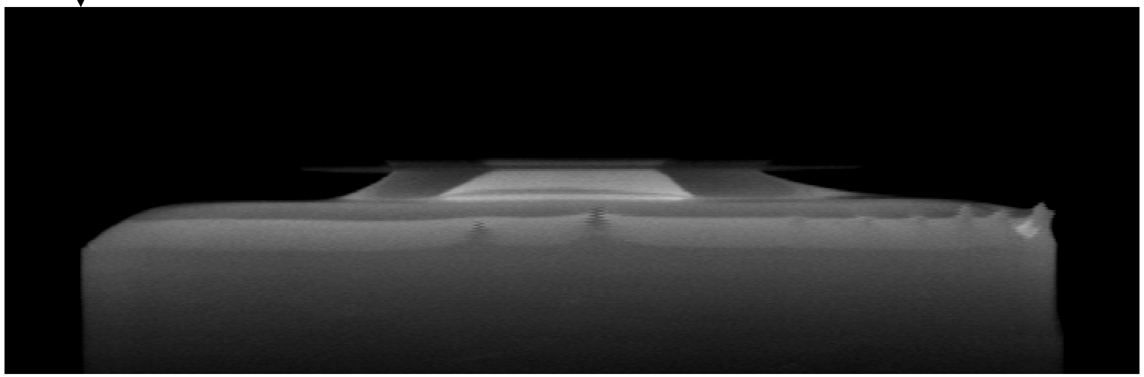
- Increasing crystal diameter

  → reducing heater power



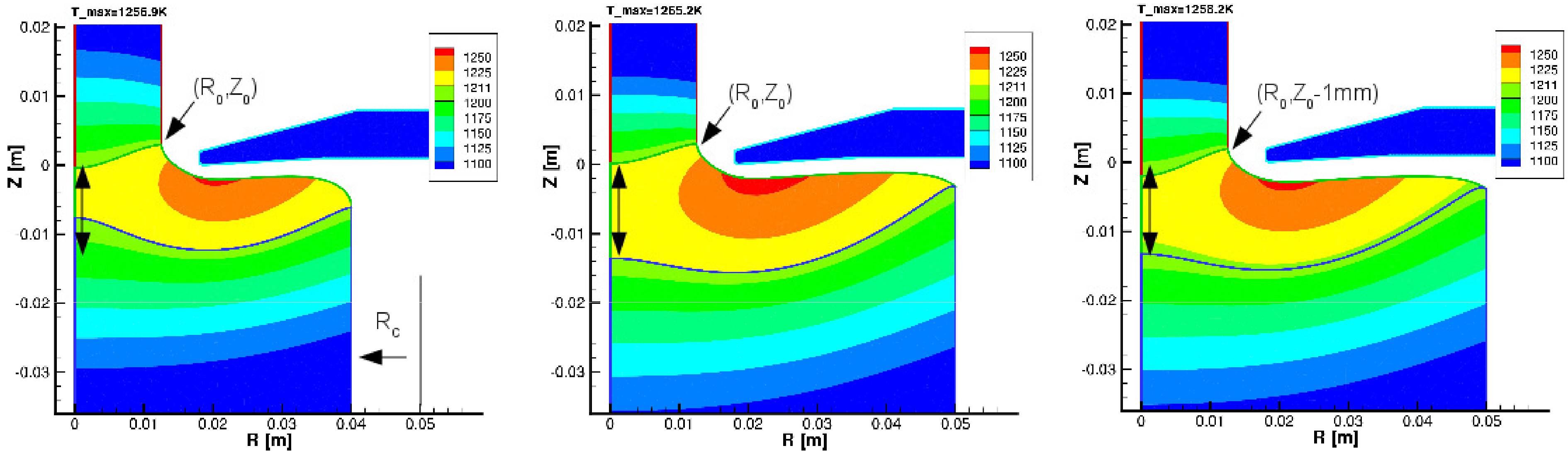
- Freezing hard to foresee

Process picture shortly before freezing



Simulation Model for Process Optimization

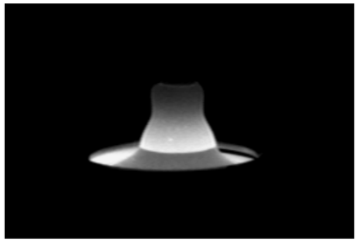
FemagFZ/PED from FemagSoft Belgium

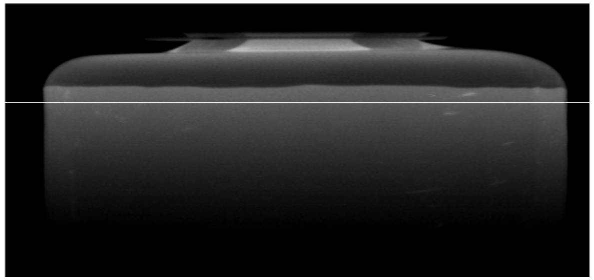


- Bigger feed rod better against freezing and spilling out (left)
- Stretched zone increases temperature gradient in the center (right)

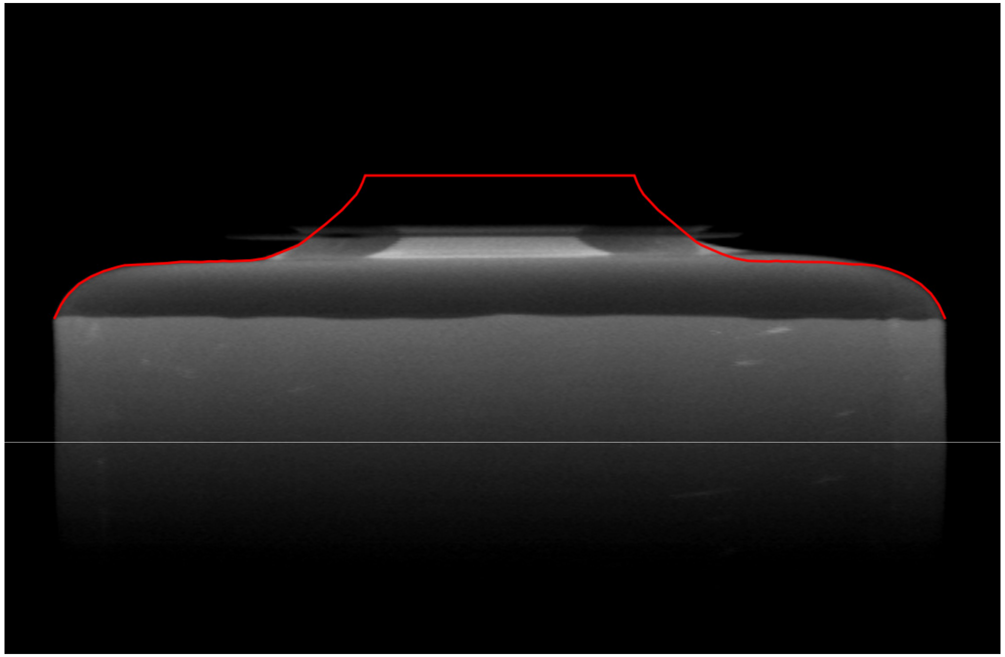
Pedestal

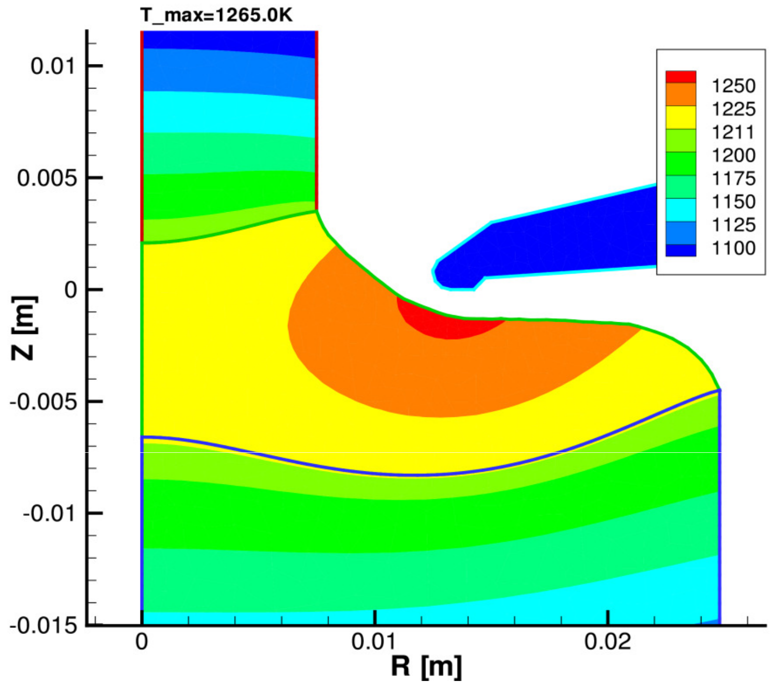
- Material: Cz germanium
- Feed rod 50mm / crystal 15mm
- Pull speed 1mm/min
- Rotation: -6min^{-1} / 15min^{-1}
- Seed <100> germanium
- Gas: argon 10 l/min





Simulation of the Temperature Field

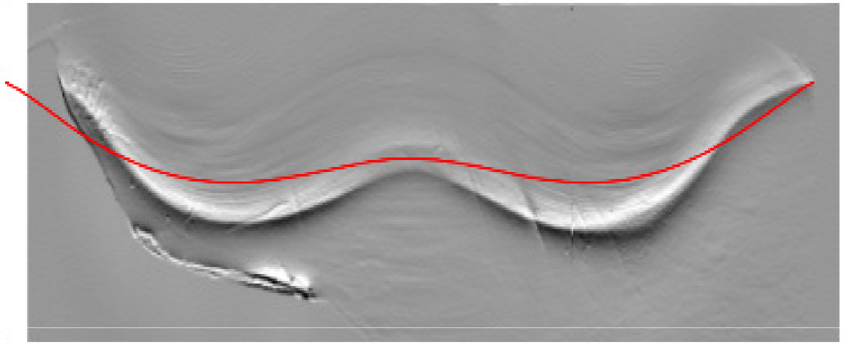




- Melt surface picked from experiment
- Melt surface unsymmetric → both sides give same results
- Simulation with model for melt surface gives slightly different results

Feed Rod Striations and Melt Point Isotherm

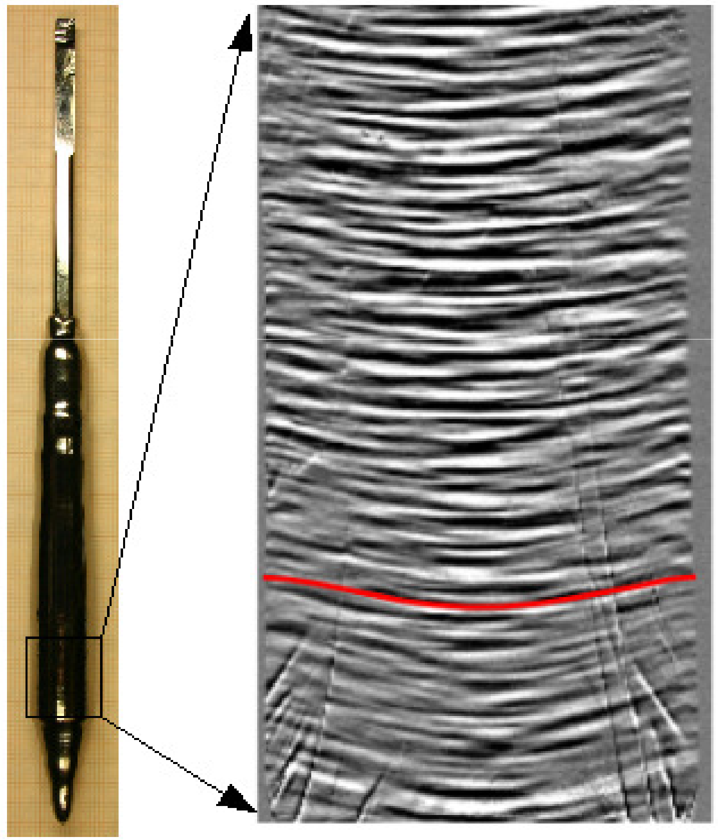
Lateral photovoltage scanning (LPS)
→ visualization of striations



- Melt point isotherm qualitatively good (W-shape)
- Minimum a little too shallow
- Calculation at the edge too steep
- Maybe melt convection must be considered

Crystal Striations and Melt Point Isotherm

- Good agreement
- For Model: melt surface taken from experiment!!



GERDA

- Shortcut for GERmanium Detector Array
  - $^{76}Ge \rightarrow$ detection of neutrinoless double beta decay
  - Done at the LNGS (Grand Sasso National Laboratory)
- Material
  - ~50kg of enriched (3.5N) GeO_2 are available (Krasnojarsk, RU)
  - Enriched material (6N) as source from PPM Pure Metals
  - Until now depleted germanium for test
- Detector Crystal of ^{76}Ge
  - 3“ <100> with few 10^{10} cm^{-3} net carrier concentration (at 77K)
  - 10 crystals needed with length of 70mm
  - Pulled with Czochralski method

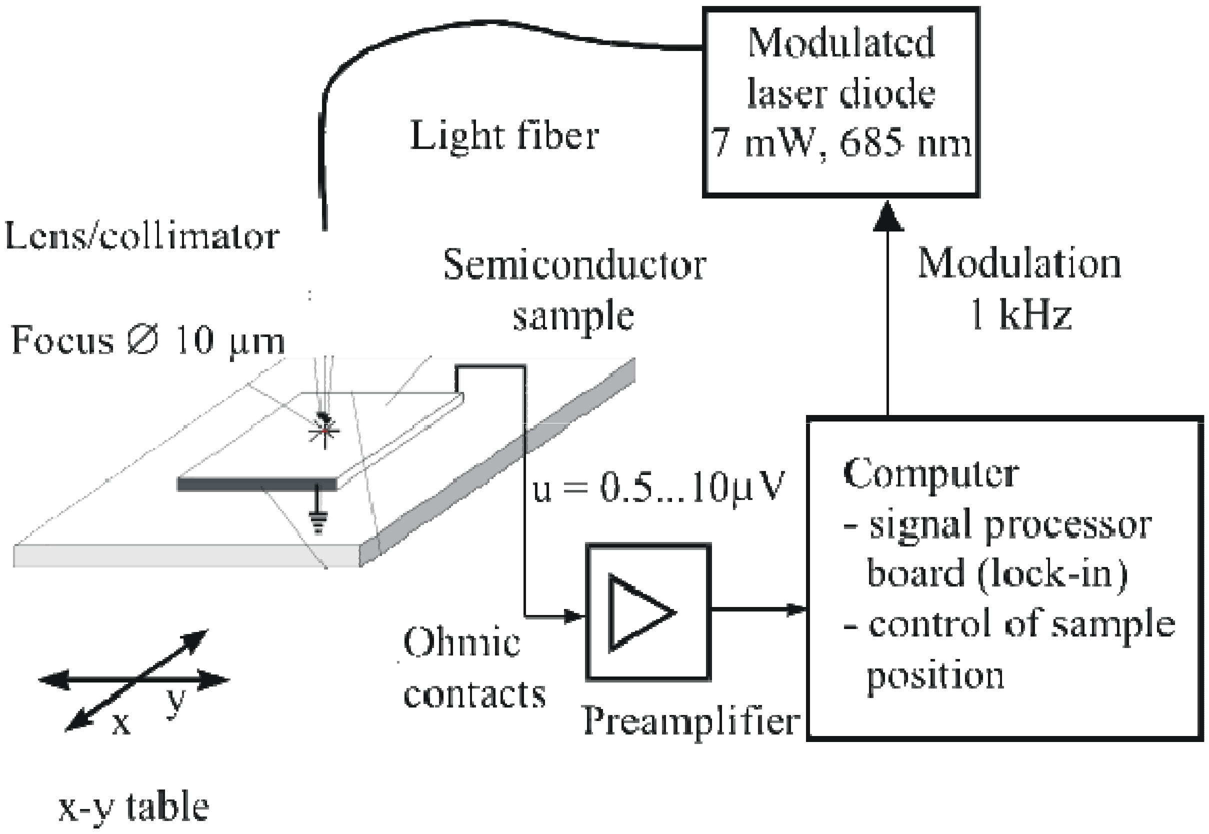
"Mini-Cz" in FZ Puller

- Tube-like induction coil
  - 3MHz generator from FZ puller
- Coil also radiation shield
  - Reduced heat losses
- Less radiativ heating of the walls
  - Only melt, crucible and susceptor are hot

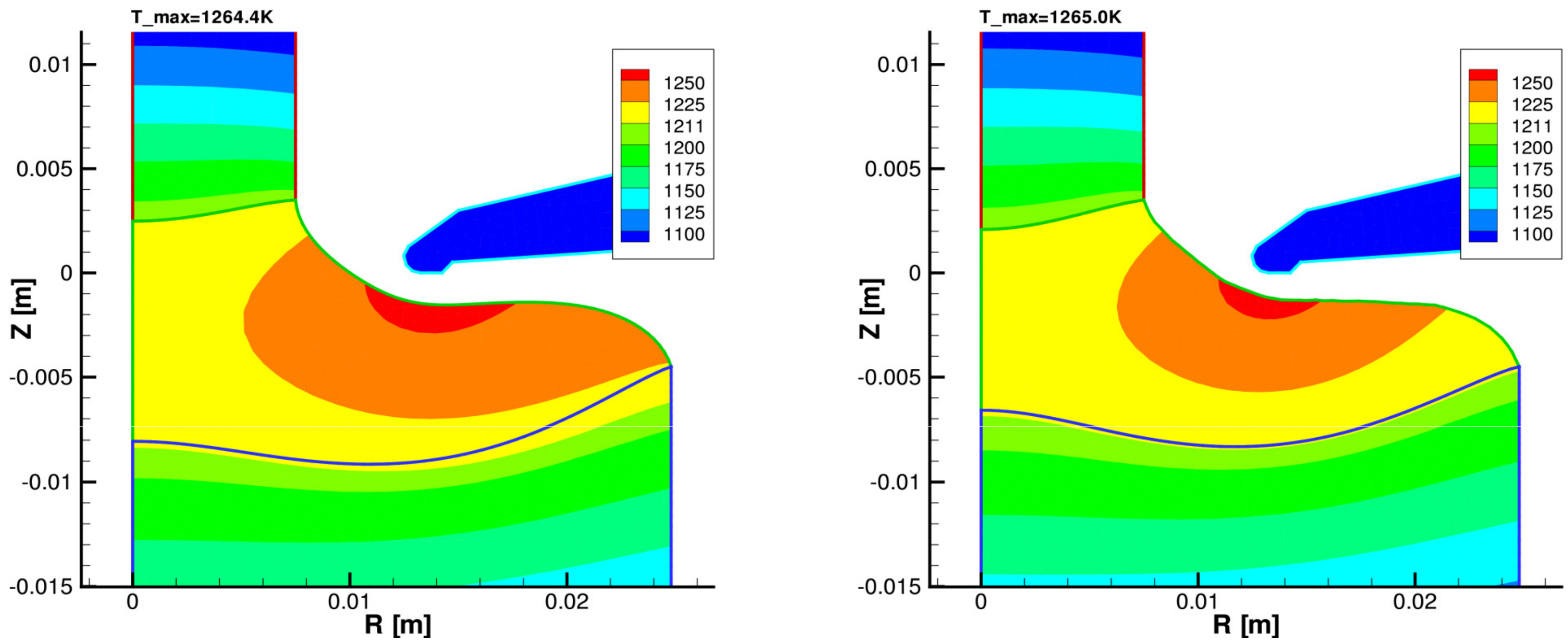
Crystal Structure Changed

- Dislocation-free crystal
  - Crystal up to 20mm
  - Dash method for necking
  - Reducing pull speed
  - After heating?
- Increasing diameter (>35mm)
  - Bigger feed rod
  - Changes of induction coil needed
- Analyzing the impurities
  - 5% Hydrogen in helium for passivation
  - Multiple zone melting?

Lateral photovoltage scanning (LPS)



Simulation des Temperaturfeldes



- Schmelzoberfläche aus Experiment bestimmt
- In Experiment nicht ganz symmetrische Schmelzoberfläche
- Simulation mit Modell-Oberfläche liefert unzureichende Übereinstimmung