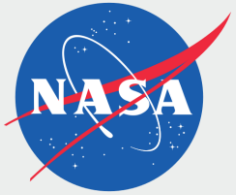
Bridgman Growth of Germanium and Germanium-Silicon Crystals under Microgravity

A. Cröll[1,2], A. Hess[1], J. Zähringer[1], T. Sorgenfrei[1],
A. Senchenkov[3], A. Egorov[3], K. Mazuruk[2], M. Volz[4]

[1] Crystallography, Albert-Ludwigs University of Freiburg, Germany
[2] RSESC, The University of Alabama in Huntsville (UAH), USA
[3] ZENKI - NIISK, Moscow, Russia
[4] EM 31, NASA Marshall Space Flight Center, Huntsville, USA



Crystallography
Geo- and Environmental Natural Sciences
Albert-Ludwigs University Freiburg

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OVERVIEW

- **Introduction and FOTON M4 flight**
- **Sample Setup and Growth Parameters**
  - **Bridgman growth of Ge:Ga with RMF**
  - **Bridgman growth of Ge:Ga with Vibration**
  - **Detached Bridgman growth of Ge-Si**
  - **Simulations**
- **Flight and Reference Crystal Analysis**
  - **Ge:Ga with RMF**
  - **Ge:Ga with Vibration**
  - **Detached growth**
- **Future ISS experiments**
- **Conclusions**

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INTRODUCTION

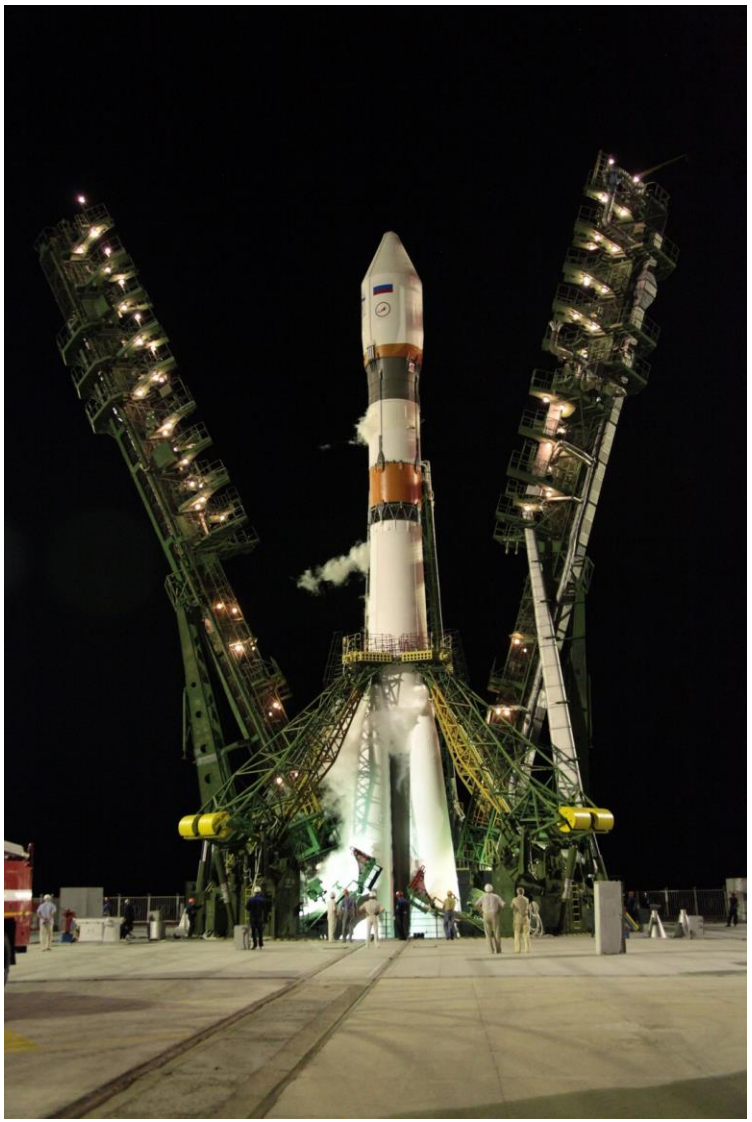
- **3 Bridgman experiments on Ge:Ga and 1 Bridgman experiment on Ge-Si were performed on the unmanned mission FOTON M4 in 2014.**
- **The experiments were part of the RDGS/ICESAGE projects of ESA/NASA/DLR**
- **Original objectives:**

  - **Analyzing segregation transitions (diffusive - laminar flow, laminar - time-dependent flow) in Ge:Ga Bridgman crystals by means of a rotating magnetic field (Exps. “K1”, “K2”)**

  - **Influencing segregation and interface curvature in Ge:Ga Bridgman crystals by means of axial vibrations (Exp. “K3”)**

  - **Detached Bridgman growth of Ge-Si (Exp. “K4”)**

FOTON M4 LAUNCH



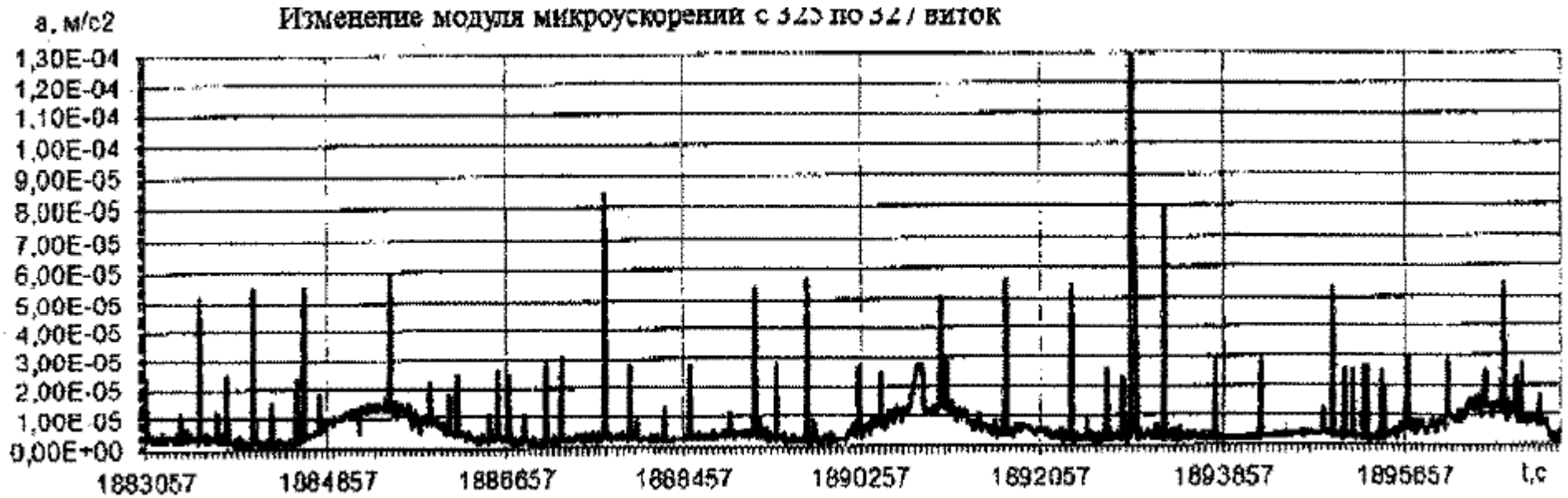
Source: www.federalspace.ru

Launch: July 18, 2014
Rocket: Soyuz 2-1a

FOTON M4 FLIGHT PARAMETERS

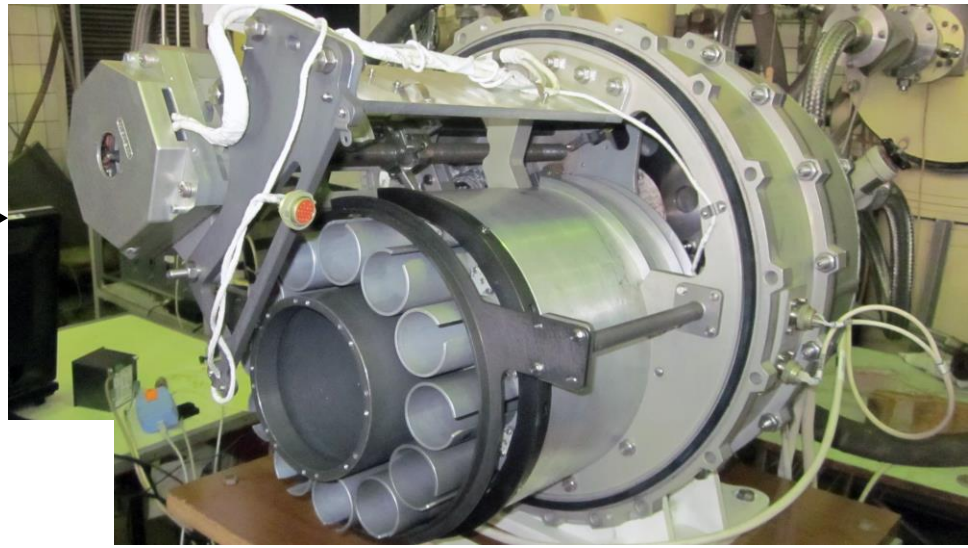
- **Launch: July 18, 2014**
- **Perigee: 258.4 km**
- **Orbital period: 92.56 min**
- **Landed: Sept. 1, 2014**
- **Apogee: 568.7 km**
- **Orbit inclination: 64,89°**

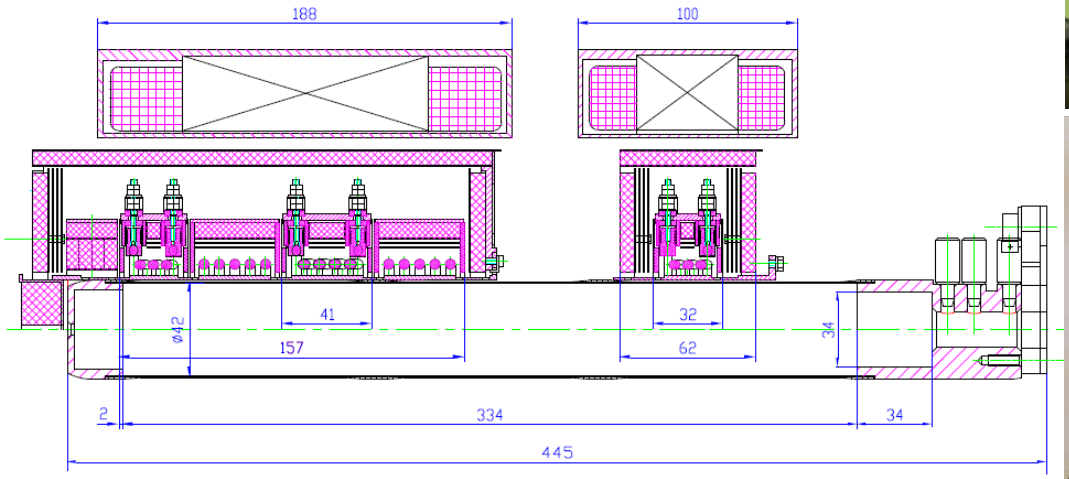
Typical µg levels

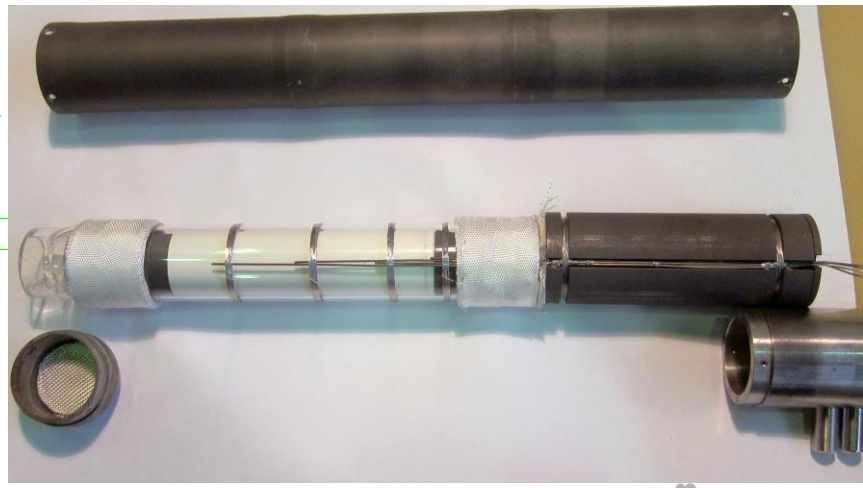


POLIZON M2 FURNACE

4(+1) Heating Zones
Vacuum furnace
Cartridge diameter 42mm
Max. ampoule diameter 36mm
Automated cartridge exchange
Rotating Magnetic Field
4 TC‘s on the ampoule (flight)







Technical performance

Long inductor:
induction from 0.1 to 1.0 mT;
frequency from 25 to 200 Hz

Short inductor:
induction from 1 to 4 mT;
frequency from 25 to 200 Hz

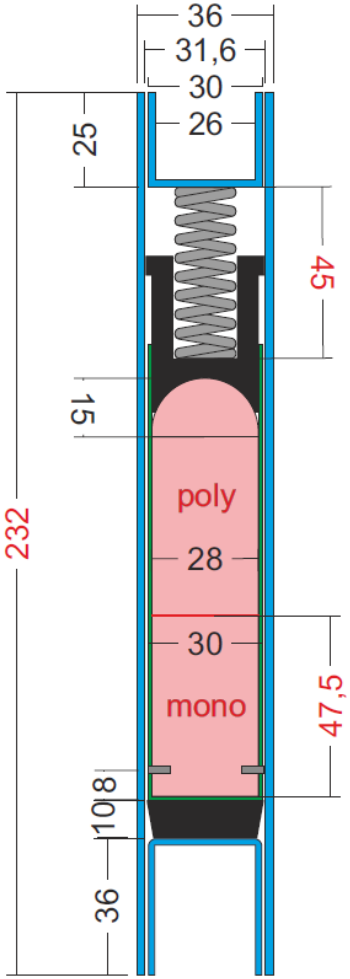
EXPERIMENT TIMELINE

Experiment, sample	Date, hh:min (MDT)	Planned duration, hh:min	Real duration, hh:min
K2 Ge:Ga	27.07.2014 17:00 – 28.07.2014 07:09	13:30	14:09
K3 Ge:Ga	28.07.2014 13:00 – 29.07.2014 03:09	13:30	14:09
K4 GeSi	29.07.2014 10:00 – 01.08.2014 00:09	61:30	62:09
K1 Ge:Ga	01.08.2014 17:00 – 01.08.2014 07:09	13:30	14:09
F1 CdZnTe:In	02.08.2014 02:00 – 08.08.2014 20:07	200:00 (100 h. by the contract)	162:07

K1/K2 SAMPLE SETUP

- Gallium-doped Germanium crystals
- {100}-oriented seeds
- Sample divided into two parts: single crystalline doped ($1 \cdot 10^{17} cm^{-3}$ Ga) lower half, undoped polycrystalline upper half
- pBN crucible, Ta fixation pins for the seed
- Graphite plug with CFC spring to avoid free melt surface
- No inert gas - vacuum

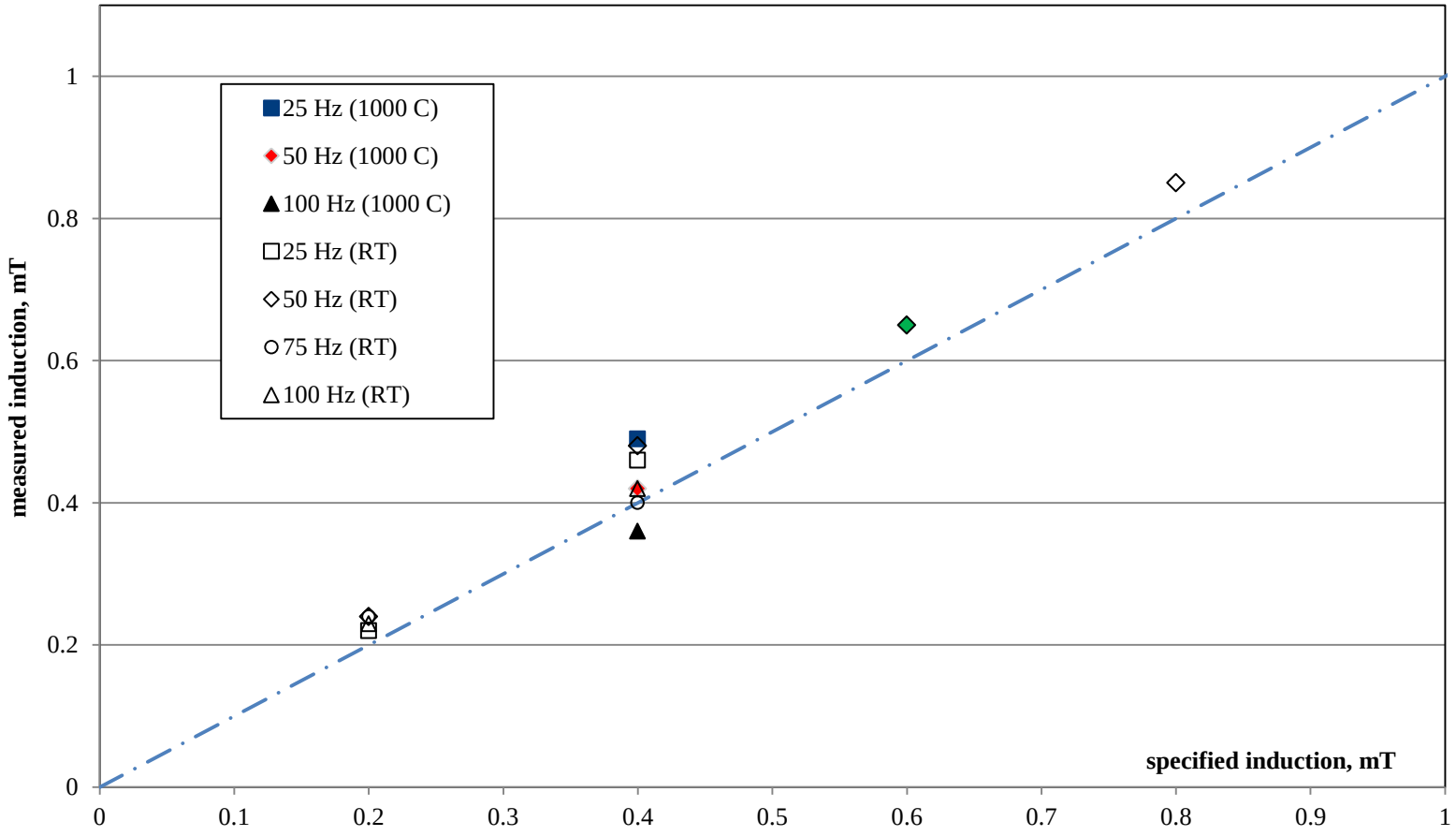
- K1: Transition from diffusive to laminar convection regime (RMF)
- K2: Transition from laminar to time-dependent convection regime and back (RMF)



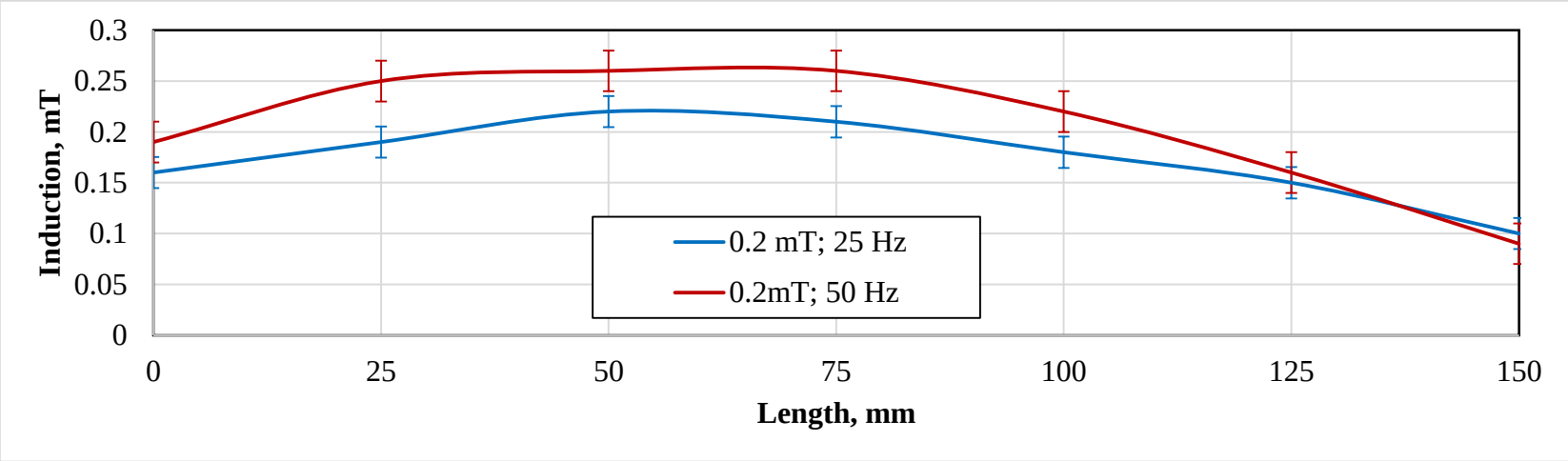
all measures in mm

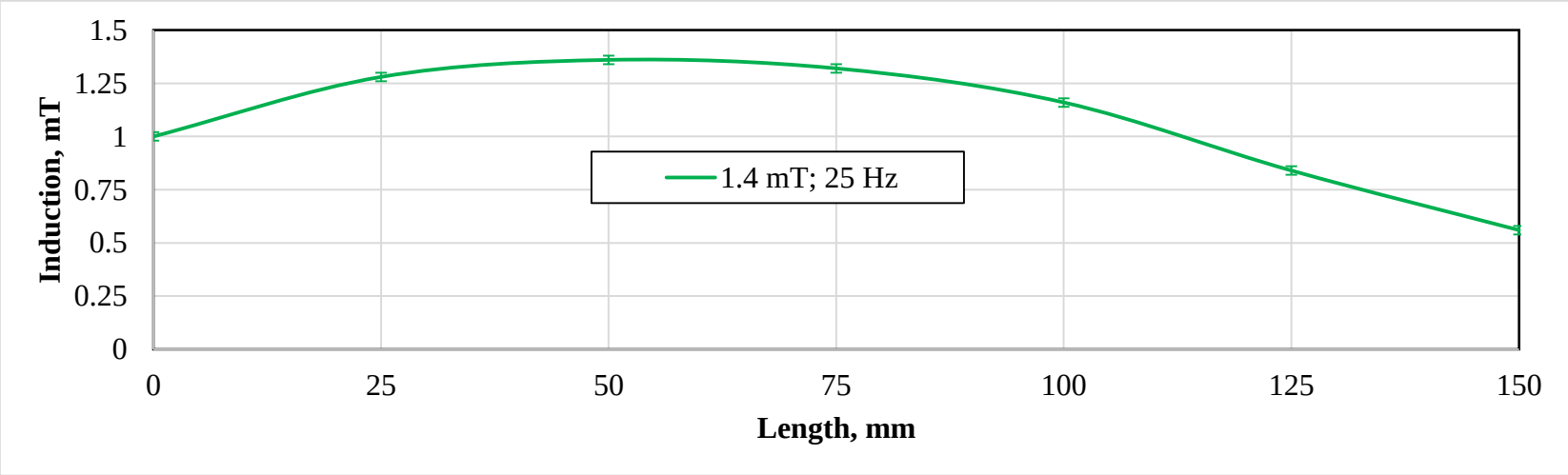
Ta
Ge
pBN
graphite
quartzglass

RMF TESTS

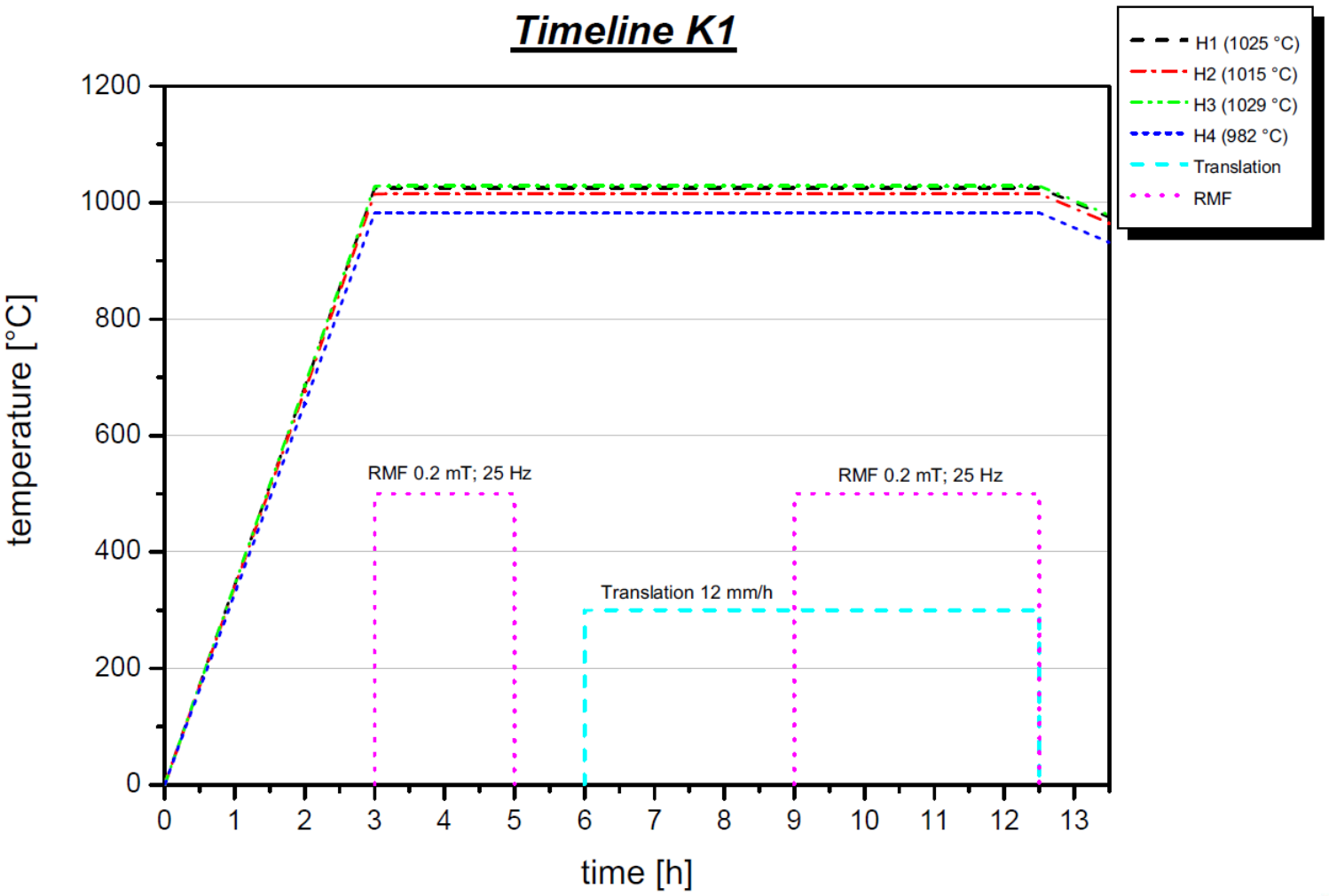

25 Hz (1000 C)
50 Hz (1000 C)
100 Hz (1000 C)
25 Hz (RT)
50 Hz (RT)
75 Hz (RT)
100 Hz (RT)
measured induction, mT
specified induction, mT
0
0.2
0.4
0.6
0.8
1
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1

RMF – INDUCTION DISTRIBUTION

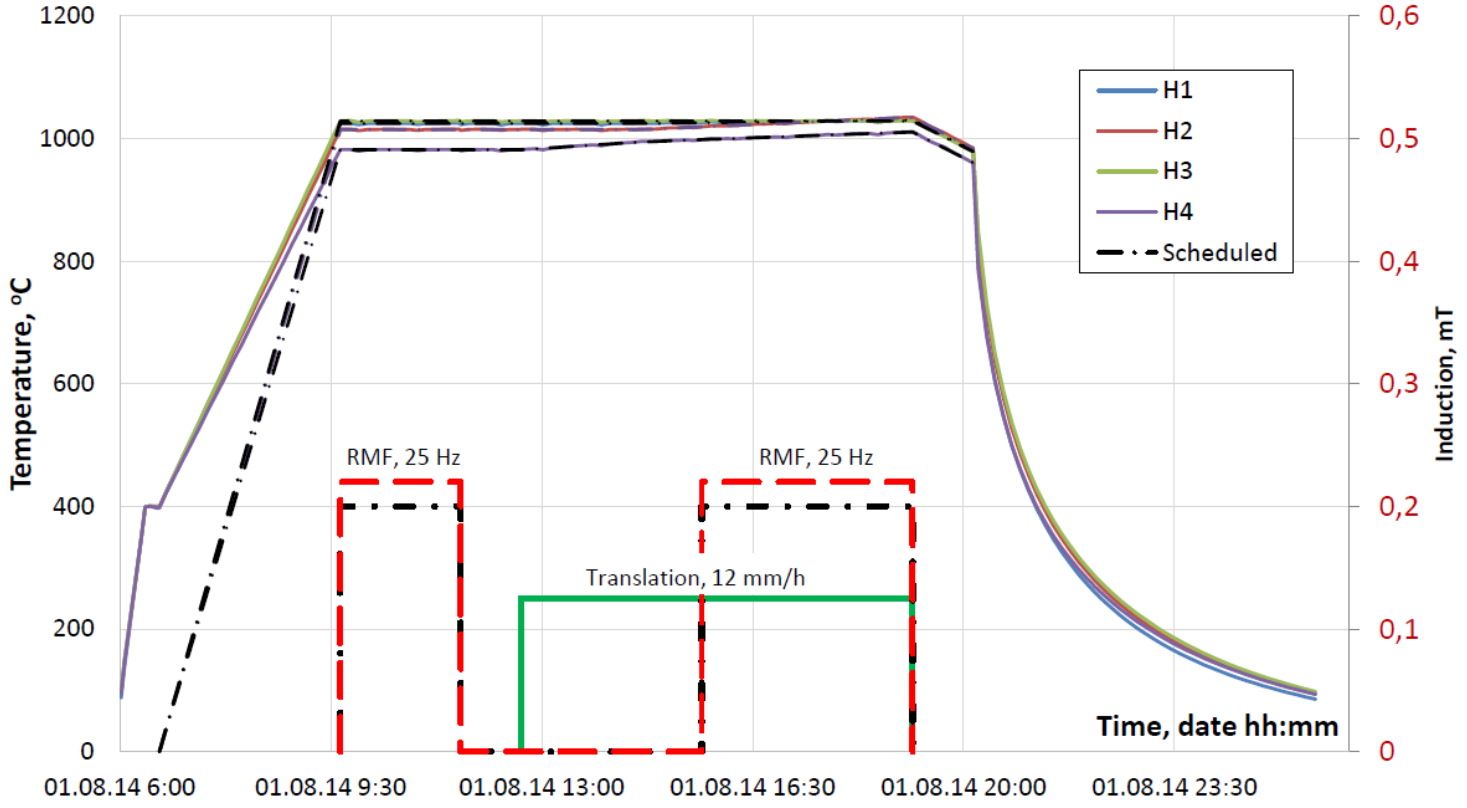




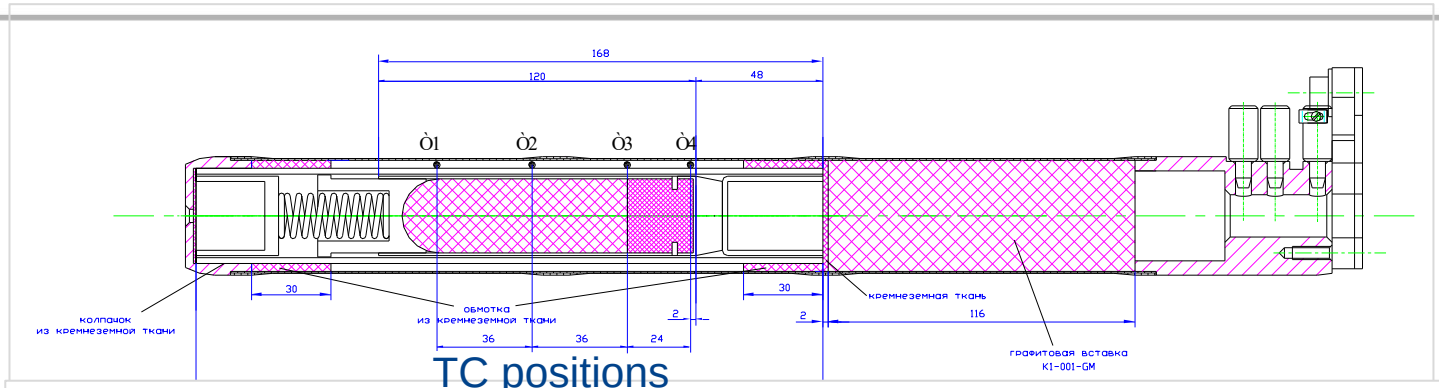
K1 GROWTH PARAMETERS



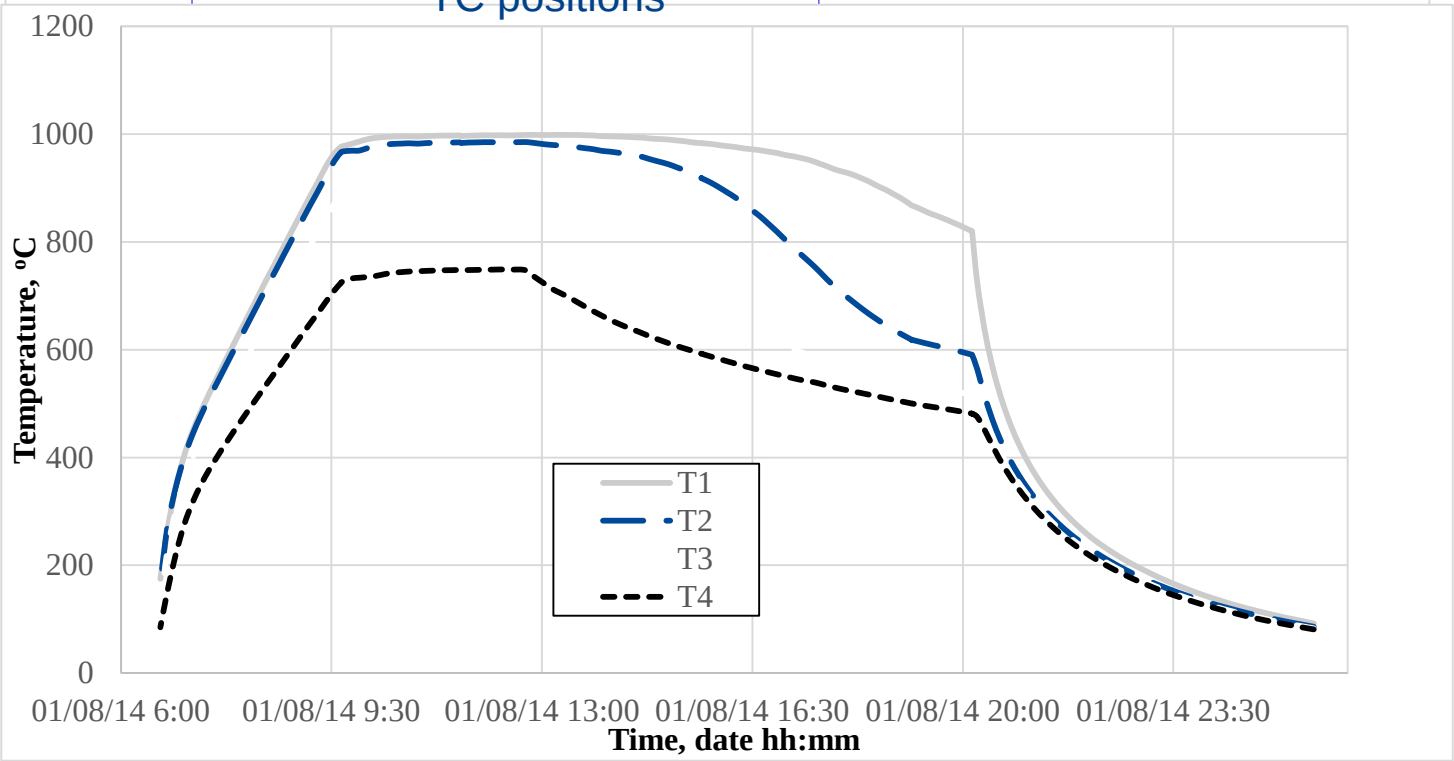
K1 PARAMETERS - MEASURED



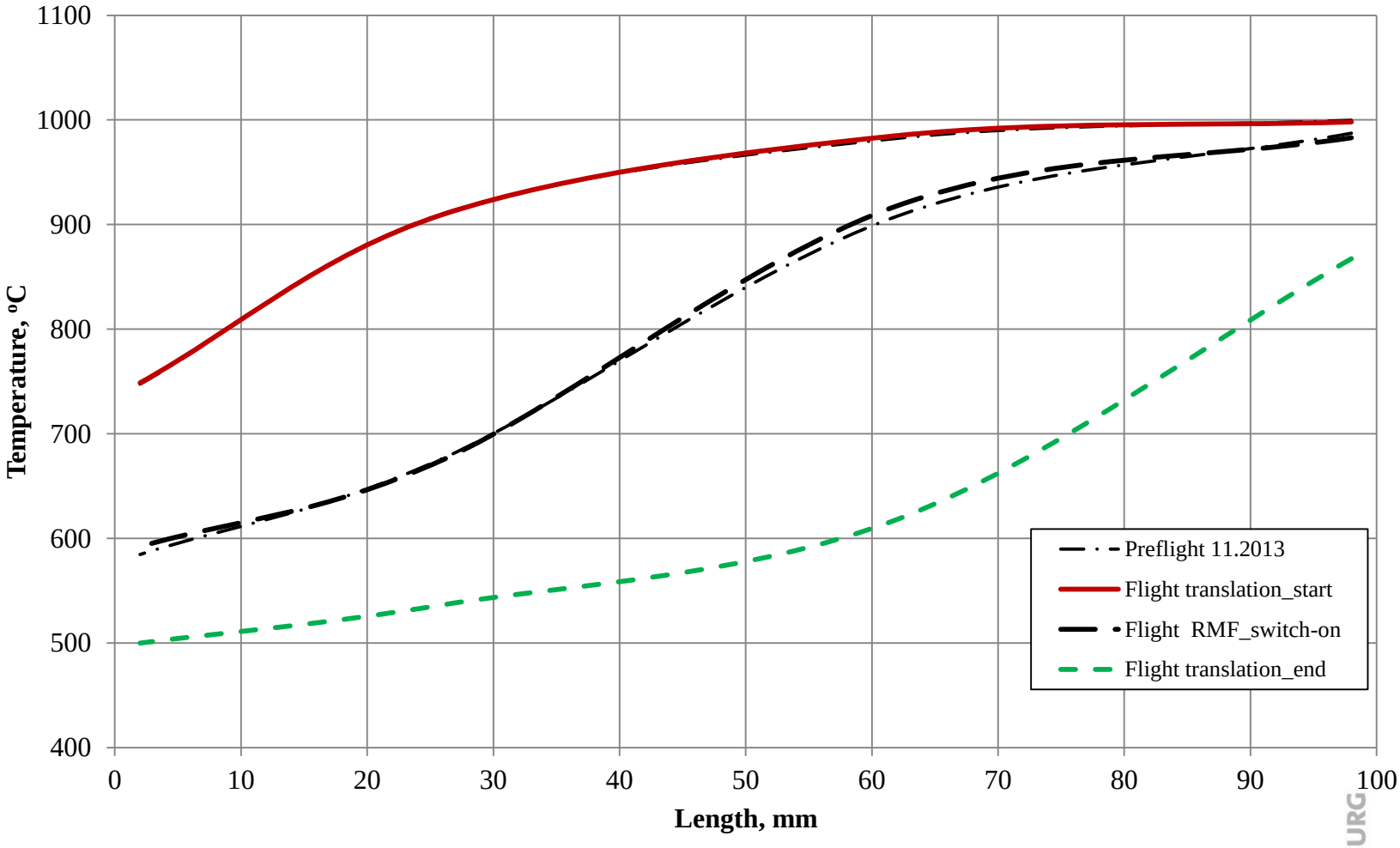
K1 TEMPERATURE PROFILES



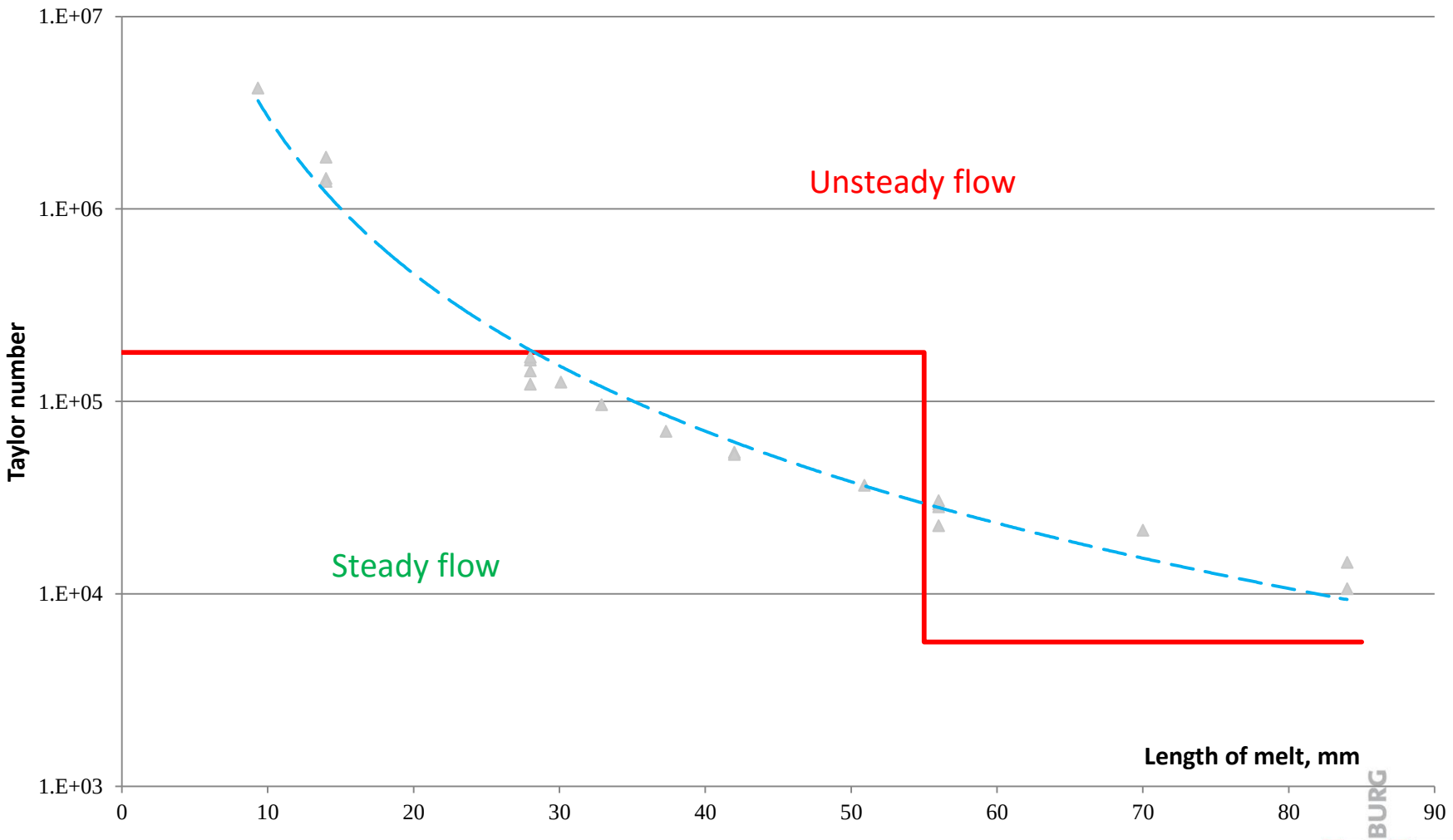
TC positions



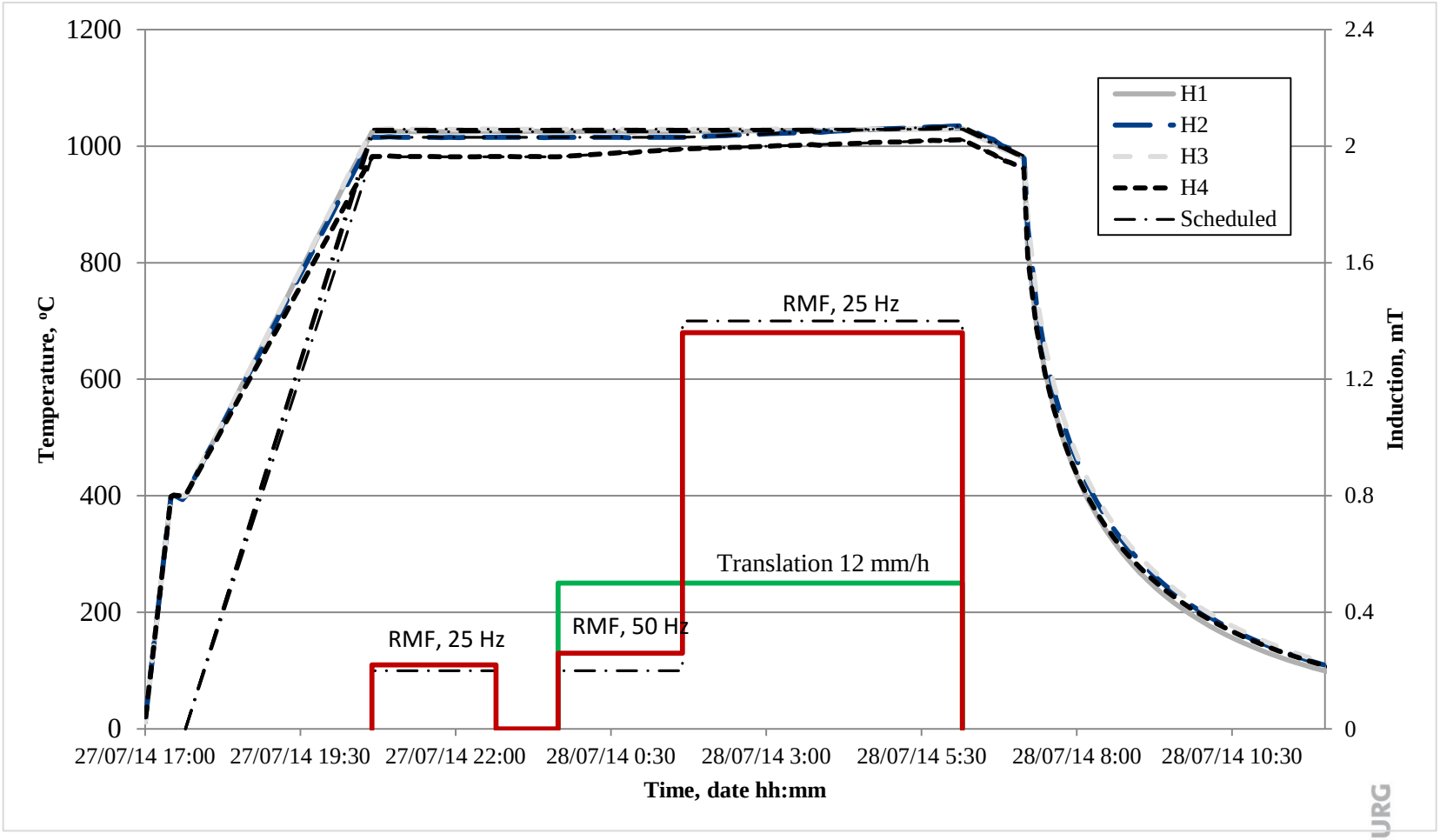
K1 TEMPERATURE PROFILES



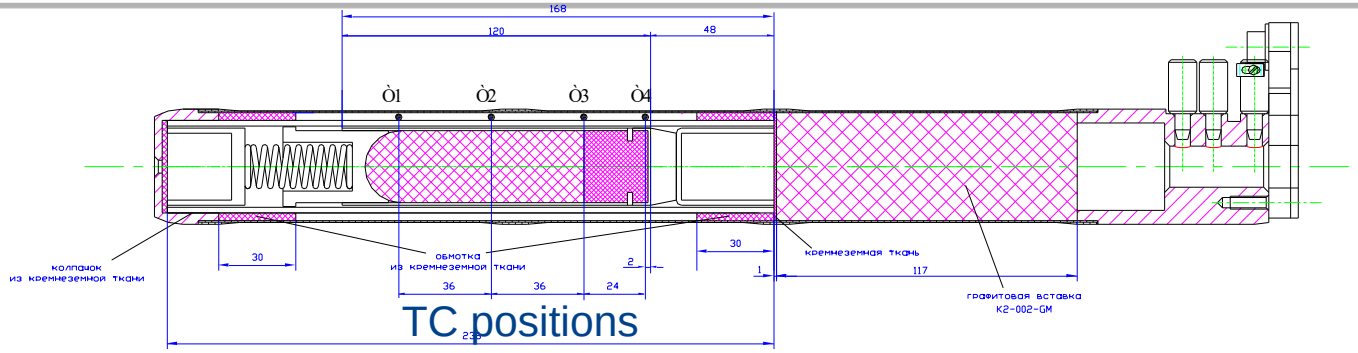
K2: CRITICAL TAYLOR NUMBER

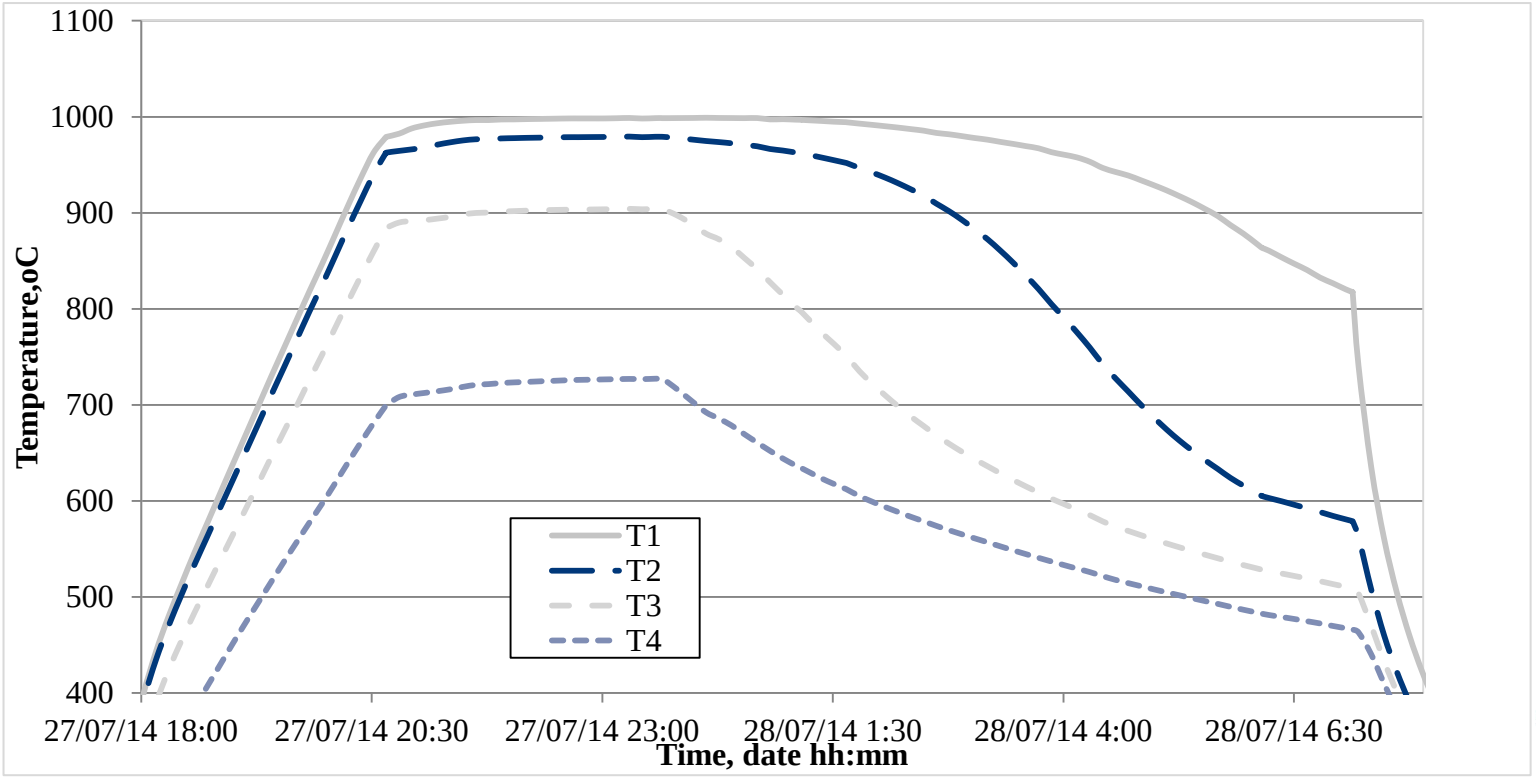


K2 PARAMETERS - MEASURED

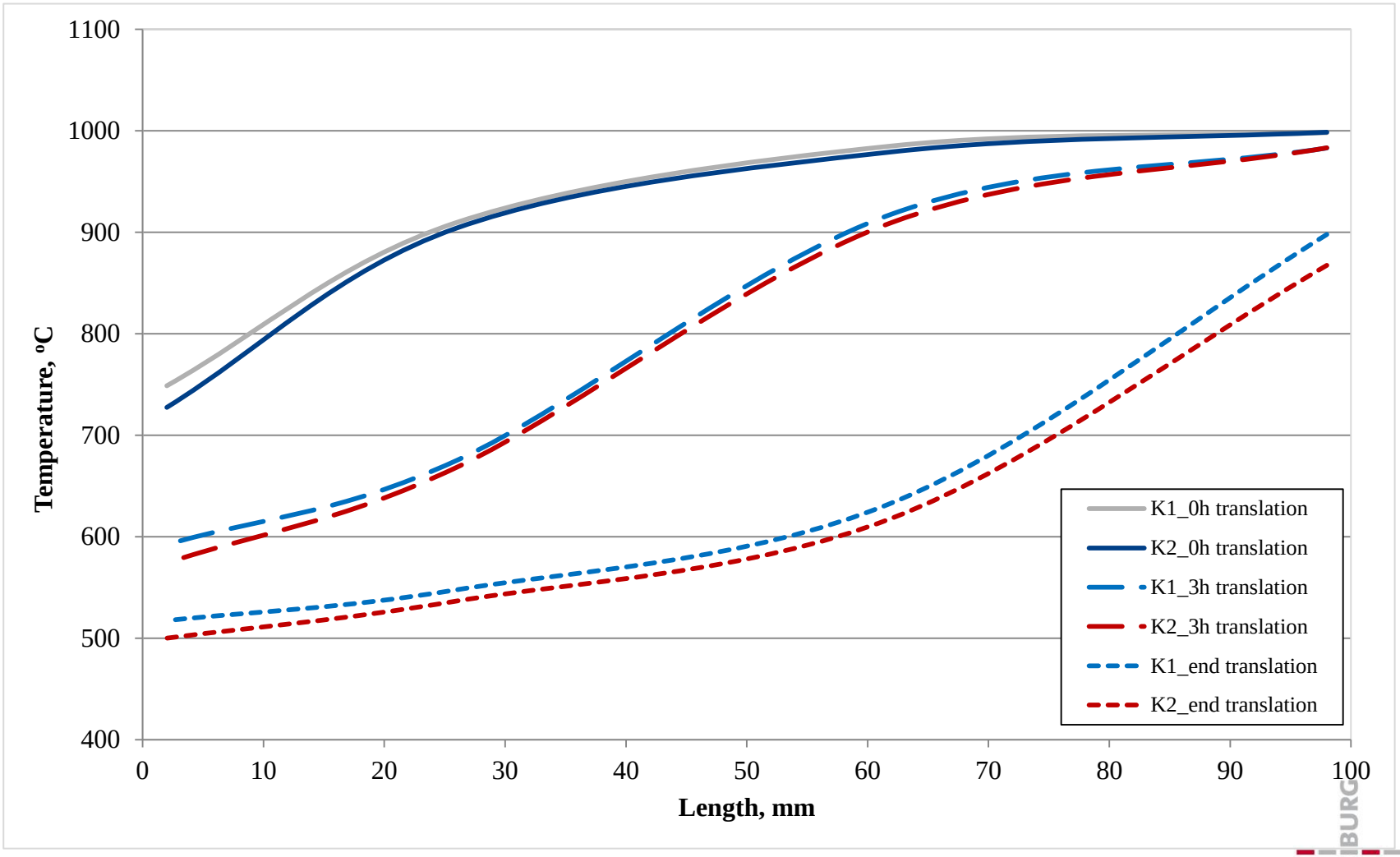


K2 TEMPERATURE PROFILES



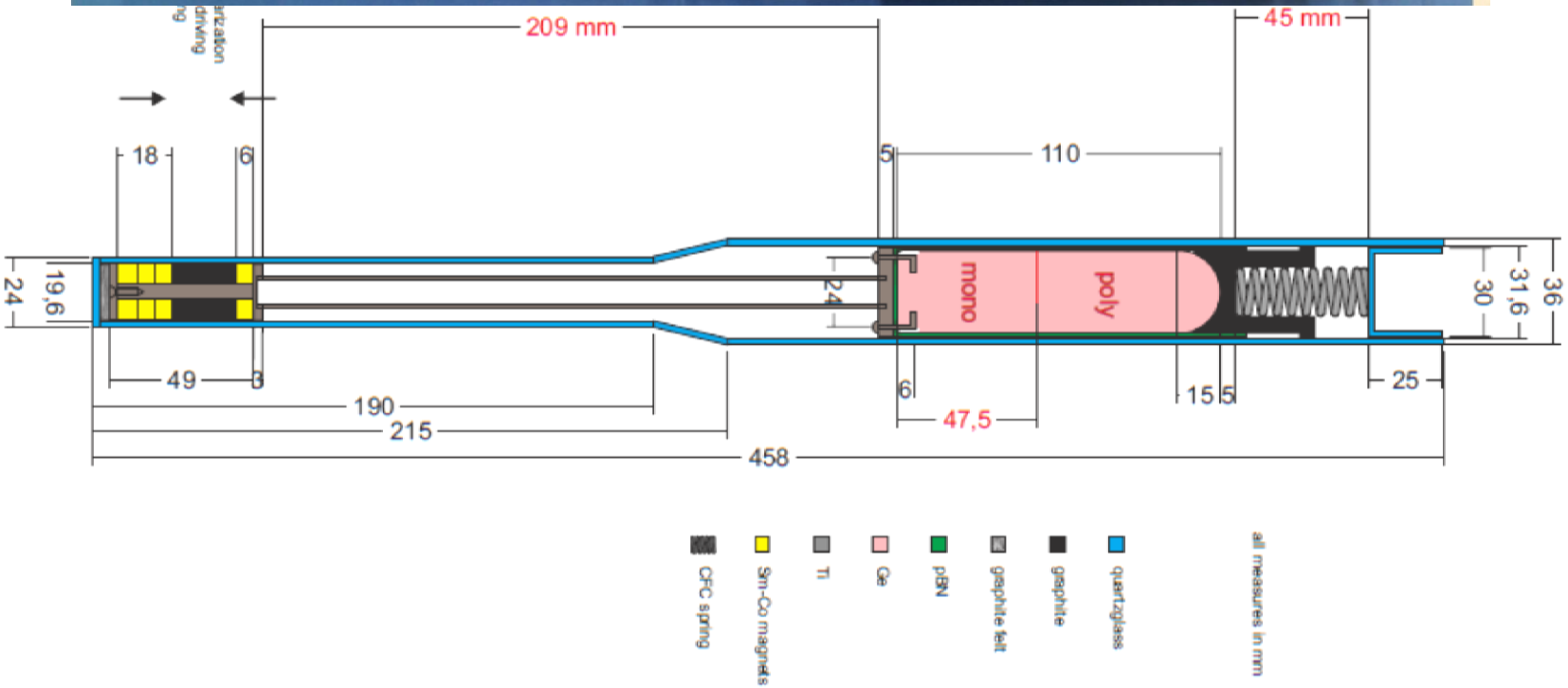


K2 TEMPERATURE PROFILES

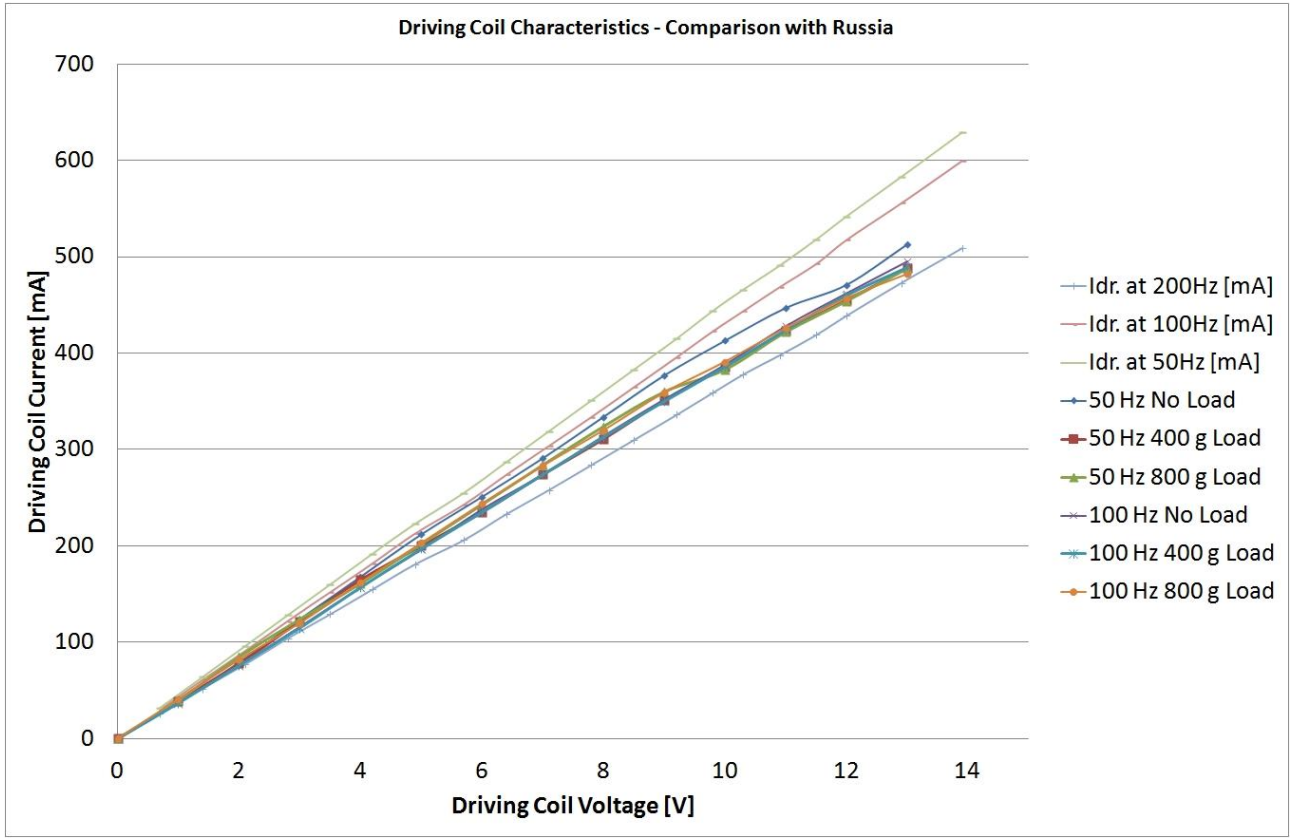


K3 SAMPLE SETUP

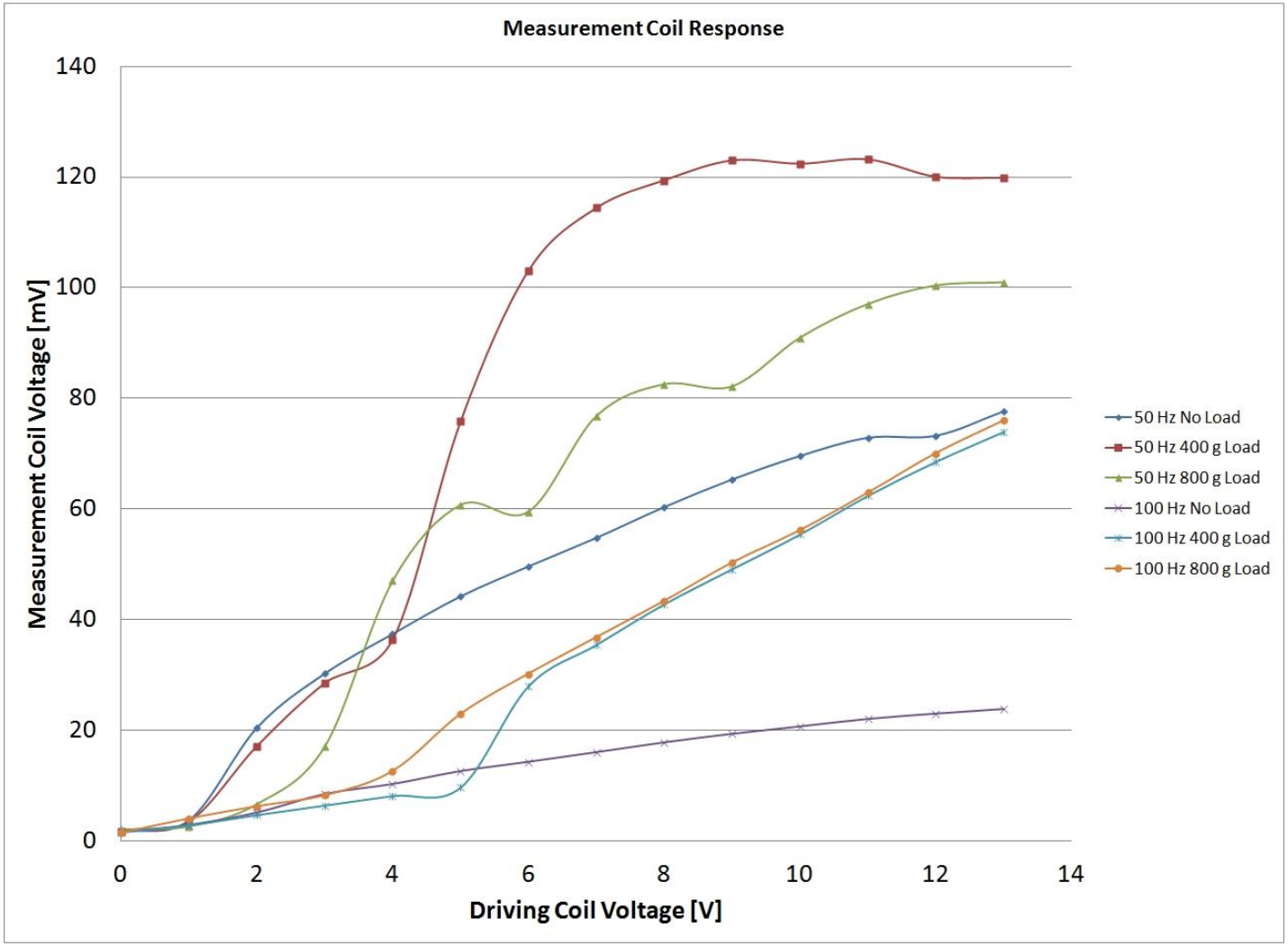
- **Gallium doped Germanium crystals, {100}-oriented seed**
- **Sample divided into a single crystalline doped ($1 \cdot 10^{17} cm^{-3}$ Ga) lower half and undoped poly-crystalline upper half**
- **pBN crucible and seed are connected to the vibration motor by a Ti tube**
- **Graphite plug with CFC spring to avoid free melt surface**
- **No inert gas - vacuum**



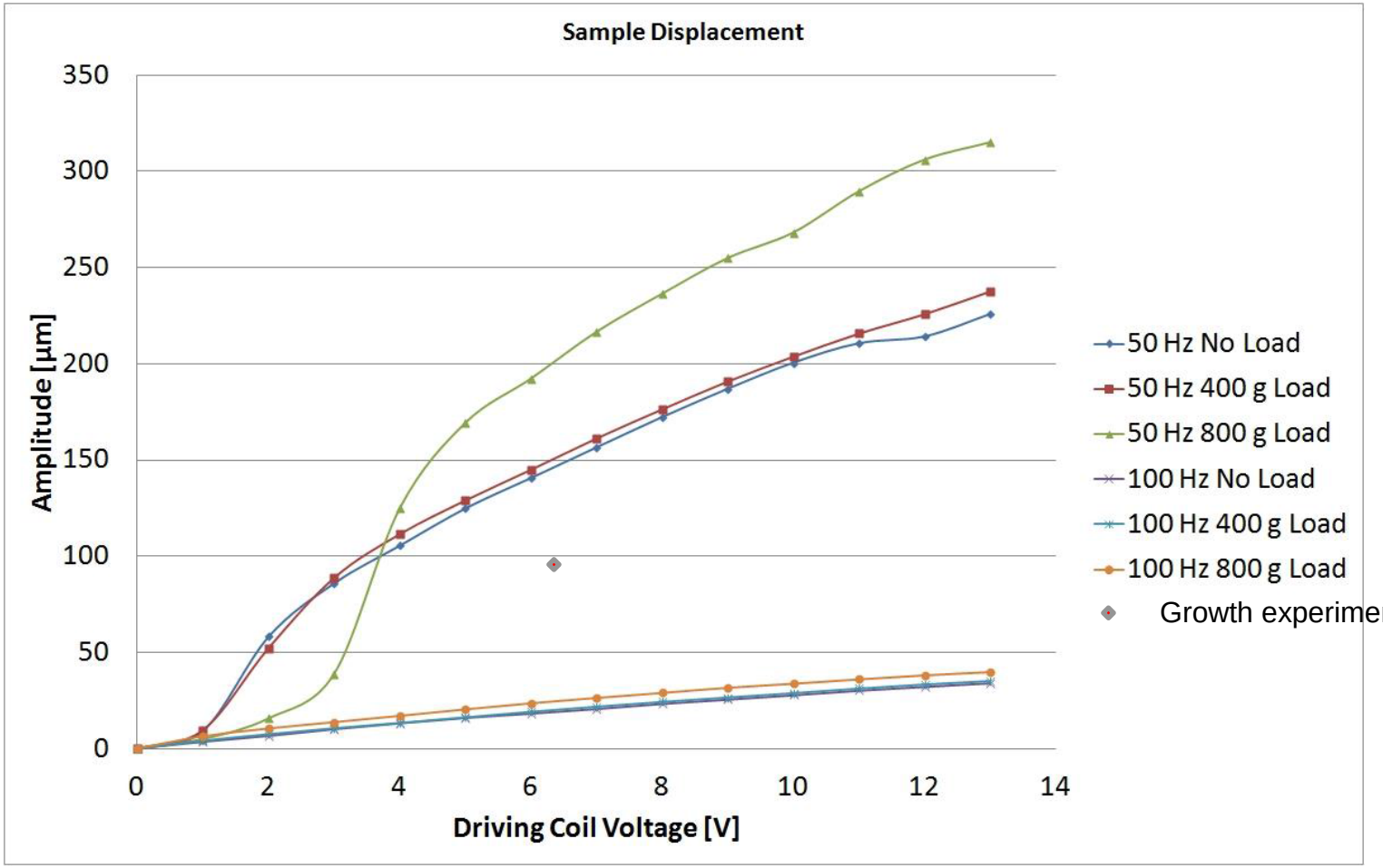
K3 VIBRATION CALIBRATION



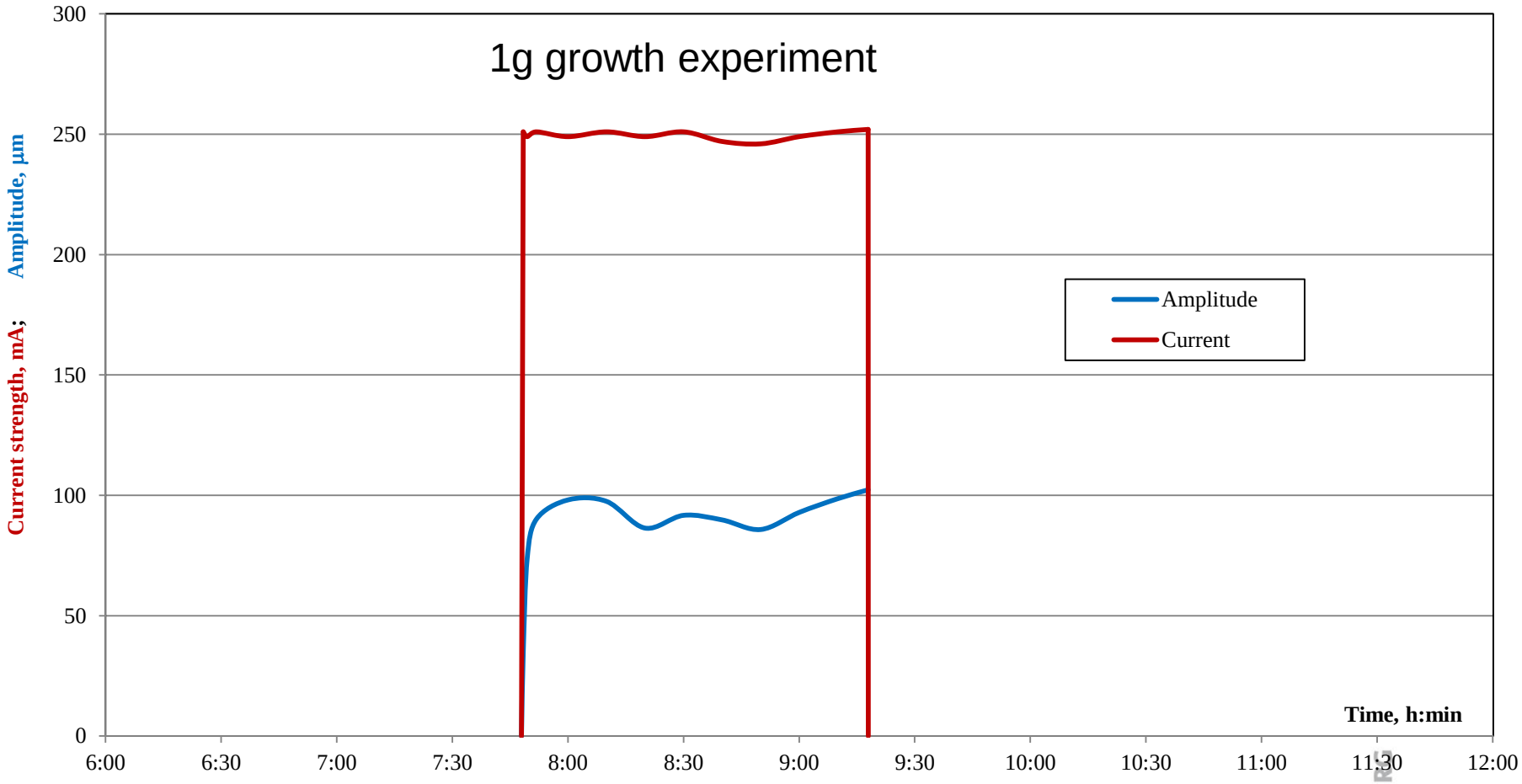
K3 VIBRATION CALIBRATION



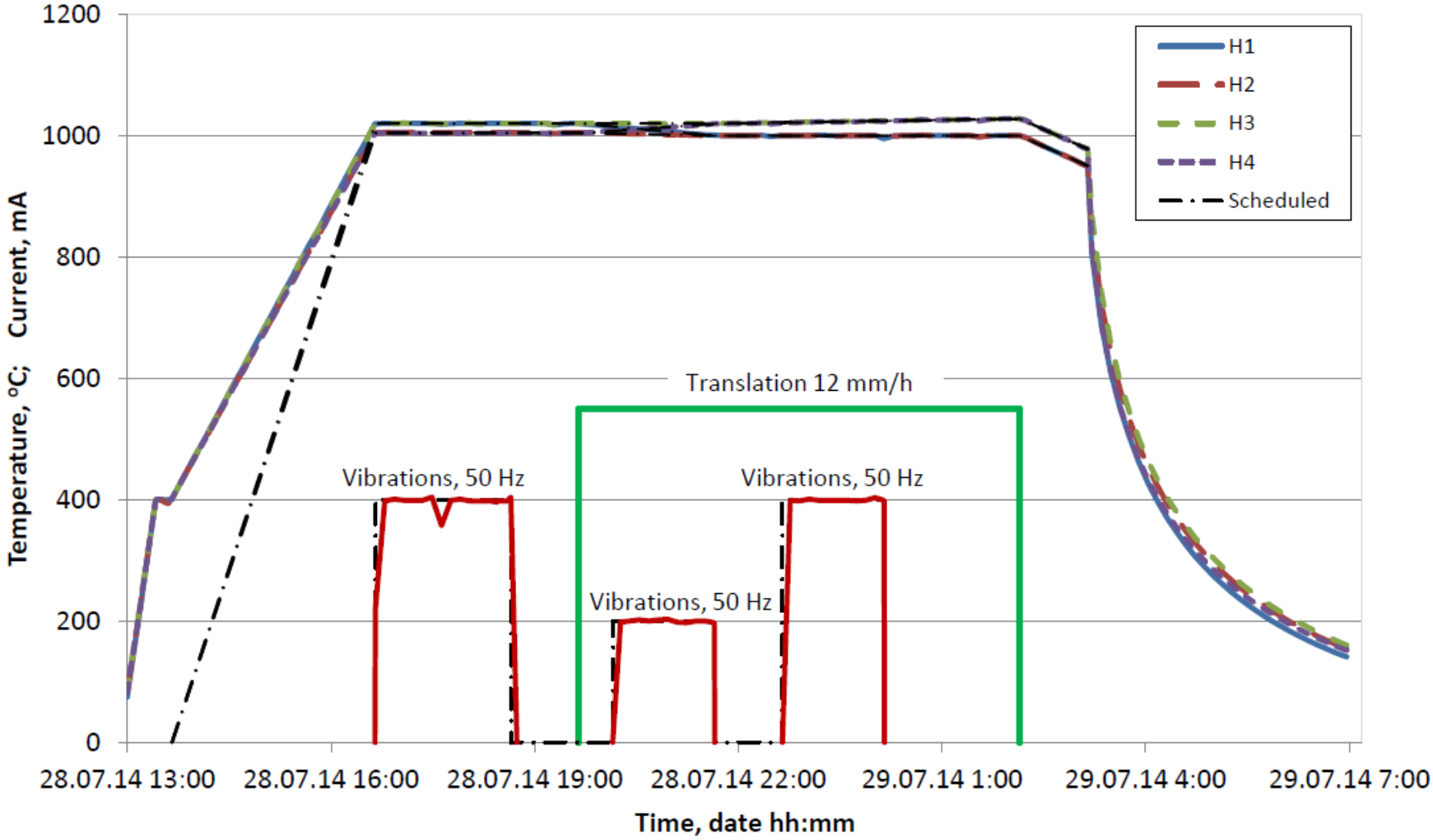
K3 VIBRATION CALIBRATION



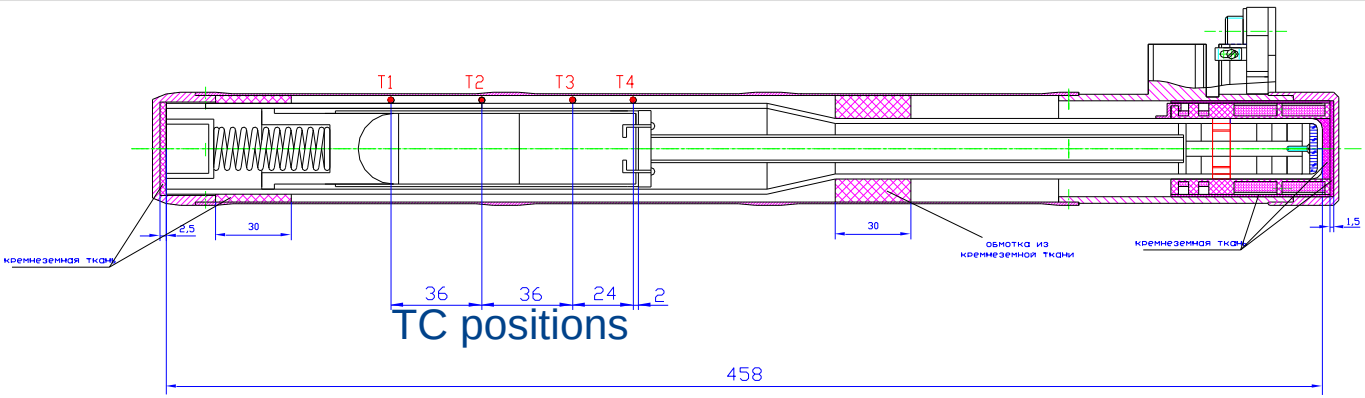
K3 VIBRATION CALIBRATION

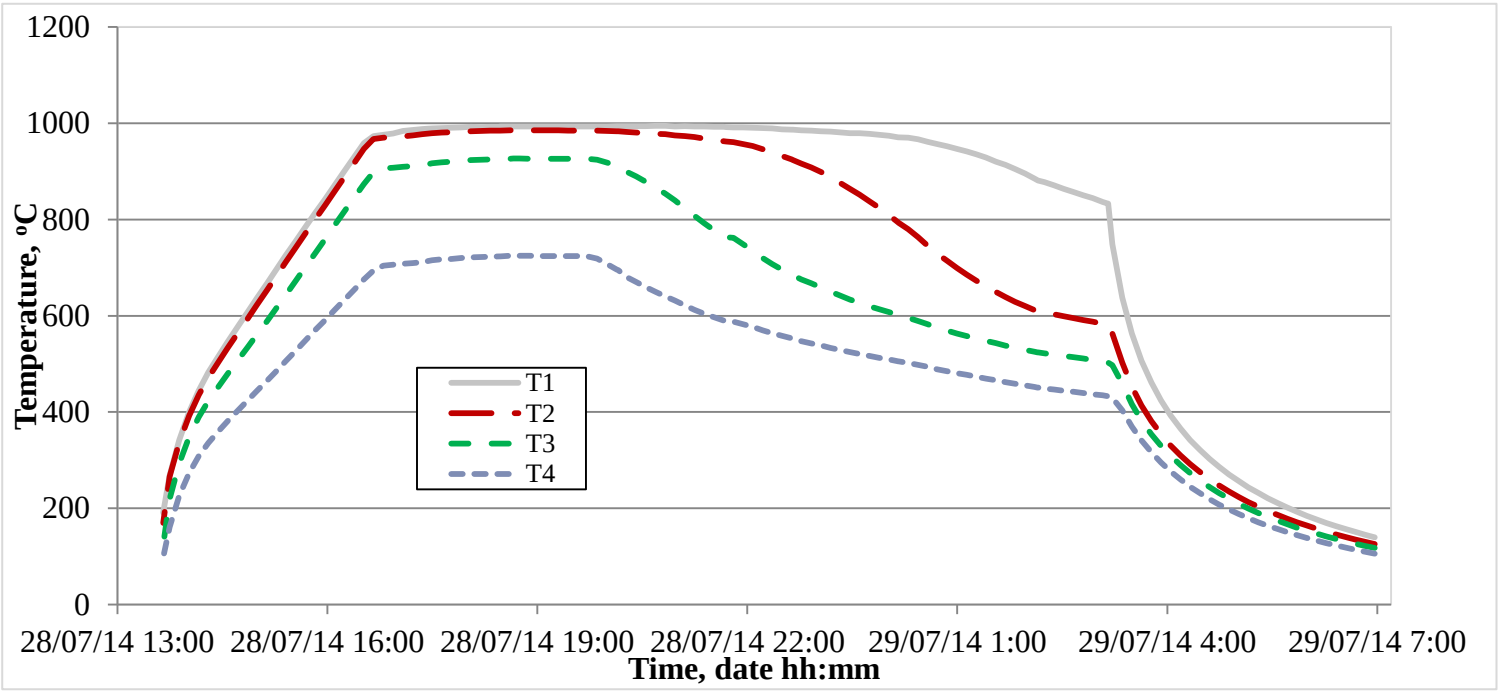


K3 PARAMETERS - MEASURED

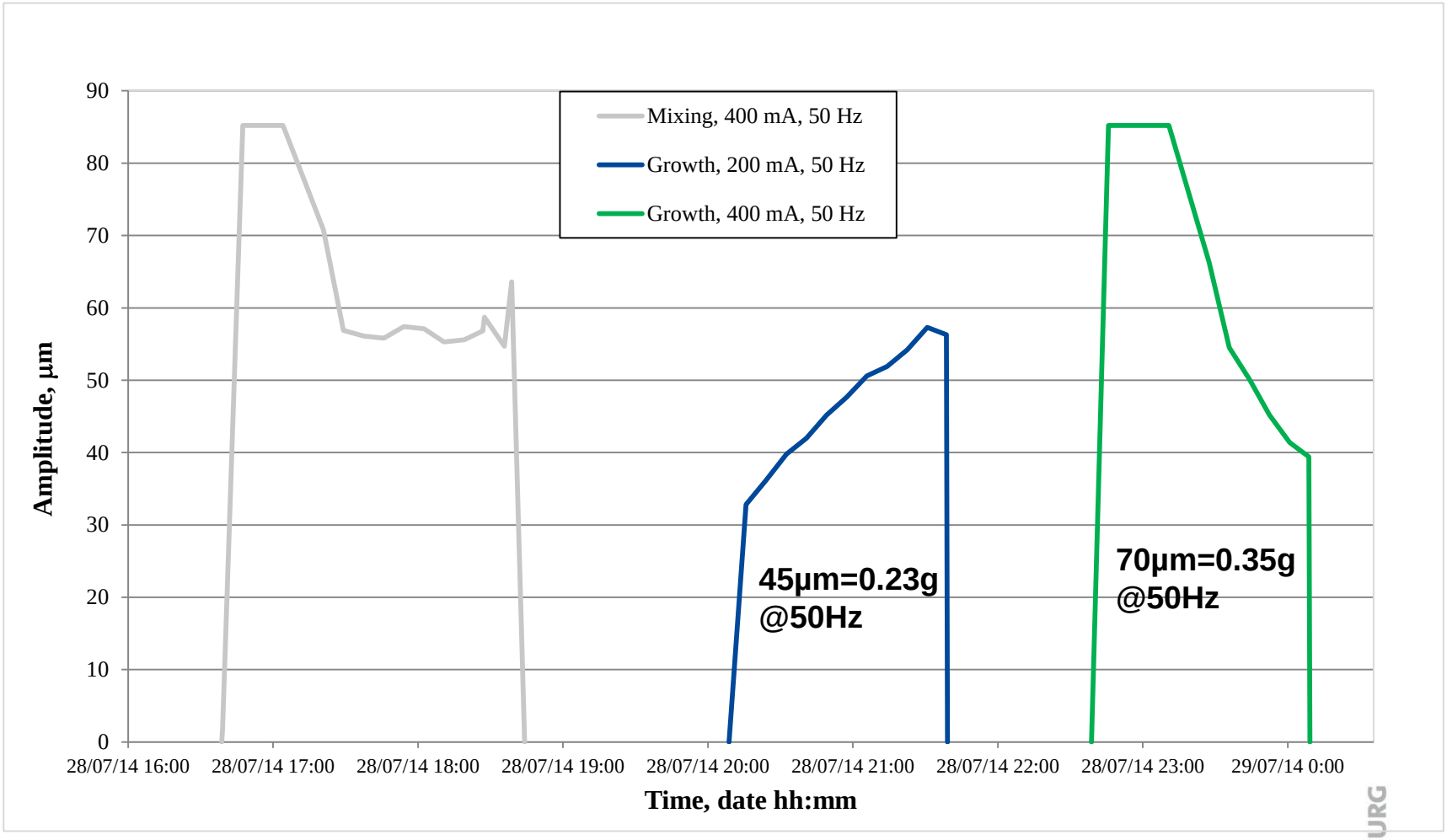


K3 TEMPERATURE PROFILES



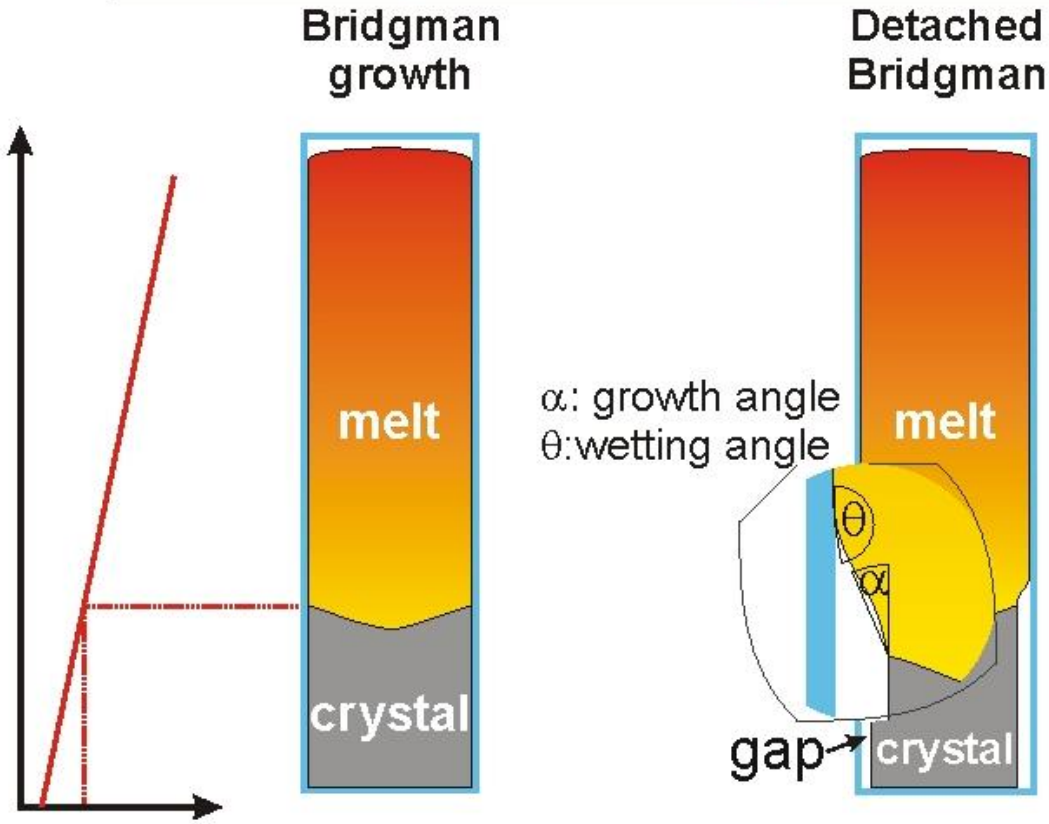


K3 VIBRATION AMPLITUDES



K4 BACKGROUND

Sufficient condition for detachment[1,2]:
$(\alpha+\theta \geq 180°)$



Advantages

- No sticking of the crystal to the ampoule wall
- Reduced stress
- Reduced dislocations
- No heterogeneous nucleation by the ampoule
- Reduced contamination

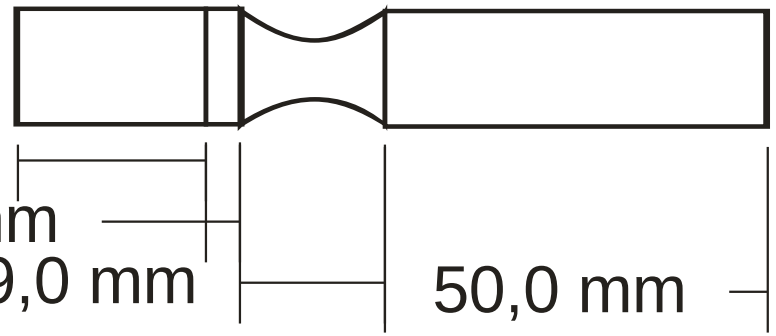
[1] V. S. Zemskov: Fiz. Khim. Obrab. Mater. 17 (1983) 56

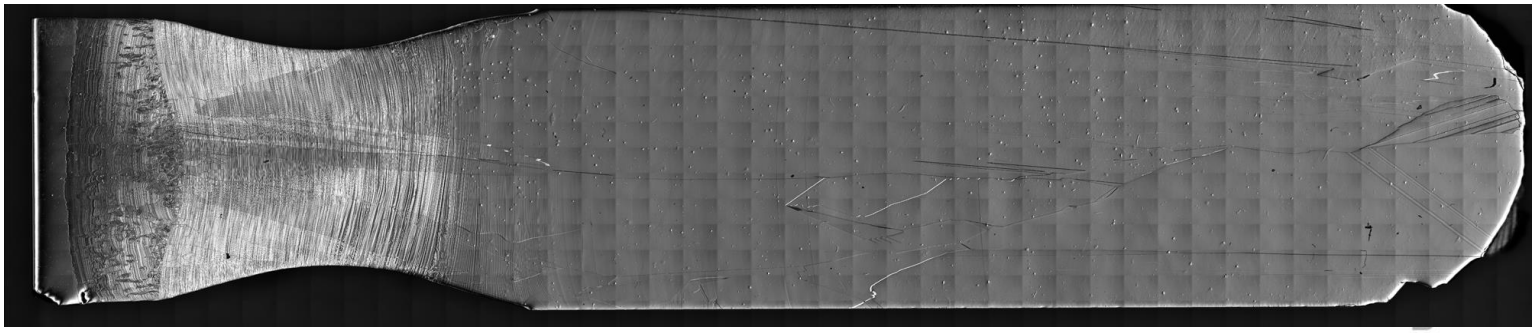
[2] T.Duffar, I.Paret-Harter, P.Dusserre: J.Crystal Growth 100 (1990) 171.

K4 BACKGROUND

FOTON M3 (2007) detached µg Bridgman experiment on Ge-Si (2%Si):

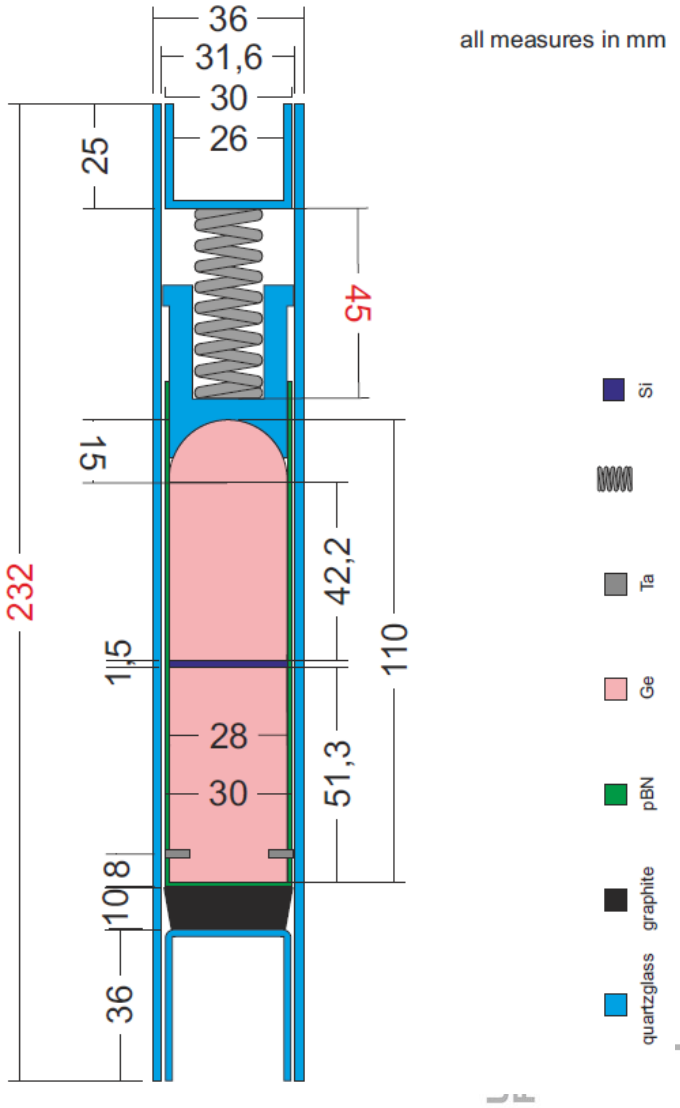
- **Initial growth w/o pulling for a few mm - „normal“ detachment**
- **Formation of a large free melt zone when pulling**
- **→ Unstable detachment**
- **→ strong thermocapillary convection**
- **→ change of interface curvature**



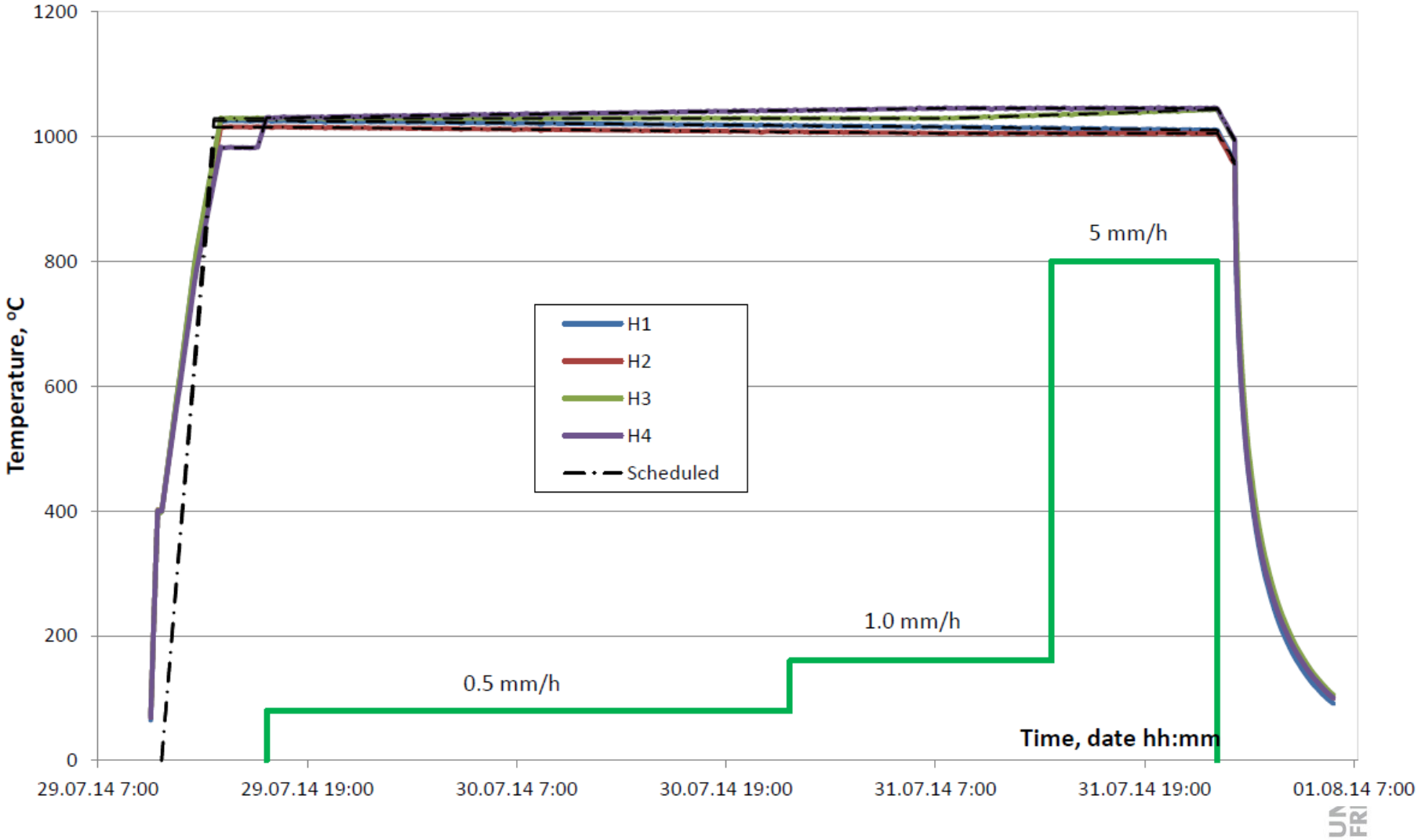


K4 SAMPLE SETUP

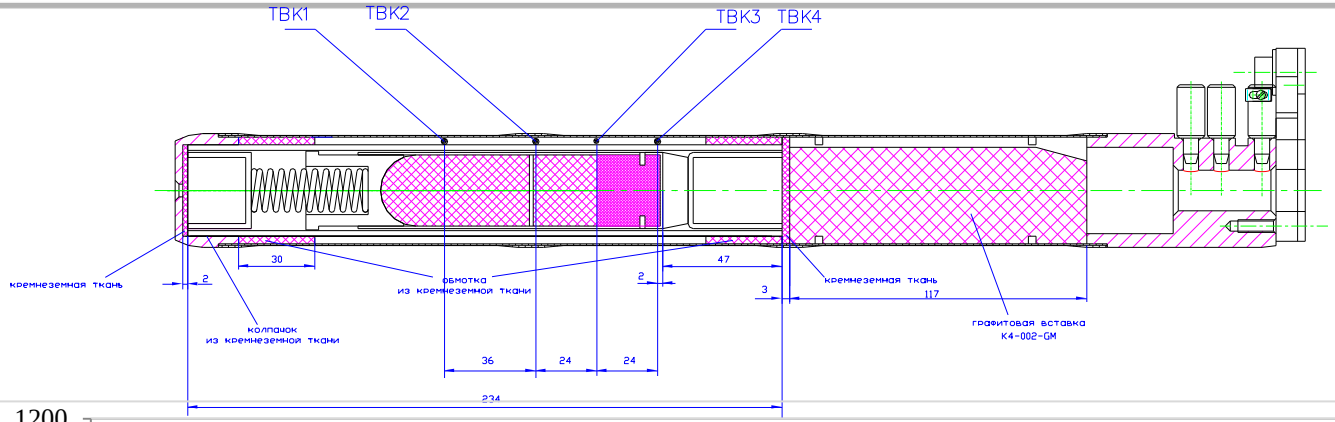
- **$Ge_{1-x}Si_x$ crystals (x≈0.03 in the melt)**
- **{100}-oriented undoped Ge as seed**
- **Sample divided into 3 parts: single crystalline undoped lower part, undoped Si wafer, single crystalline undoped upper Ge part**
- **pBN crucible, Ta fixation pins for the seed**
- **Quartz glass plug to avoid SiC formation**
- **No inert gas -vacuum**
- ***No* pressure difference between top and bottom volumes (vacuum, holes for seed fixation)**

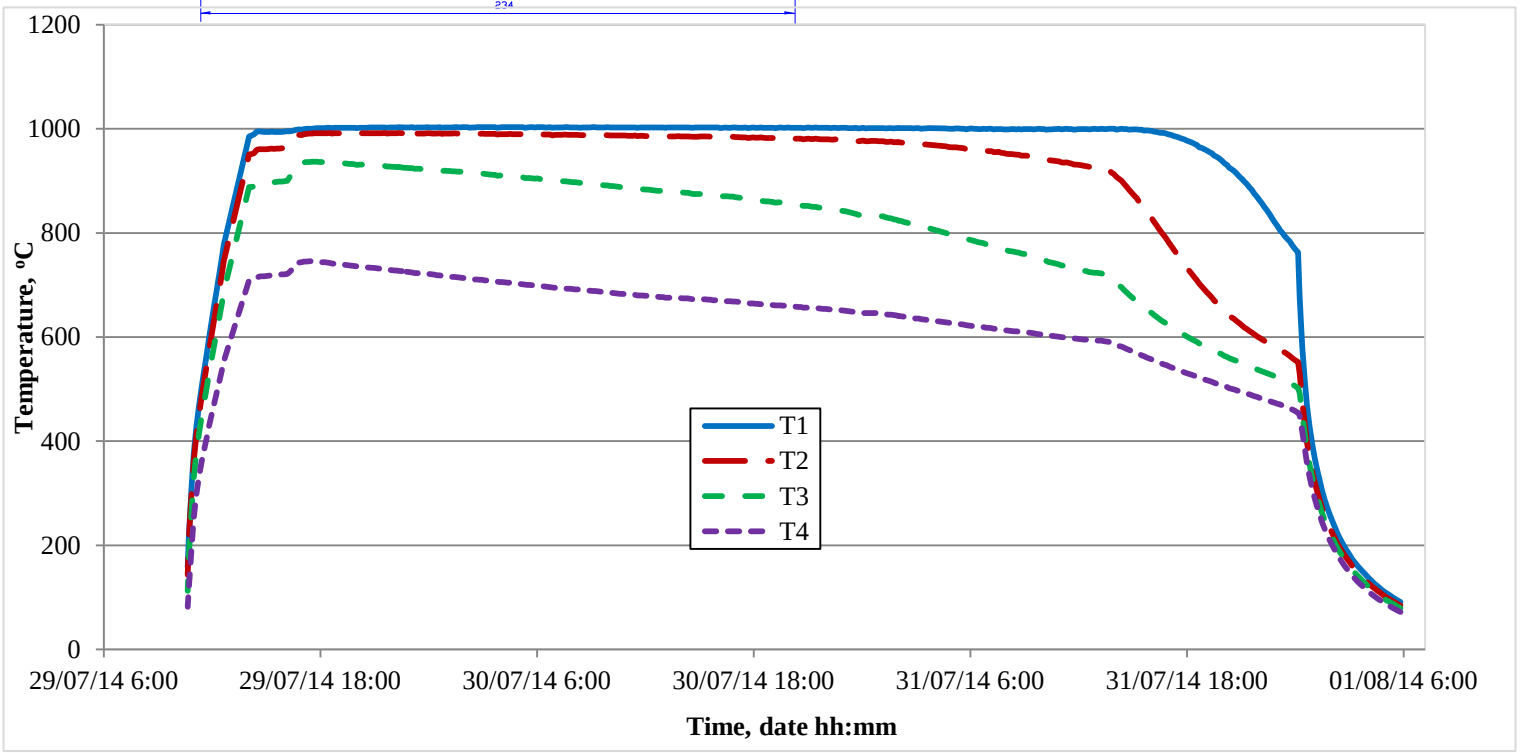


K4 PARAMETERS - MEASURED



K4 TEMPERATURE PROFILES

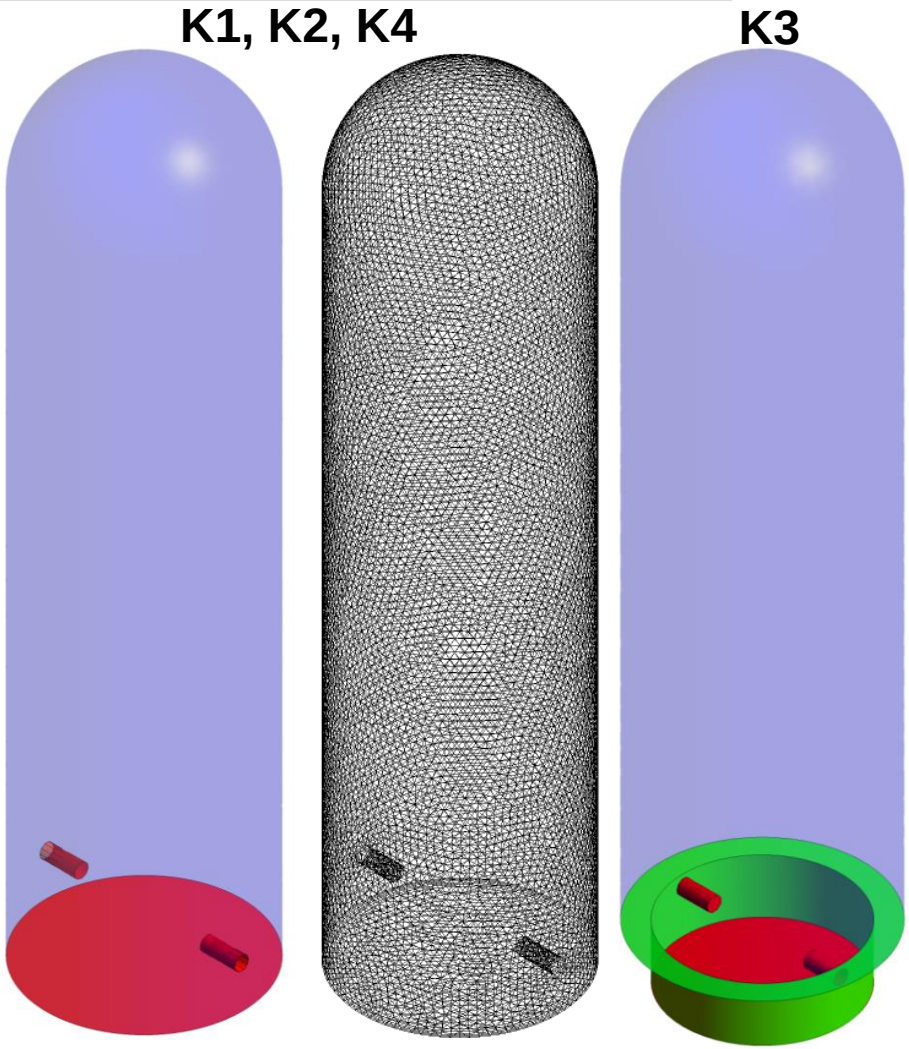




SIMULATIONS

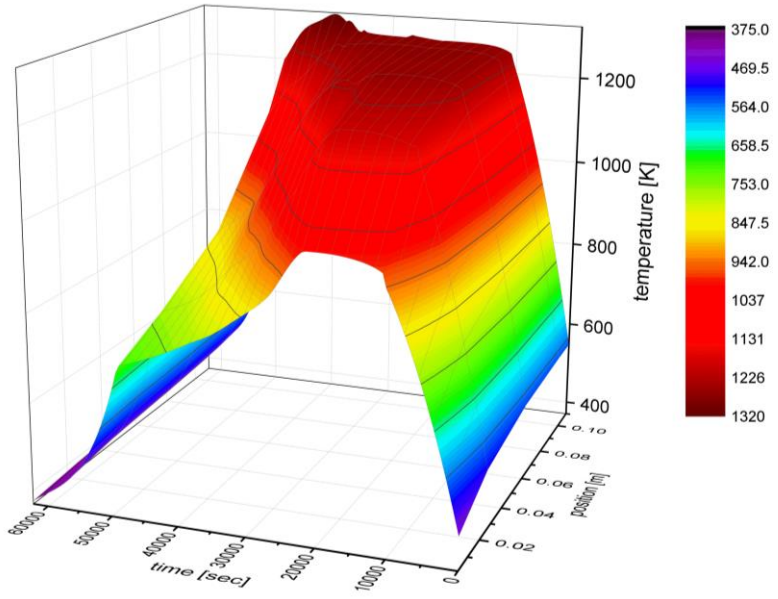
- **Geometry based on FM/RM ampoules (only melt and crystal/seed)**
- **Defined heat flux (crucible bottom, mounting holes)**
- **Time dependent temperature profiles T(t,y) (melt/crucible, UDF/C++)**

- **Low resolution / high resolution grid ~200.000 cells / ~400.000 cells**

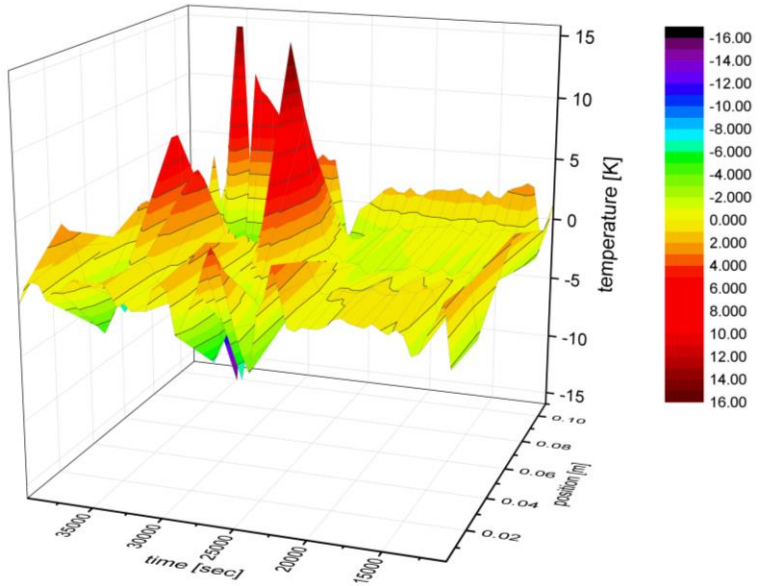


SIMULATIONS K1/K2

temperature distribution T(t,y)



divergence from measured data



SIMULATIONS K1/K2

- **1g along -$\vec{y}$ (UDF/C++)**

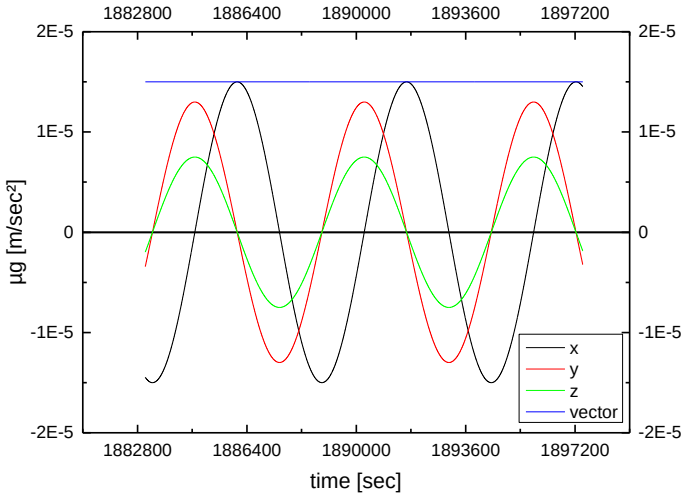
  K1-009-RM, K2-007-RM

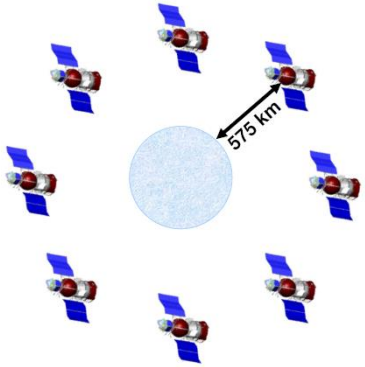
- **Rotating µg-vector (UDF/C++)**

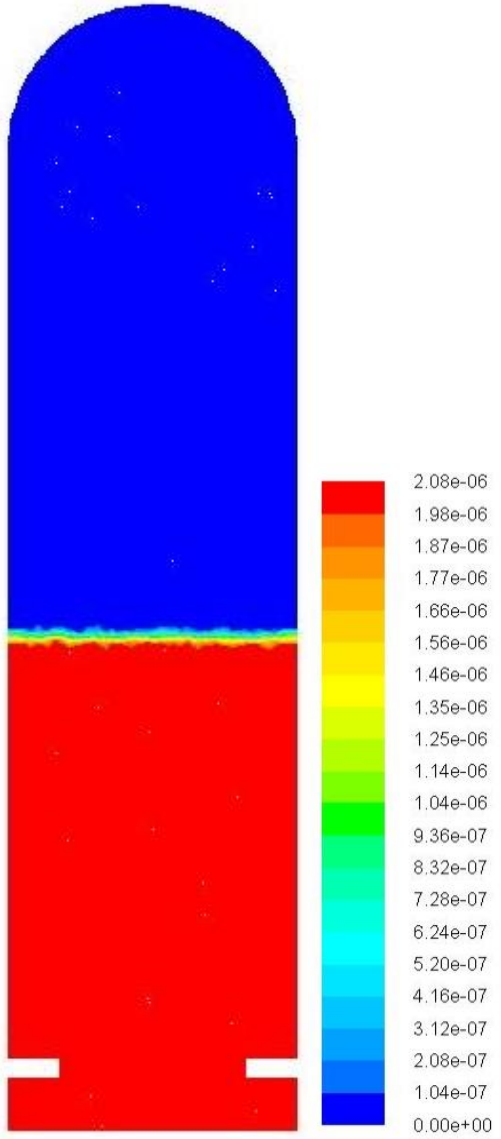
  based on flight data

  Ga Doping (Ansys Fluent species module)

- **RMF (Ansys Fluent MHD module)**







SIMULATIONS K3

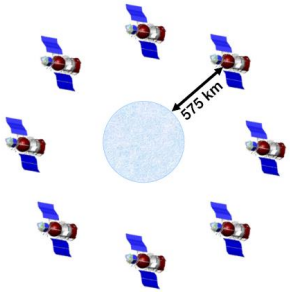
- 1g along $-\vec{y}$ (UDF/C++)

  K3-006-RM

- Rotating µg-vector (UDF/C++)

  based on flight data

  K3-004-FM

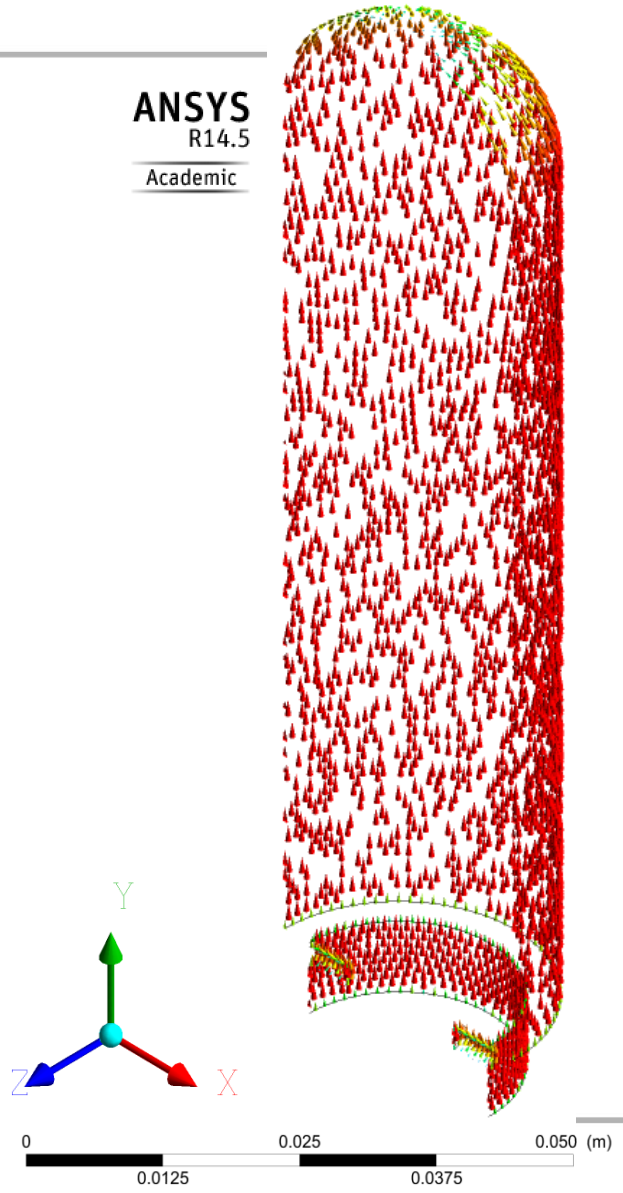


- Ga Doping

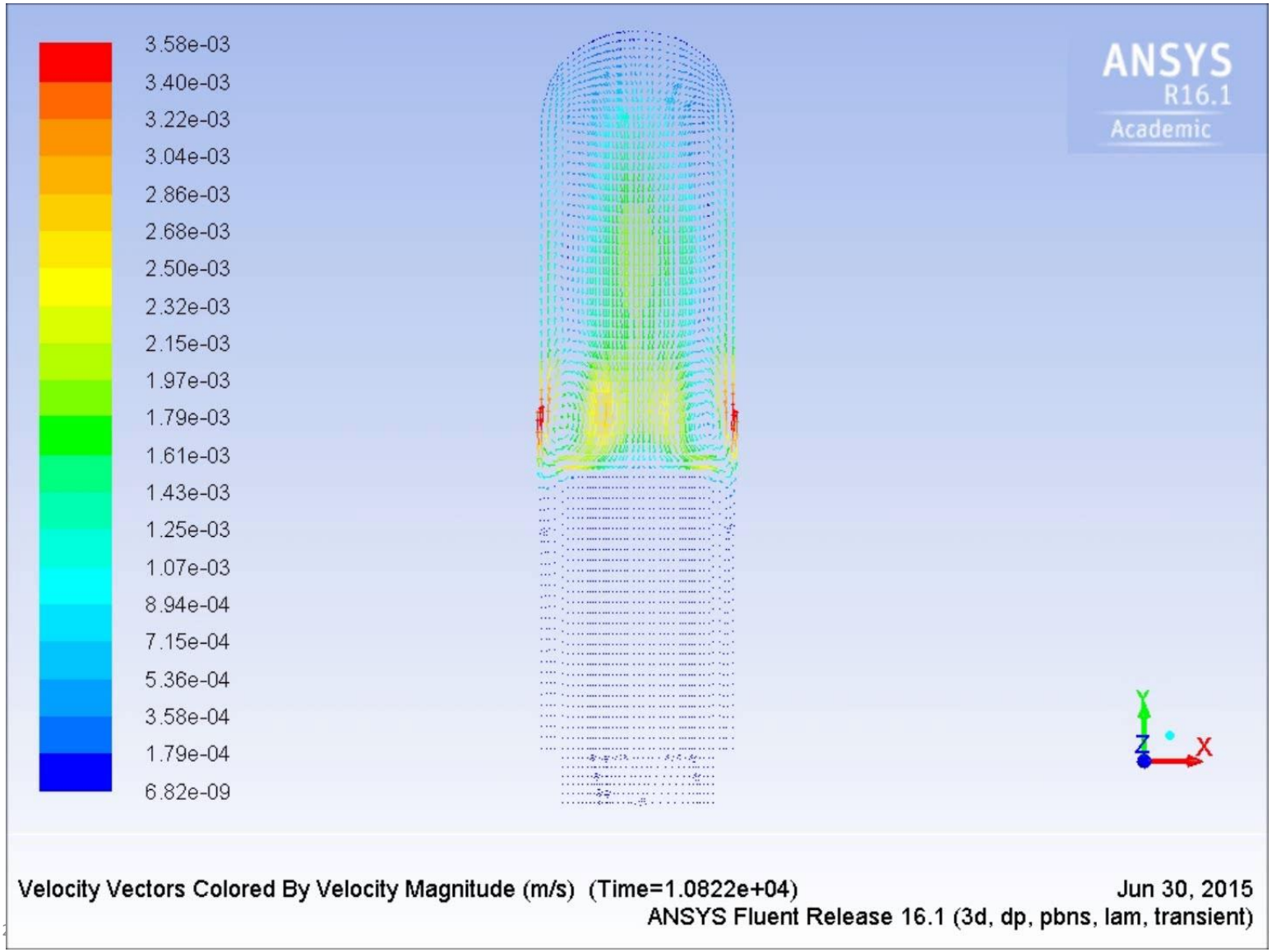
  (Ansys Fluent species module)

- Vibration (UDF/C++)

$$v(t) = A\, 2\pi f \cos(2\pi f t)$$



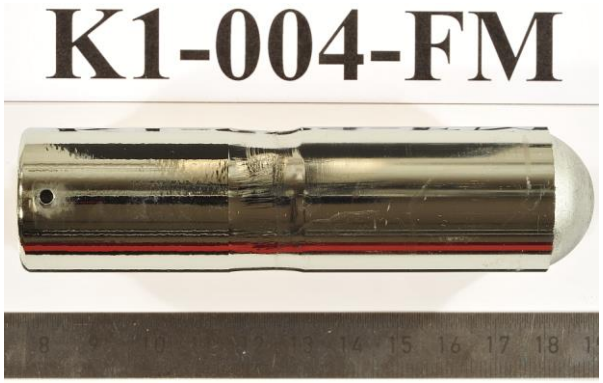
SIMULATIONS K3

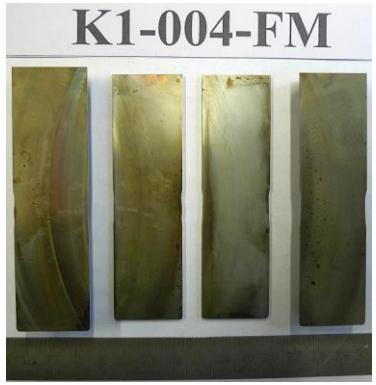


UNI FREIBURG

CRYSTAL PREPARATION

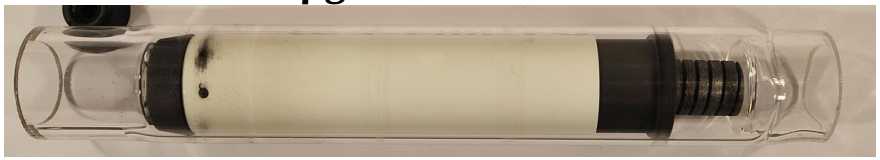
- **Visual Inspection of the ampoule after the experiment**
- **Disassembly of all ampoule parts**
- **Visual Inspection of the crystal**
- **Axial section by inner diameter saw (IKZ Berlin)**
- **Grinding and polishing**
- **Etching (striations)**
- **Analysis (Profilometer, NDIC microscopy, 4-point-probe, EDX, X-ray topography, …)**

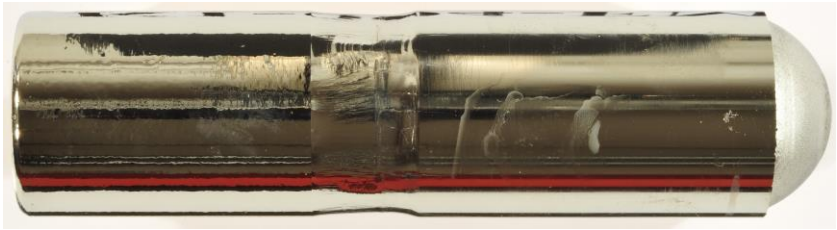


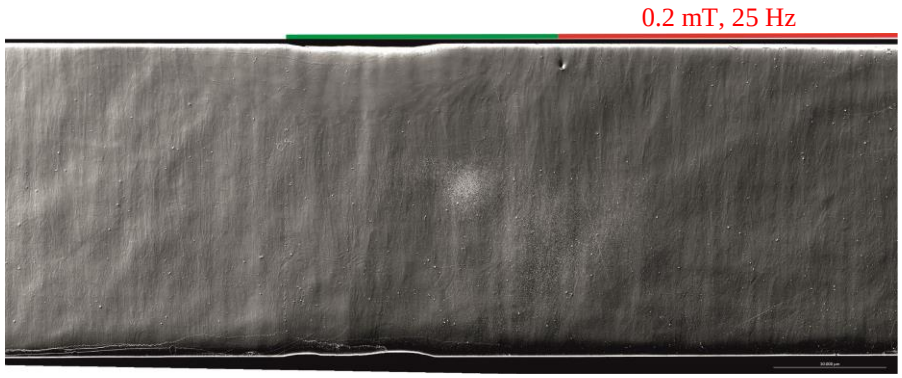


K1 - RESULTS

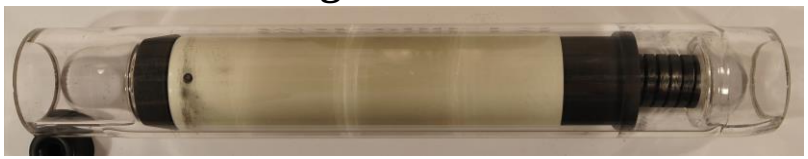
µg: K1-004-FM

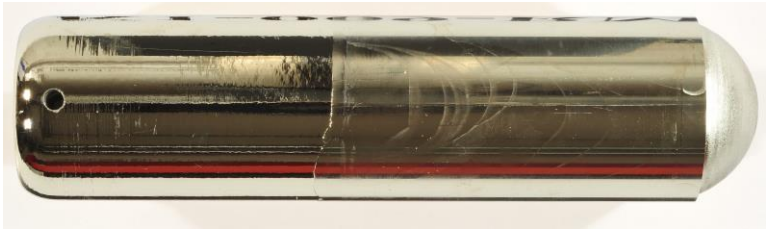






1g: K1-009-RM

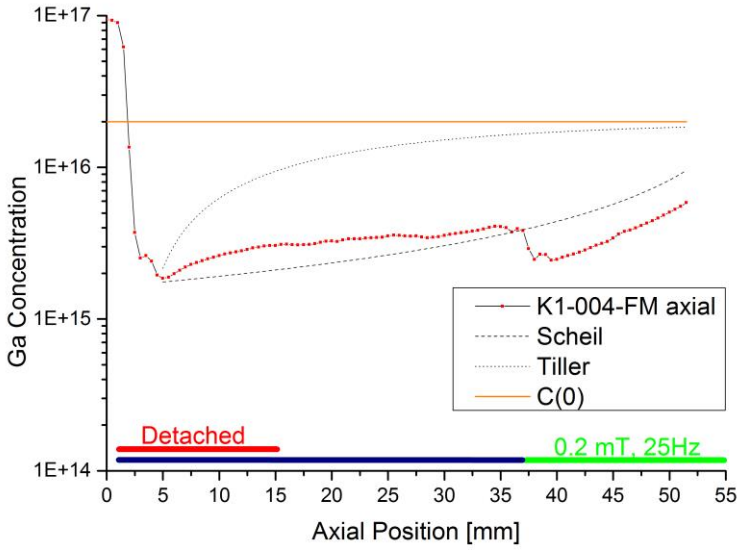




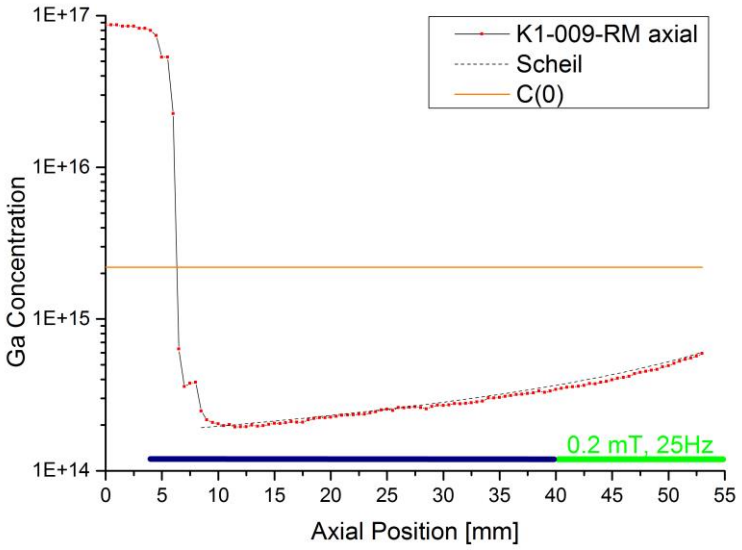
- **Detachment of the flight crystal *despite* the CFC spring**
- **Both µg and 1g samples are single crystals**
- **No dopant striations visible in the grown crystals**

K1: AXIAL SEGREGATION

µg: K1-004-FM

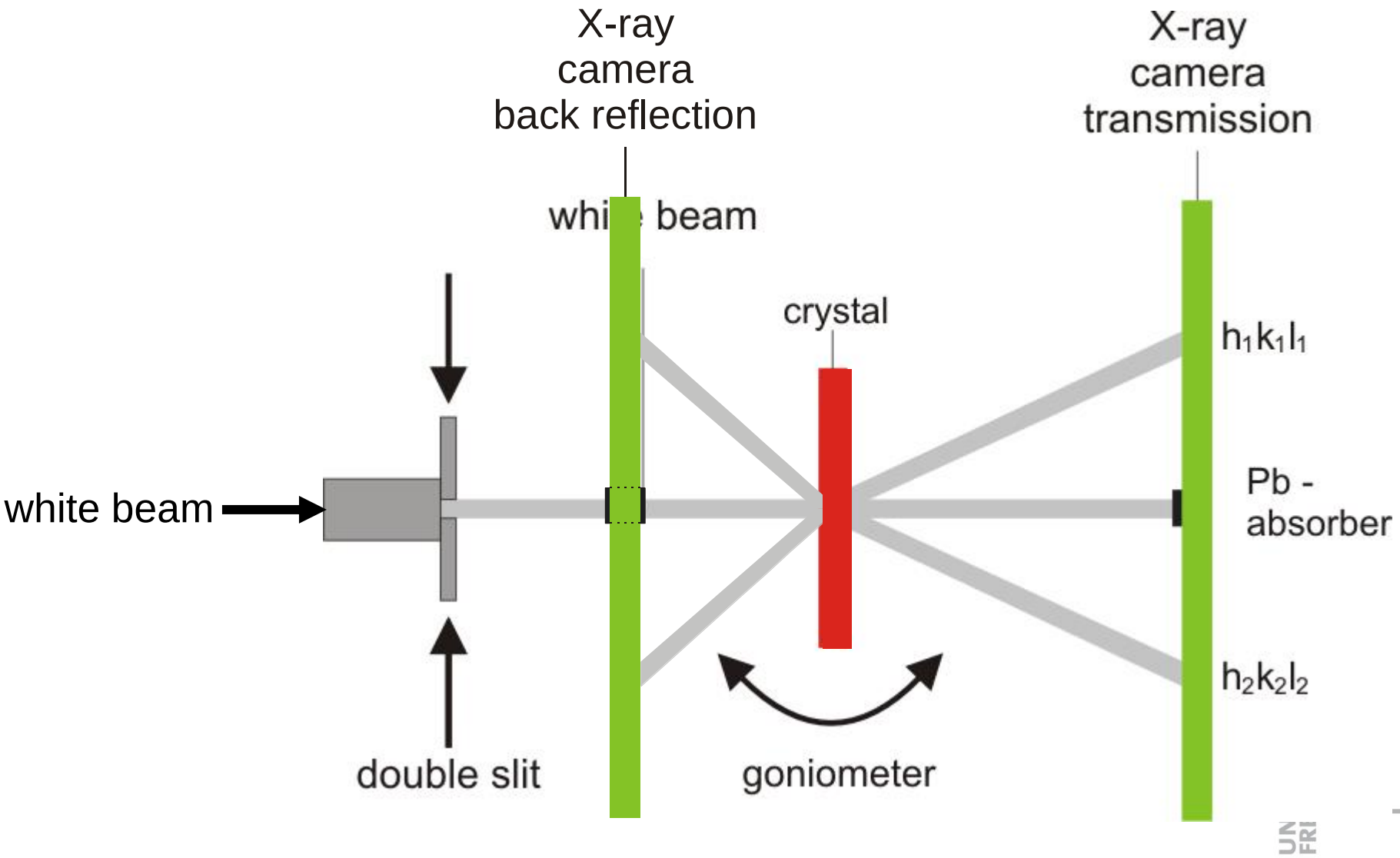


1g: K1-009-RM

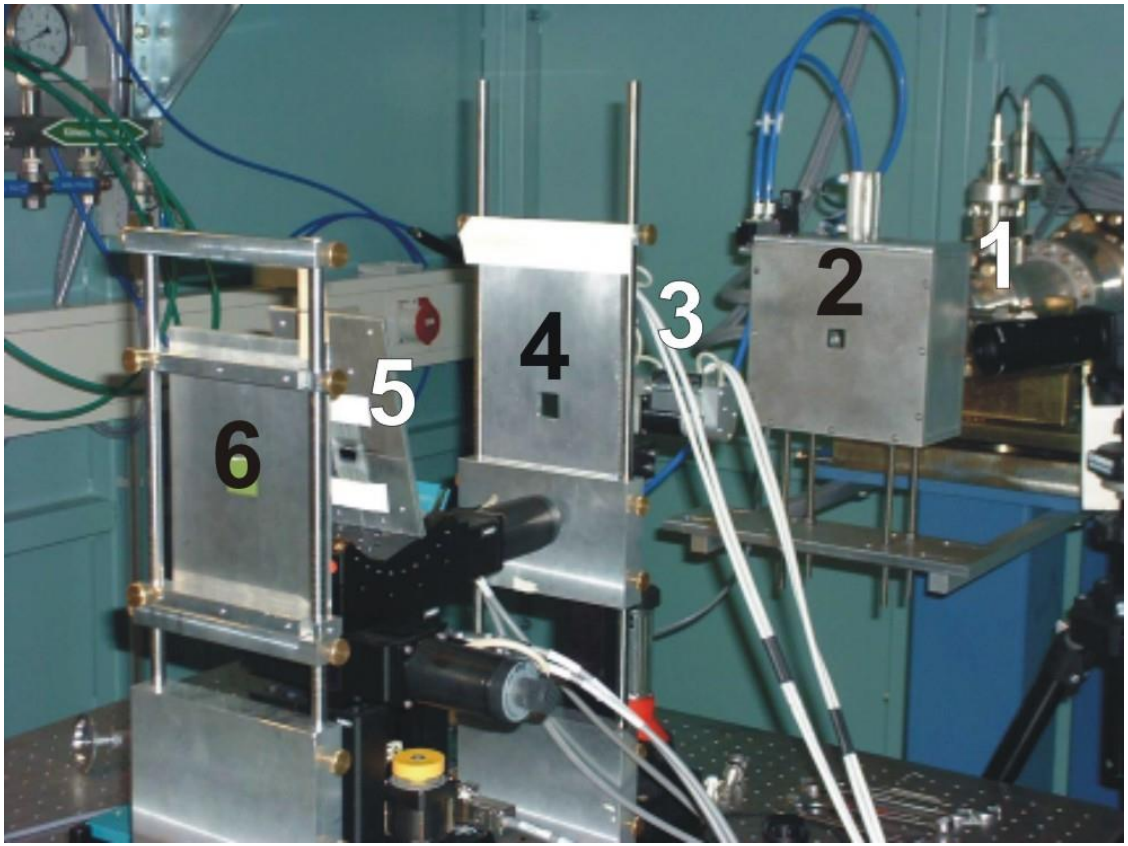


- **µg crystal shows mostly diffusive behaviour in the detached region and a decrease in Ga concentration at the beginning of the rotating magnetic field phase**
- **The curvature changes from mostly diffusive behaviour (Tiller) to complete mixing (Scheil)**
- **Reference crystals show the typical distribution for complete mixing, no visible change at the switching point of the rotating magnetic field**

LAUE X-RAY TOPOGRAPHY



X-RAY TOPOGRAPHY AT ANKA, KIT



(1) Be-window

(2) Fast shutter

(3) Double slit

(4) Back reflection film camera

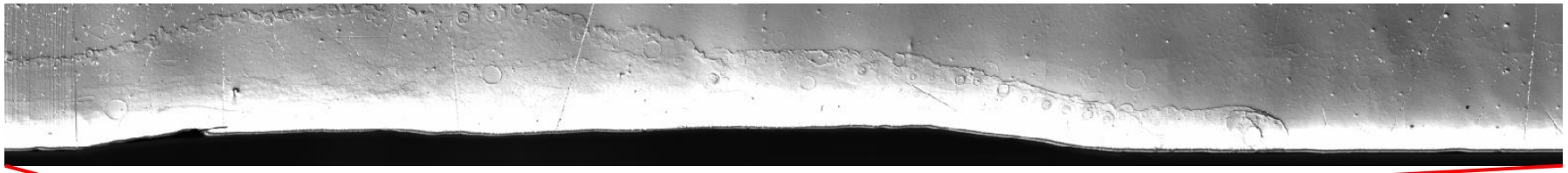
(5) Sample on two-circle goniometer

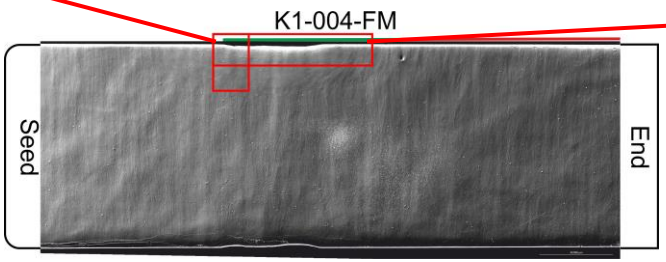
(6) Transmission film camera

K1: DISLOCATIONS

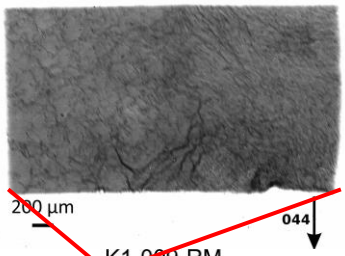
Synchrotron topography image µg

NDIC image µg



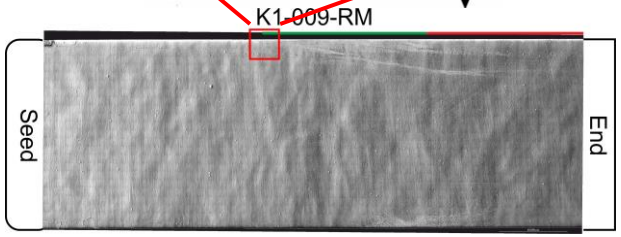


Dislocation density µg:
$3 \cdot 10^2$ - $5 \cdot 10^3$ cm^{-2}



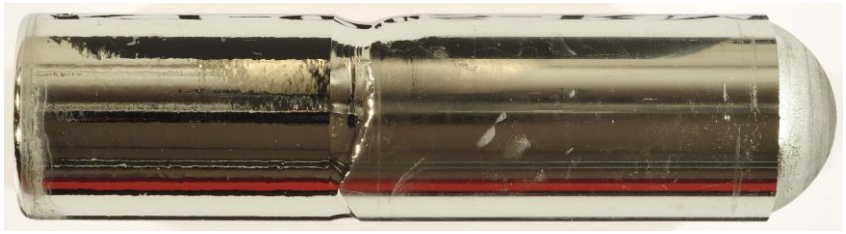
Synchrotron topography image 1g

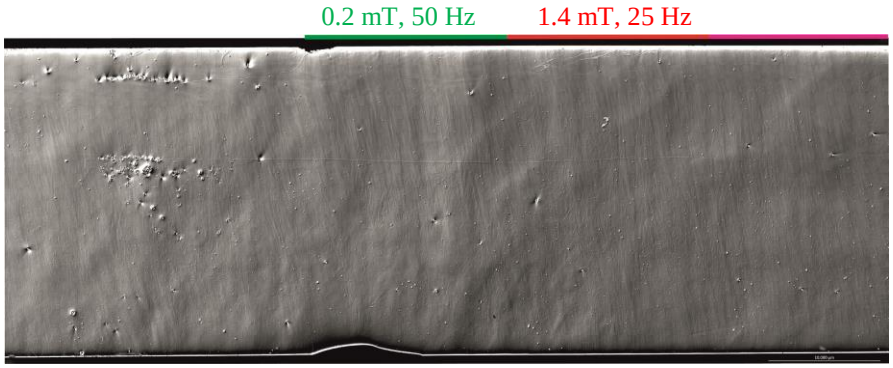
Dislocation density 1g:
≈ $5 \cdot 10^4$ cm^{-2}



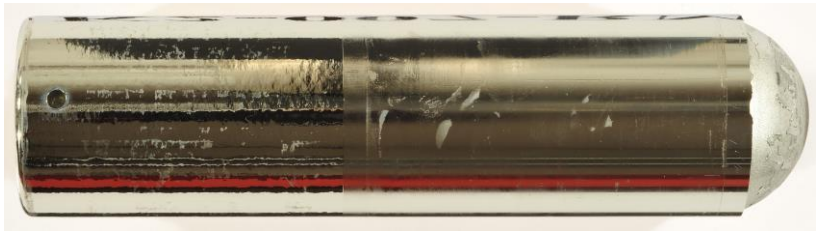
K2 - RESULTS

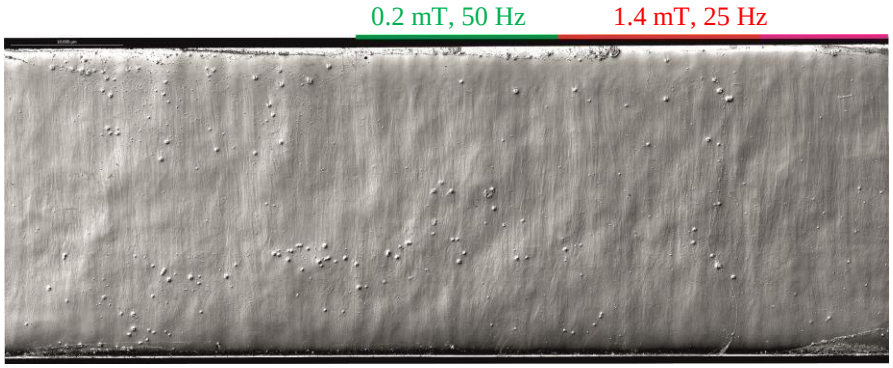
µg: K1-005-RM





1g: K2-007-RM

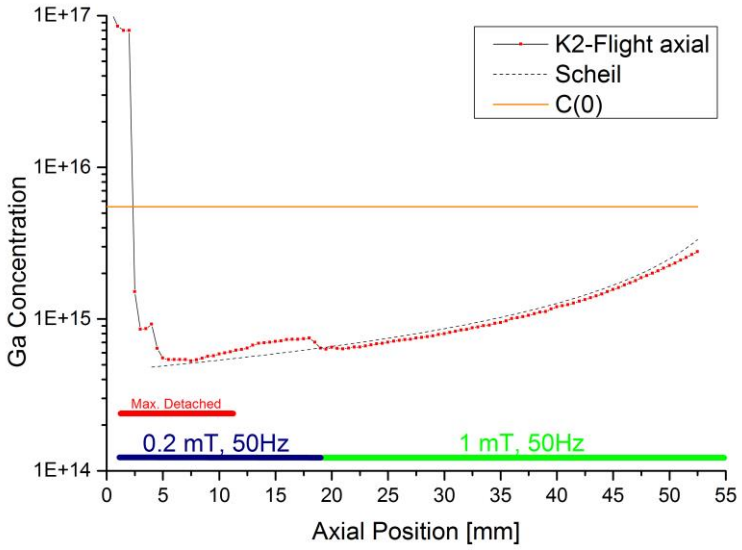




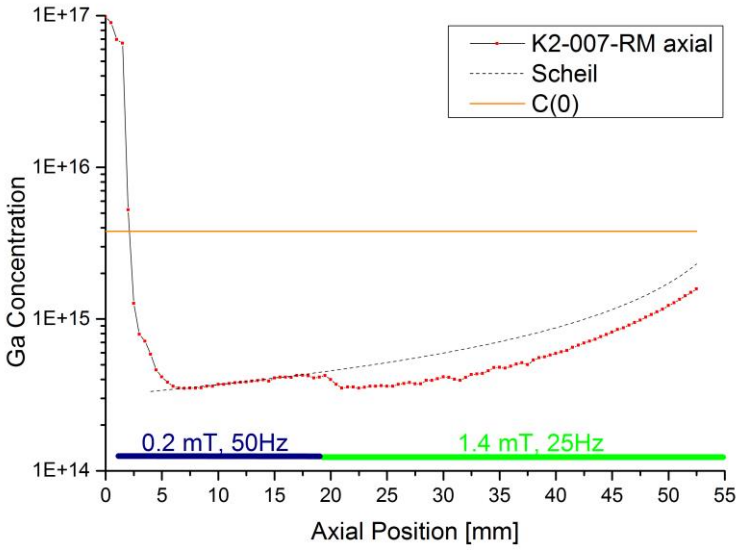
- **Detachment of the flight crystal despite the CFC spring**
- **Both µg and 1g samples are single crystals**
- **No striations visible in the grown crystals**

K2: AXIAL SEGREGATION

µg: K1-005-RM



1g: K2-007-RM

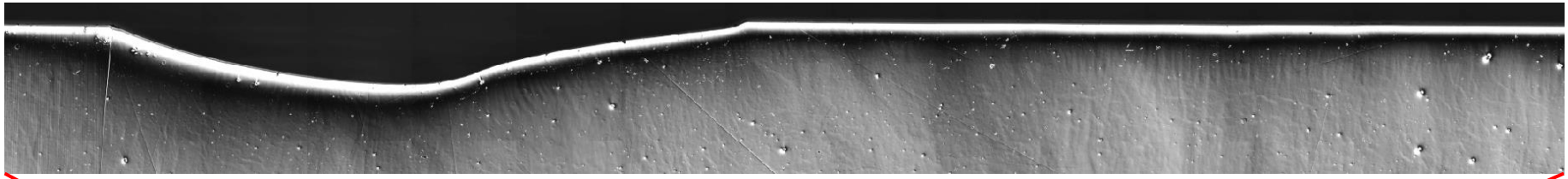


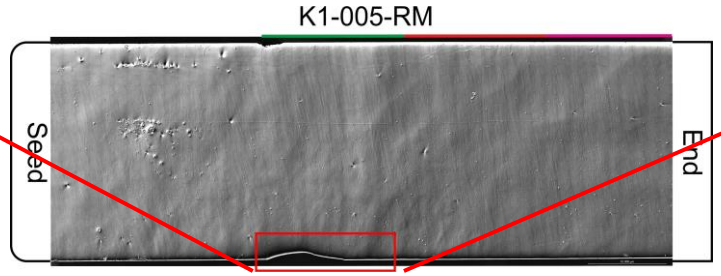
- **Both µg and 1g crystals show similar overall behavior**
- **A small deviation during the first growth stage in the µg-crystal**
- **Drop at switching point of the rotating magnetic field in both cases**

K2: DISLOCATIONS

Synchrotron topography image µg

NDIC image µg

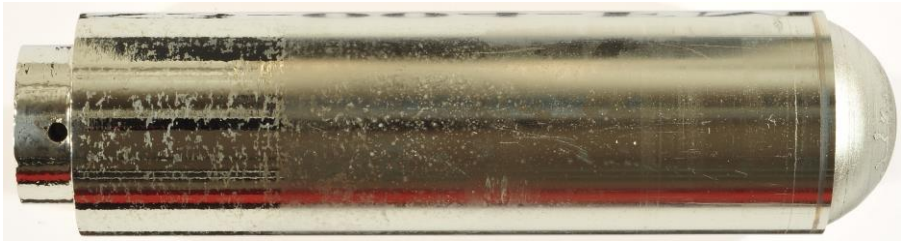


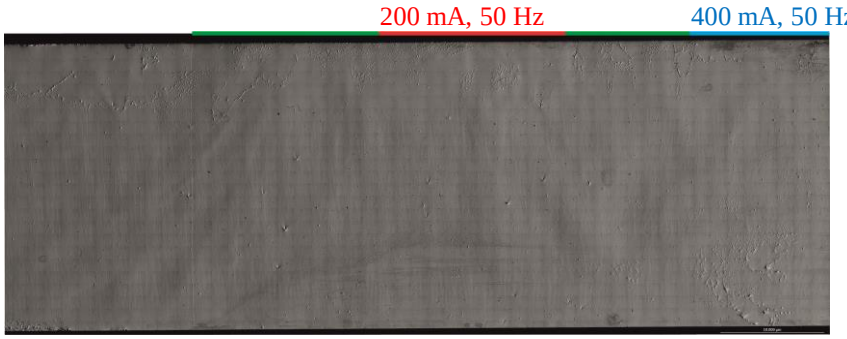


Dislocation density µg:
$3 \cdot 10^3$ - $8 \cdot 10^3$ cm^{-2}

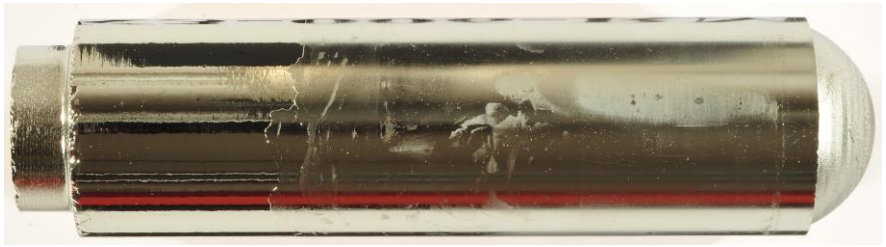
K3 - RESULTS

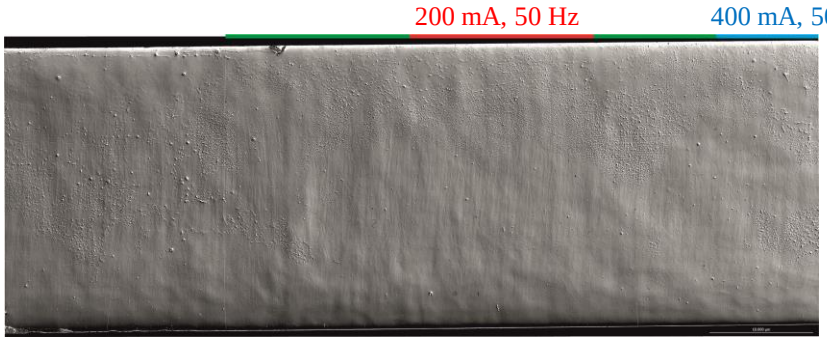
µg: K3-004-FM





1g: K3-006-RM

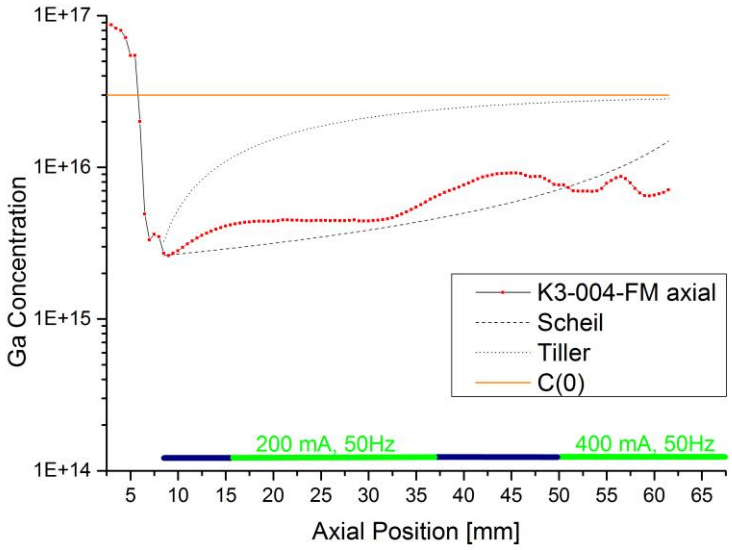




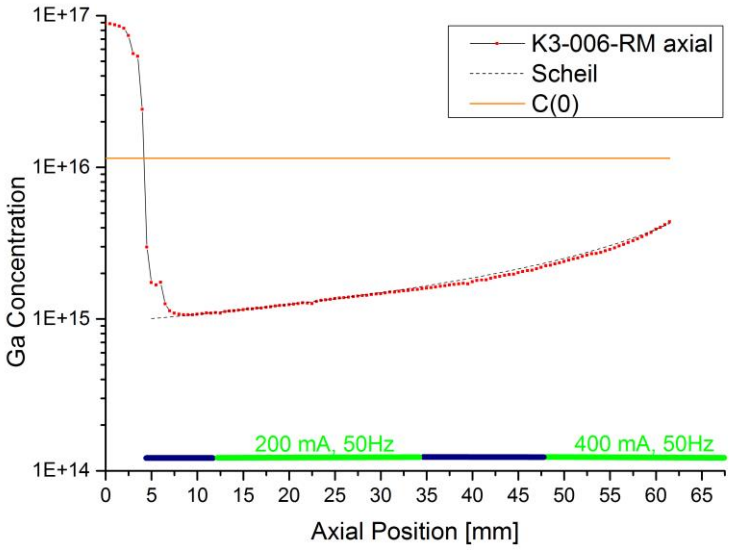
- **Flight sample starts to become polycrystalline from one side, reference sample is single crystalline**
- **No striations visible in the grown crystals**

K3: AXIAL SEGREGATION

µg: K3-004-FM

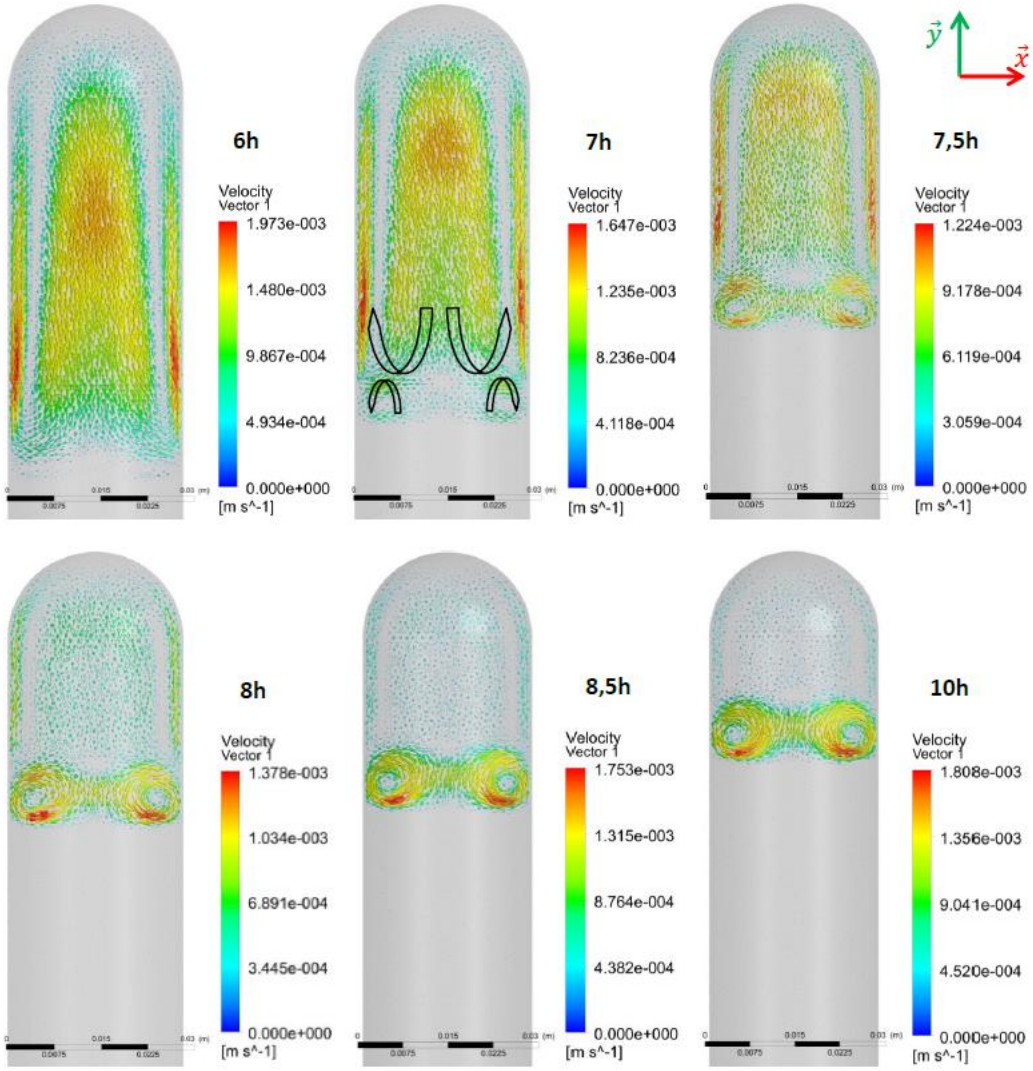


1g: K3-006-RM

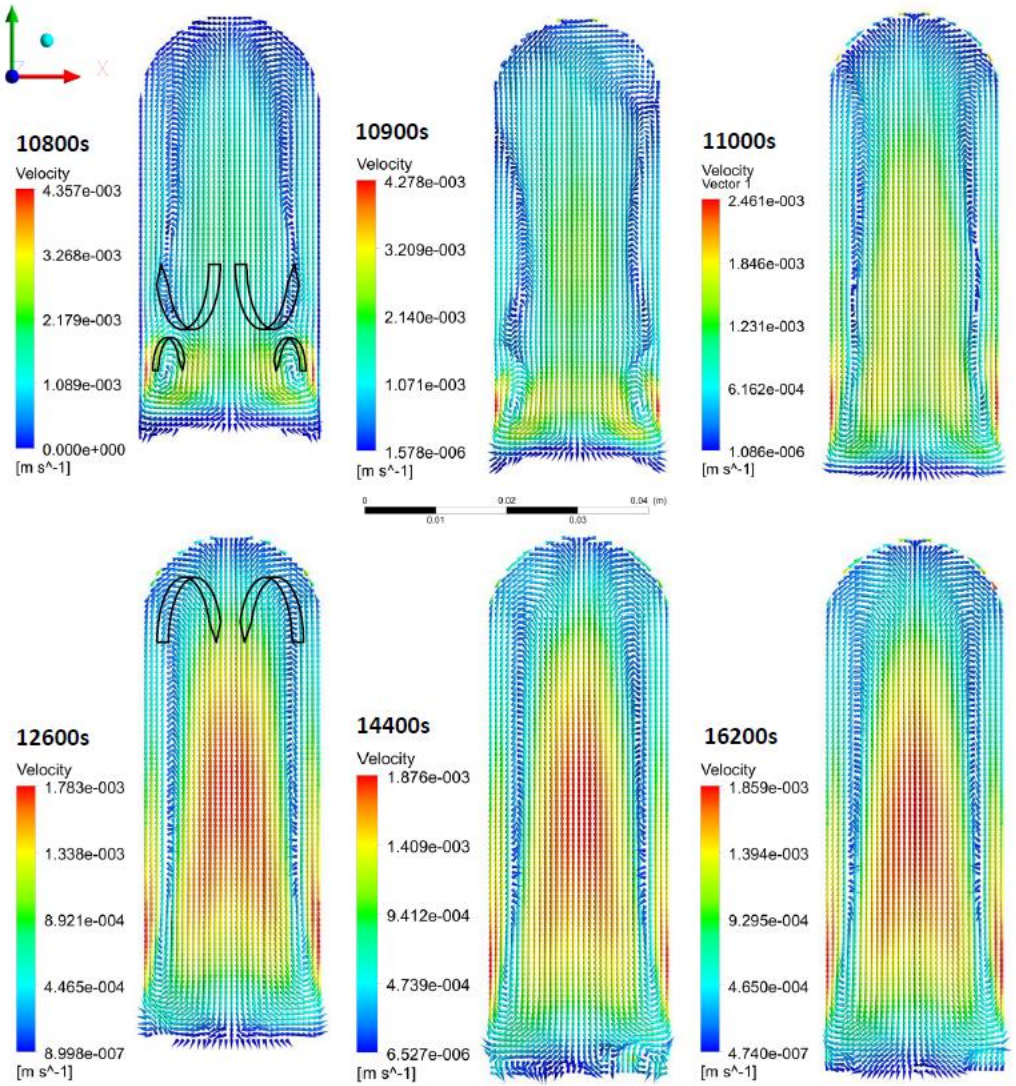


- **The µg crystal shows a constant concentration during the 1st vibration stage and a decrease in Ga concentration at the beginning of the 2nd, but with disturbances**
- **Vibration shows an effect on segregation - the resulting profile is neither Scheil or Tiller-like**
- **The reference crystal shows the typical distribution for complete mixing. No visible change during vibration → buoyancy convection is stronger**

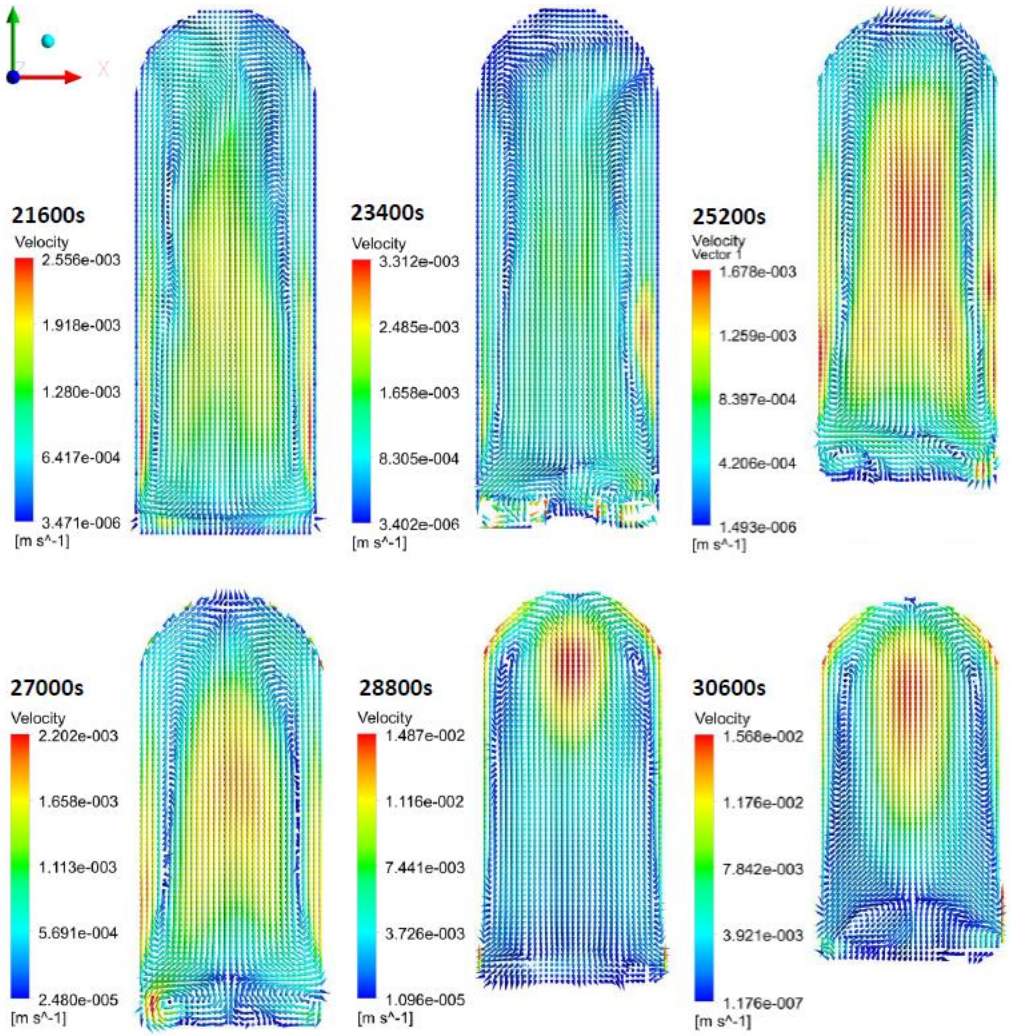
SIMULATIONS K3 – 1g – no vibration



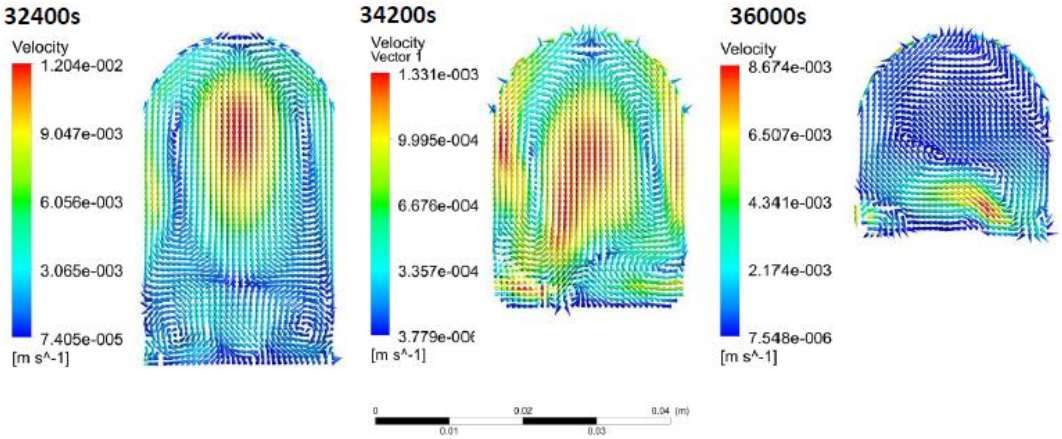
SIMULATIONS K3 – 1g



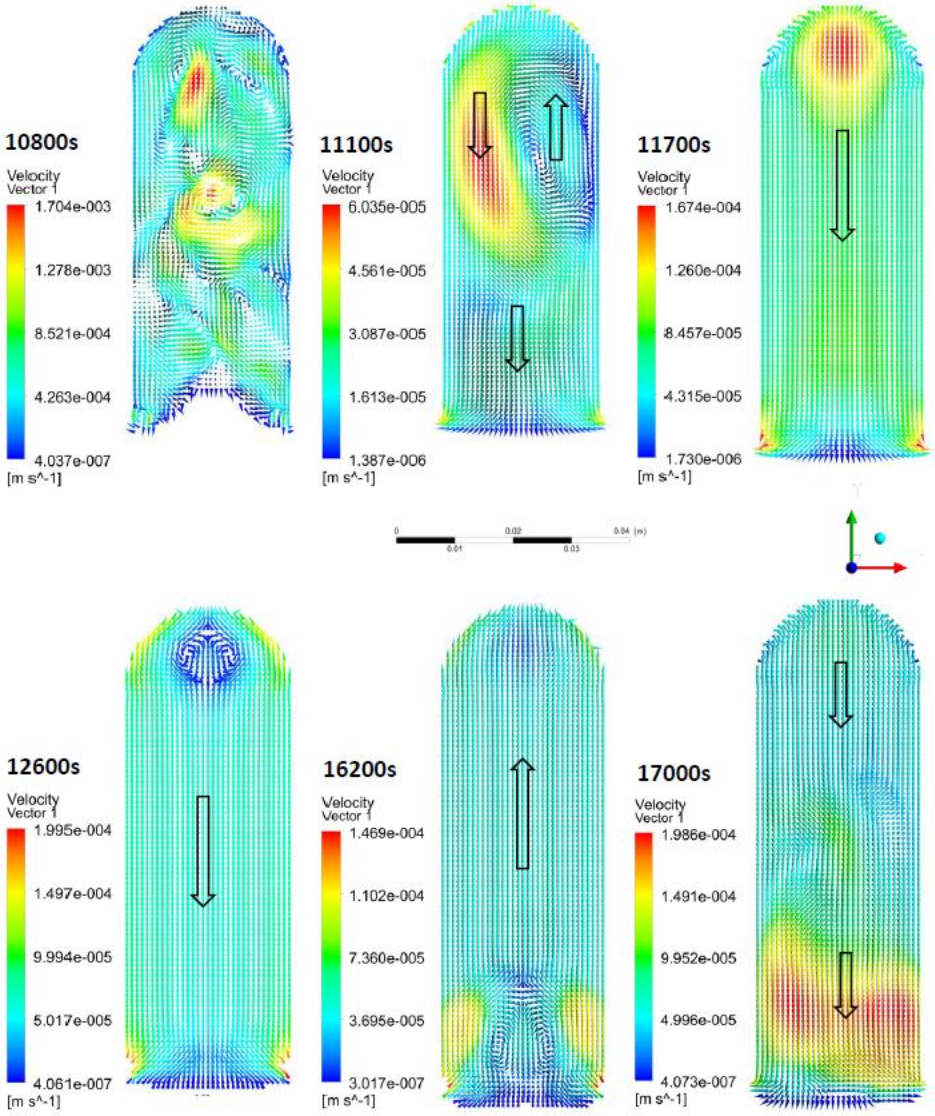
SIMULATIONS K3 – 1g cont'd



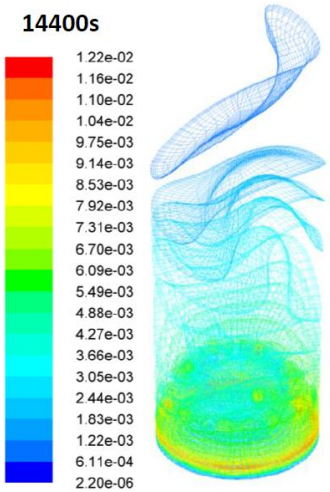
SIMULATIONS K3 – 1g cont'd

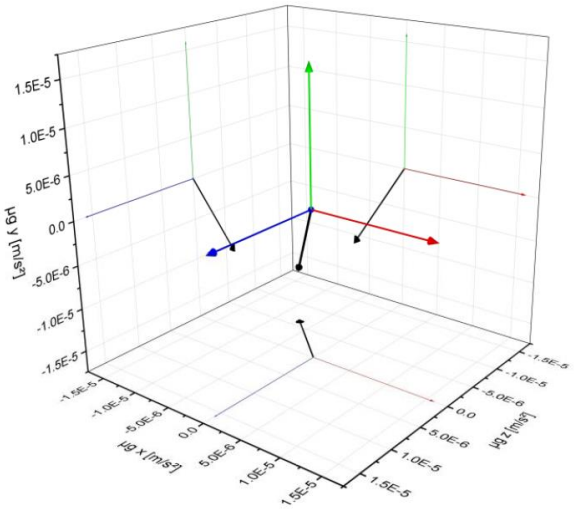


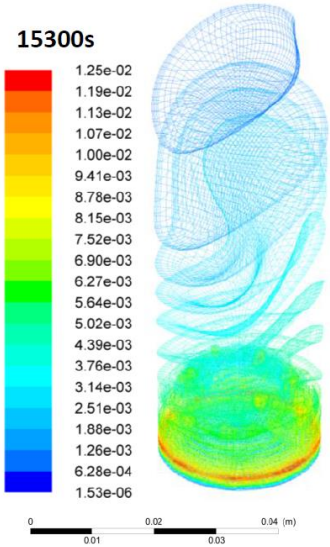
SIMULATIONS K3 – µg

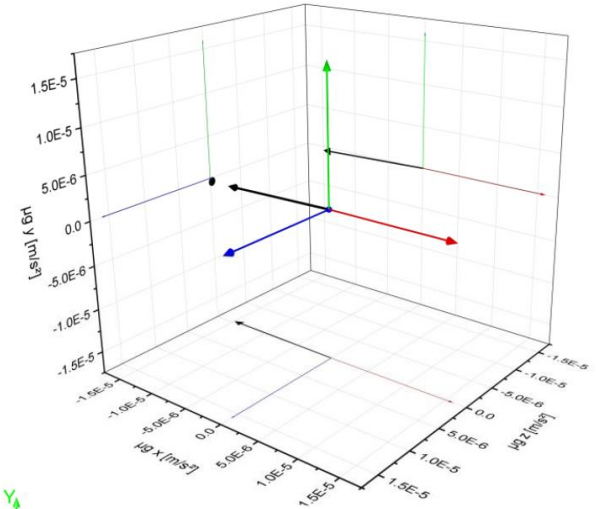


SIMULATIONS K3-µg-Ga concentration



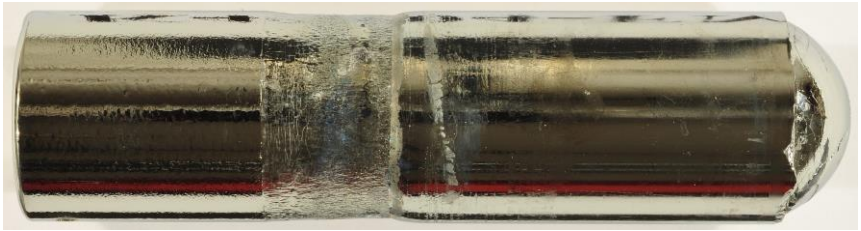


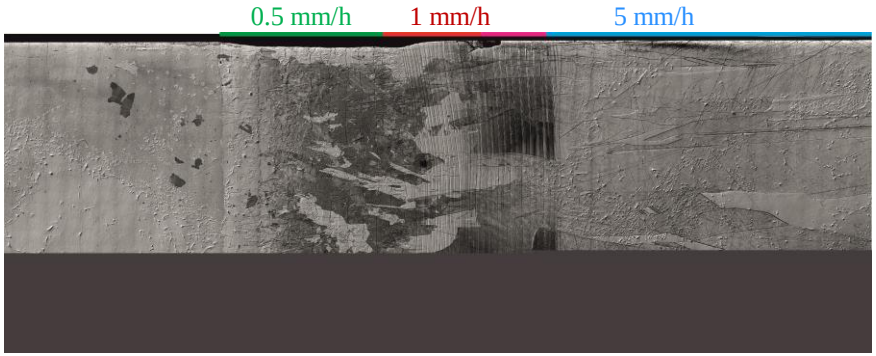




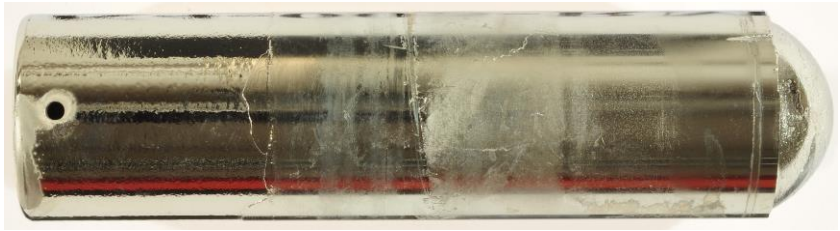
K4 - RESULTS

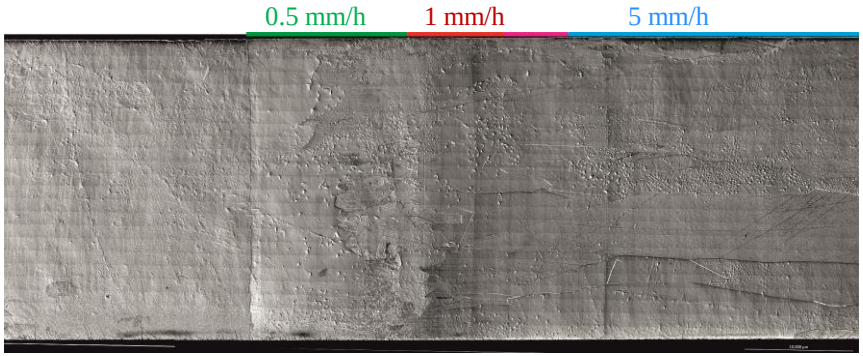
µg: K4-004-FM





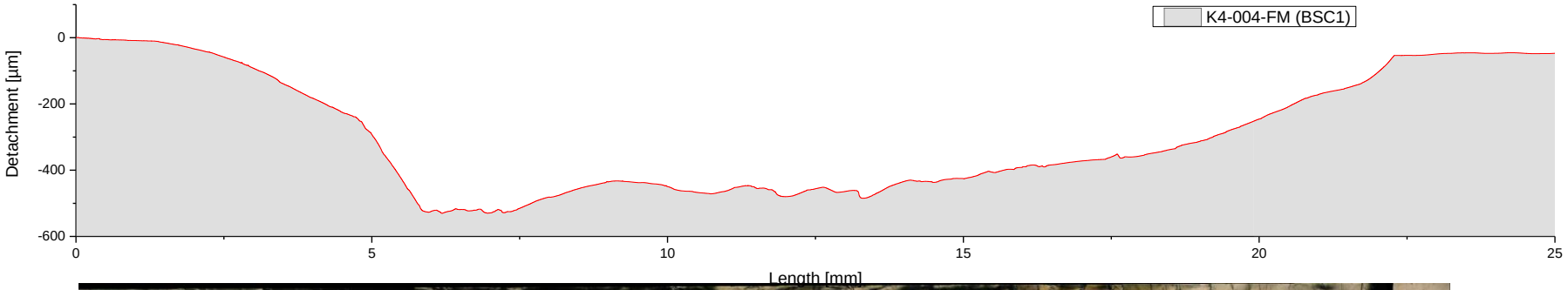
1g: K4-005-RM

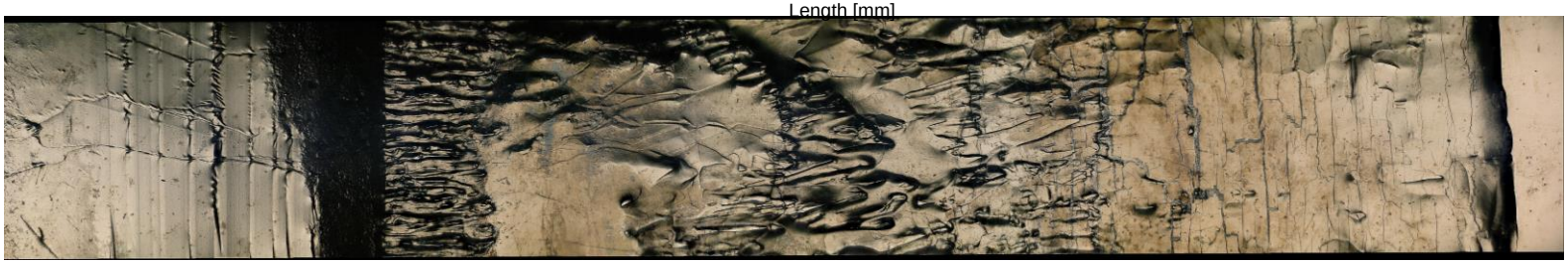




- **Successful detachment over 21.4mm → wetting angle is sufficient for detachment w/o pressure difference**
- **Polycrystalline growth after 3 mm (µg) and 7 mm (1g) due to constitutional supercooling**
- **Both samples show strong striations, more visible in the flight sample**
- **Striations are also visible in the attached area (!)**

DETACHMENT



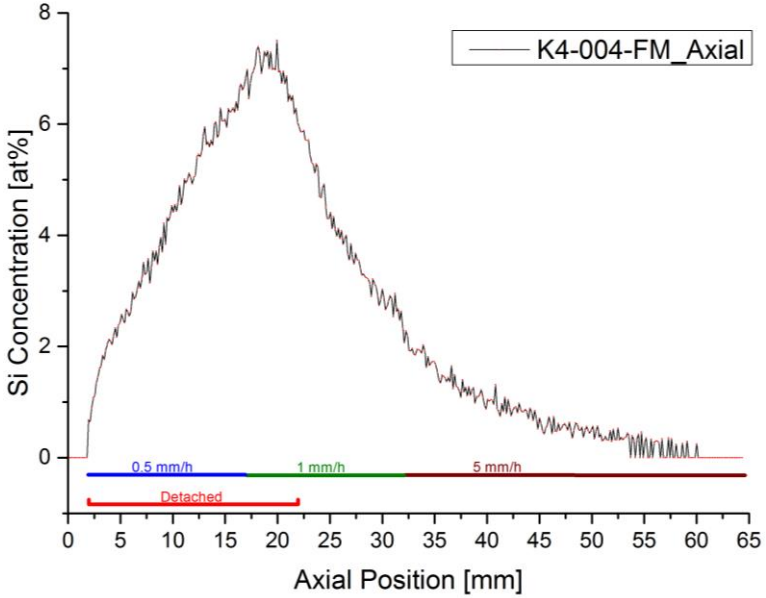


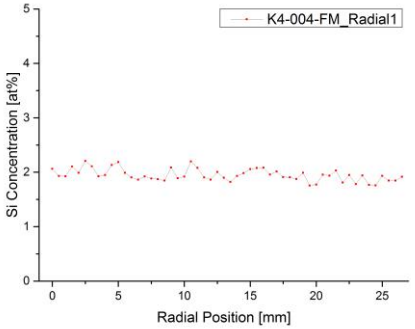
Sample	Mean Max. Detachment [µm]	Max. Length [mm]	Min. Length [mm]
K1-004-FM	450	14.5	13.3
K2-Flight	500 (strong variation)	12.1	1.3
K4-004-FM	500	21.4	21.0

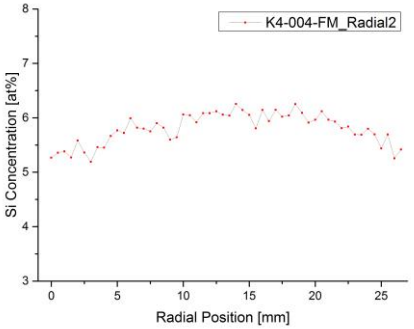
- **Profiler measurements on 10 different radial positions (only one 1 example shown)**

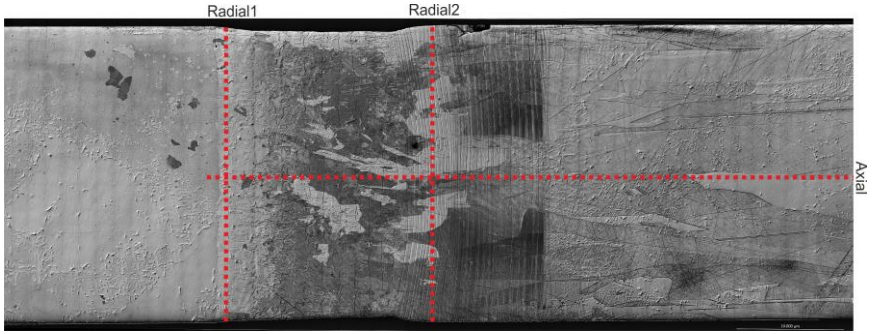
K4: AXIAL AND RADIAL SEGREGATION

µg: K4-004-FM





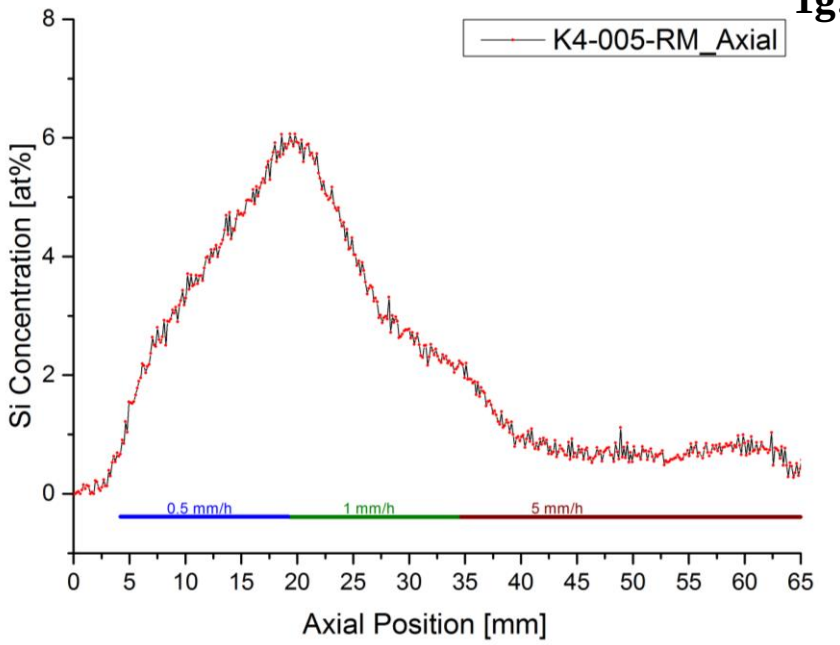


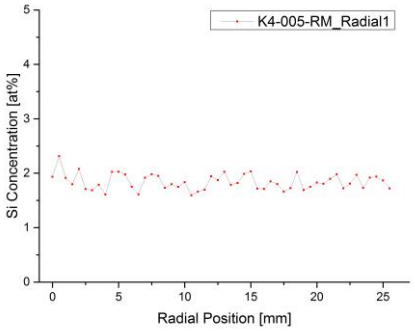


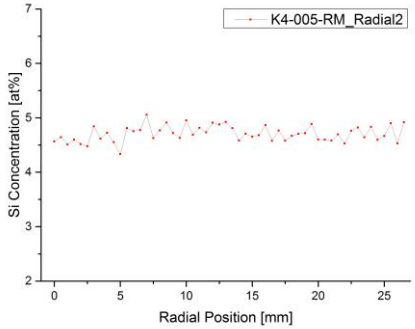
- **Only ~3 mm of single crystal region due to constitutional supercooling**
- **Higher increase of Si content compared to previous experiments due to use of rotating magnetic field + detachment (solutocapillary flow), also increased max. value**
- **Increase over the whole detachment region**
- **Radial distribution follows the visible striations**

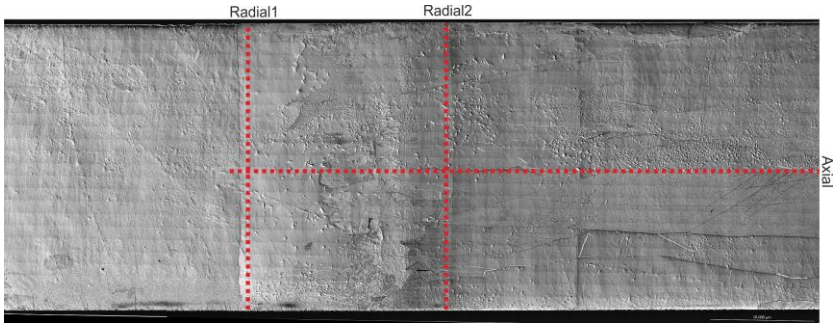
K4: AXIAL AND RADIAL SEGREGATION

1g: K4-005-RM





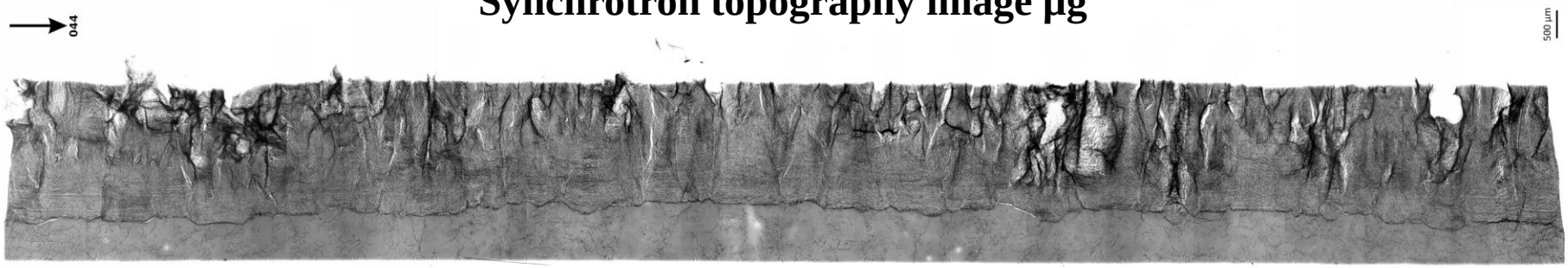




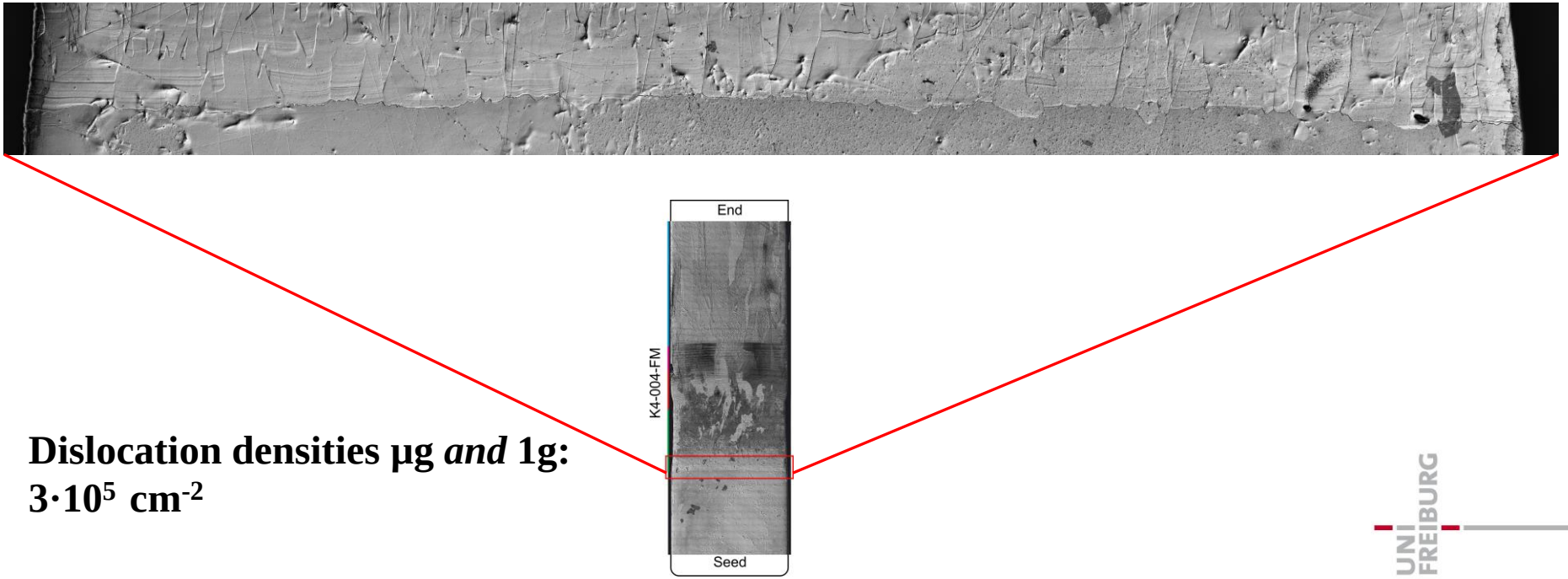
- **Only ~7 mm of single crystal region, also constitutional supercooling visible**
- **Higher increase of Si content compared to test experiments due to use of a rotating magnetic field, but lower than µg sample, also increased max. value**
- **Increase only until switching point, 2nd switching point more noticeable here**
- **Radial distribution follows the visible striations**

K4: DISLOCATIONS µg

Synchrotron topography image µg



NDIC image µg

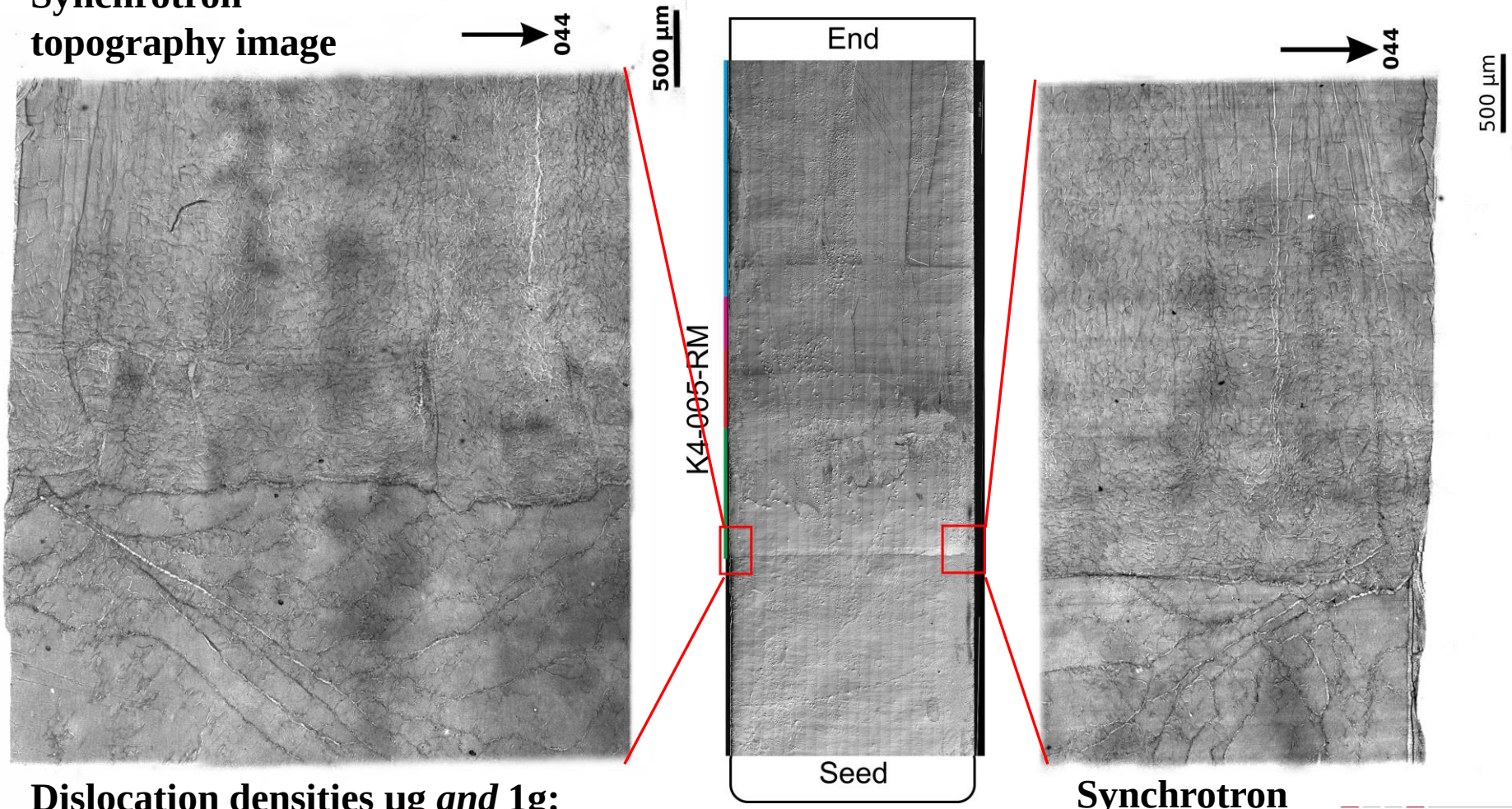


Dislocation densities µg *and* 1g:
$3 \cdot 10^5$ cm^{-2}

K4: DISLOCATIONS 1g

Synchrotron topography image

NDIC image



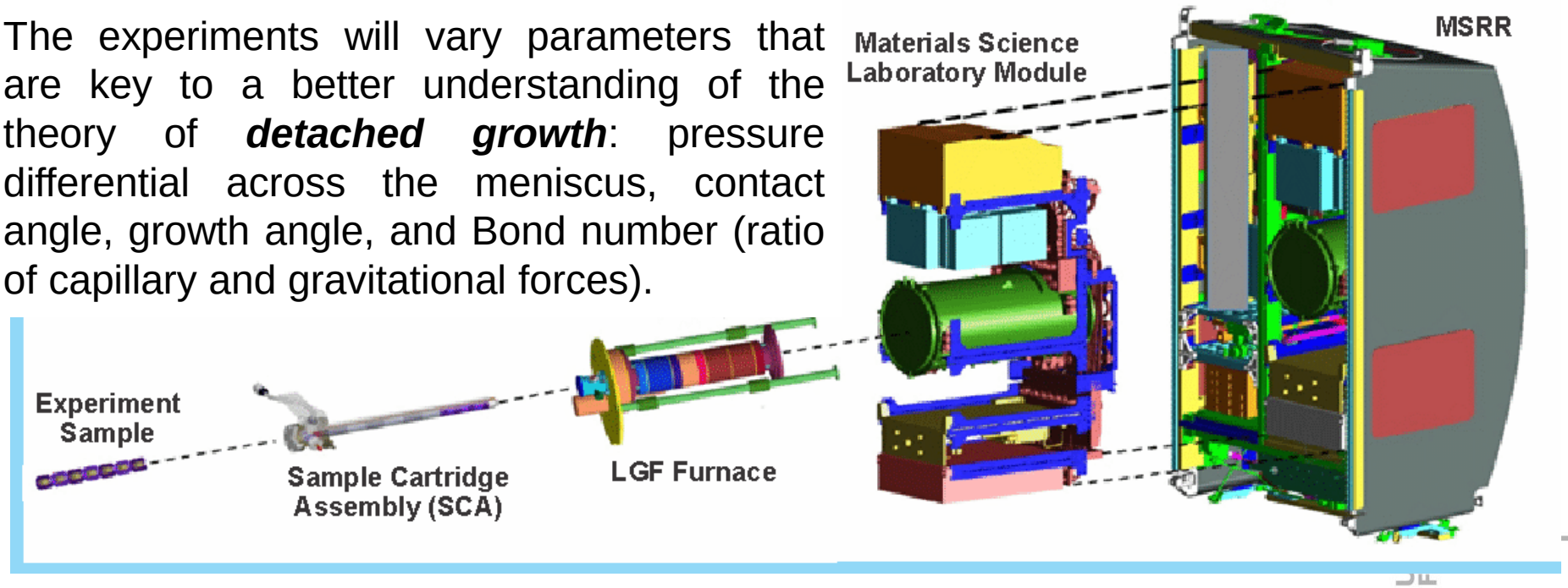
Dislocation densities µg *and* 1g: $3 \cdot 10^5$ cm^{-2}

Synchrotron topography image

ICESAGE: FUTURE ISS EXPERIMENTS

A series of 10 $Ge_{1-x}Si_x$ (x: 0-0.02) samples will be processed in the Low Gradient Furnace (LGF) in the Materials Science Research Rack (MSRR) on the ISS. The samples are currently scheduled to be launched to the ISS in 2017.

The experiments will vary parameters that are key to a better understanding of the theory of ***detached growth***: pressure differential across the meniscus, contact angle, growth angle, and Bond number (ratio of capillary and gravitational forces).



CONCLUSIONS

- **All experiments on FOTON M4 were successful and yielded crystals for analysis**
- **Both the K1 and K2 crystals grew partially detached**
- **The K4 µg crystal is symmetrically detached over the whole circumference and over 21.4 mm length, whereas the 1g reference crystal is attached**
- **The K3 vibration experiment crystals show a visible effect on the segregation in the µg crystal, not visible in the 1g crystal**
- **An experimental parametric study of detachment ("ICESAGE") is planned for 2017/18 on the ISS**

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UNI FREIBURG

THE UNIVERSITY OF ALABAMA IN HUNTSVILLE

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