31st Annual Meeting of the American Society for Gravitational and Space Research
Alexandria, Virginia
November 11-14, 2015

Crystal Growth of Germanium-Silicon Alloys on the ISS

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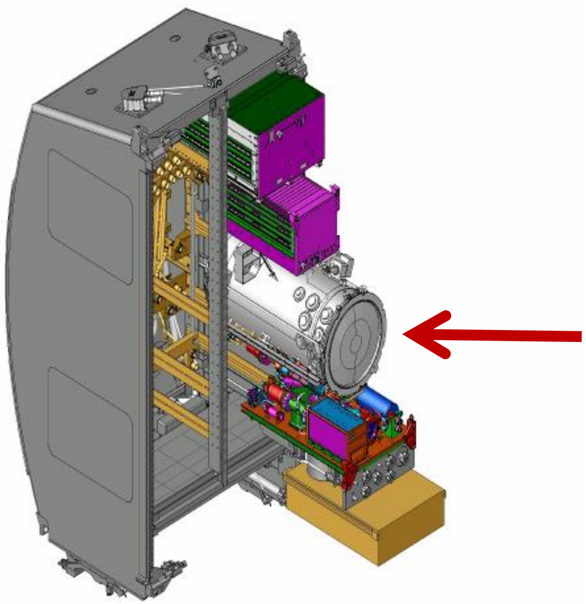
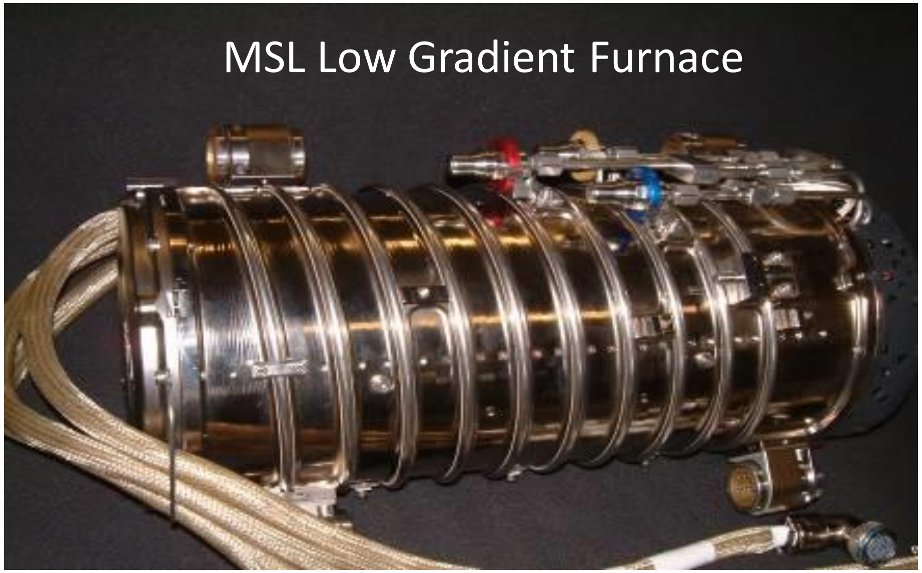
ICESAGE Flight Investigation

- “Influence of Containment on the Growth of Silicon-Germanium” (ICESAGE) is a NASA Materials Science Flight Investigation
- ICESAGE is a collaborative investigation between NASA and the European Space Agency (ESA)
- The ICESAGE experiments will be conducted in the Low Gradient Furnace (LGF) in the Materials Science Laboratory on the International Space Station (ISS)



Materials Science Laboratory

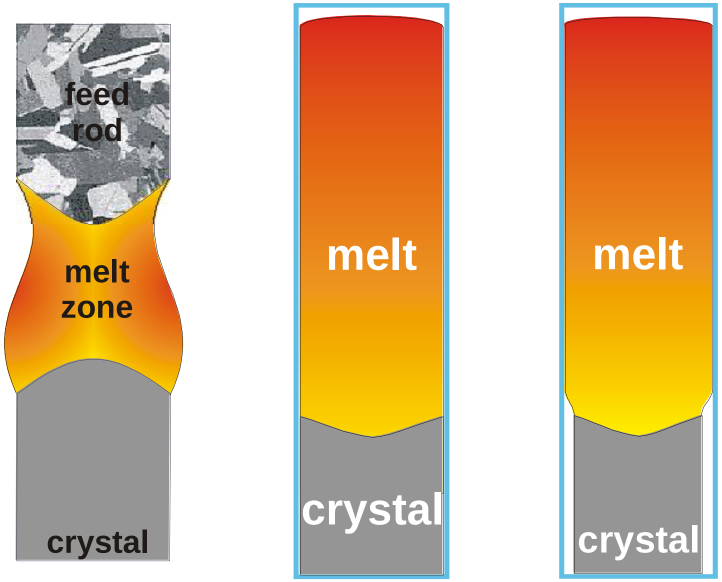


MSL Low Gradient Furnace

Overview of the Investigation

This investigation involves the comparison of results achieved from three types of crystal growth of germanium and germanium-silicon alloys:

- Float zone growth
- Bridgman growth
- Detached Bridgman growth

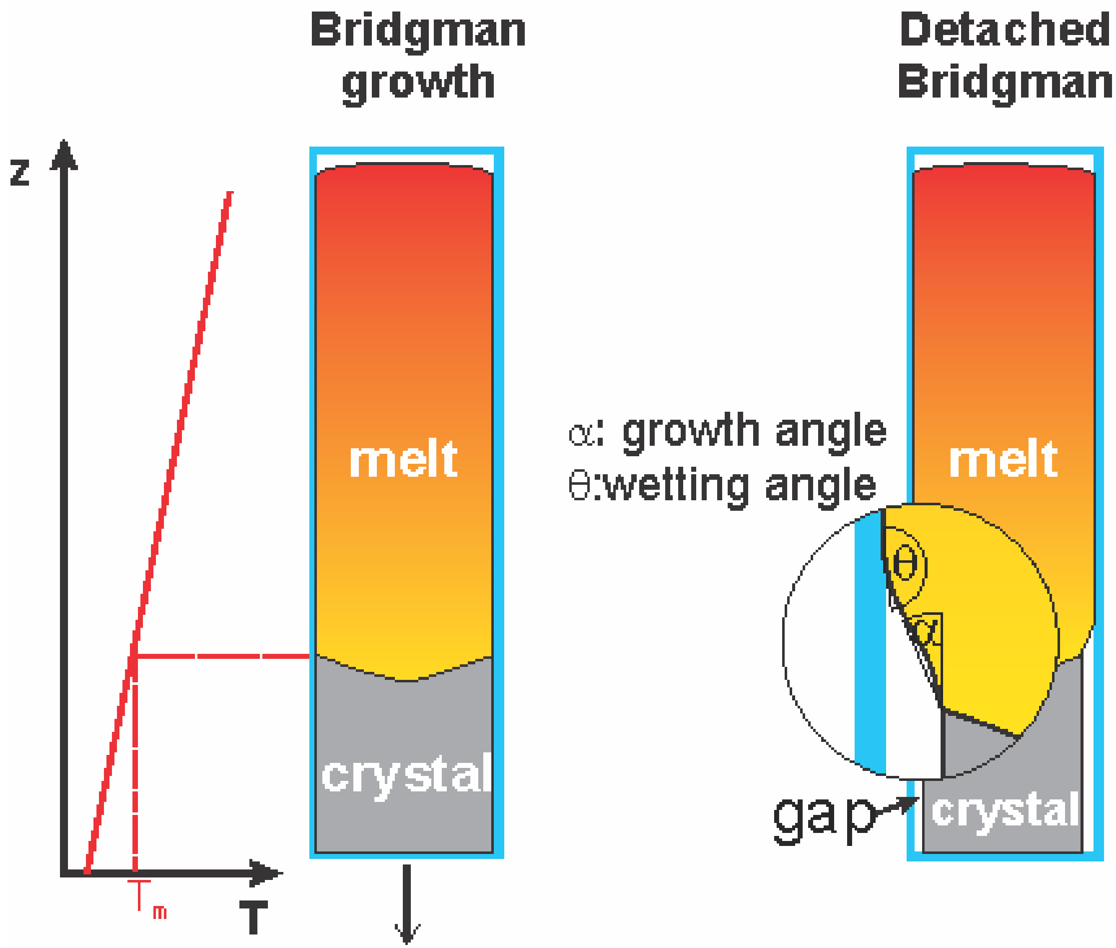


The fundamental goal of the proposed research is to determine the influence of containment on the processing-induced defects and impurity incorporation in germanium-silicon (GeSi) crystals (silicon concentration in the solid up to 5 at%) for three different growth configurations in order to quantitatively assess the improvements of crystal quality possible by detached growth.

What is Detached Bridgman Growth?

Sufficient condition for detachment[1,2]:

$$(\alpha+\theta \geq 180°)$$



Advantages

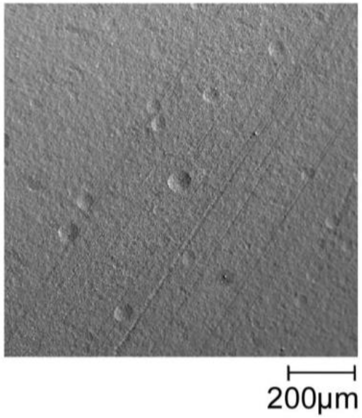
- No sticking of the crystal to the ampoule wall
- Reduced stress
- Reduced dislocations
- No heterogeneous nucleation by the ampoule
- Reduced contamination

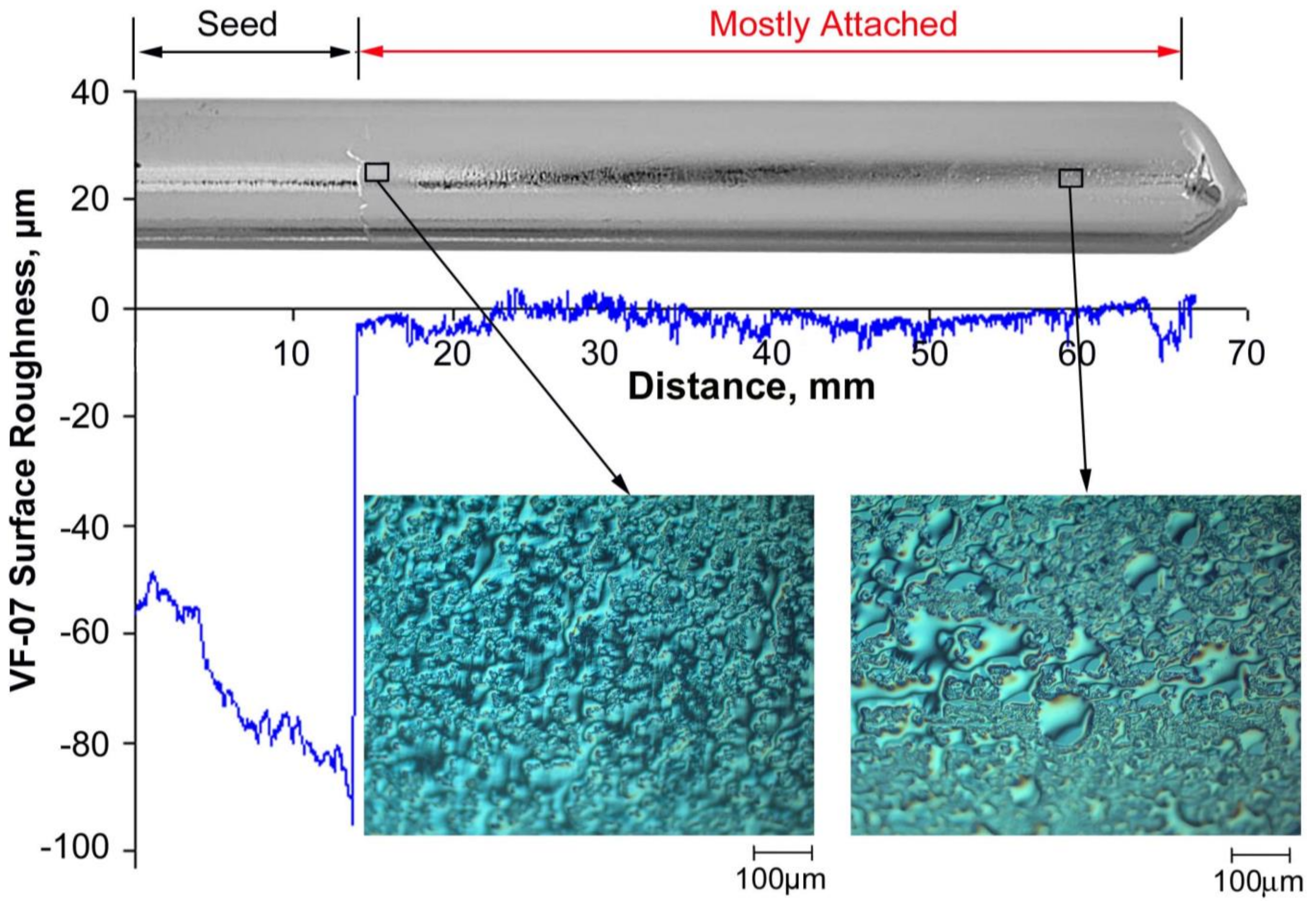
[1] V. S. Zemskov: Fiz. Khim. Obrab. Mater. 17 (1983) 56

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

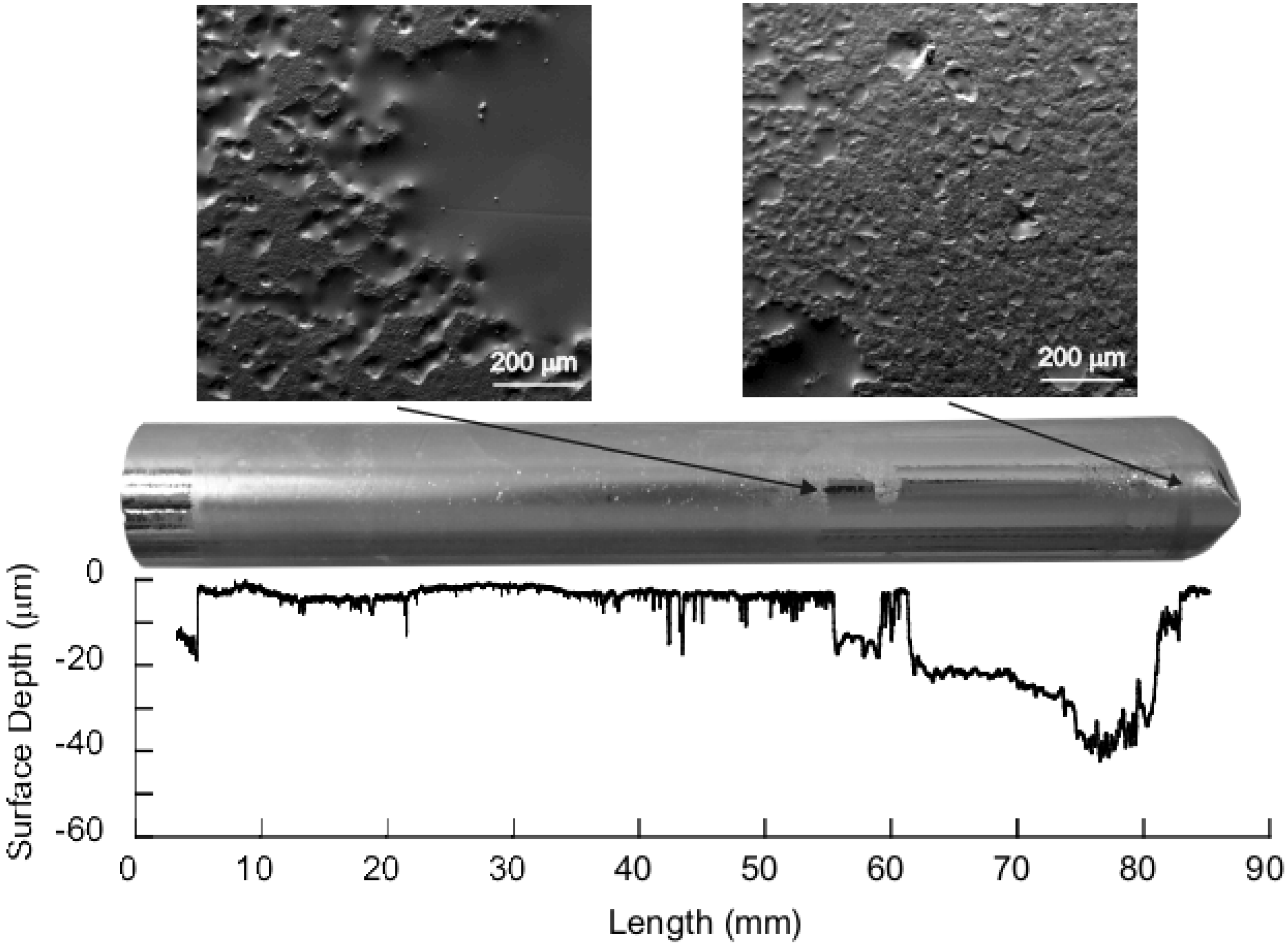
"Attached" Germanium

pBN Ampoule Surface



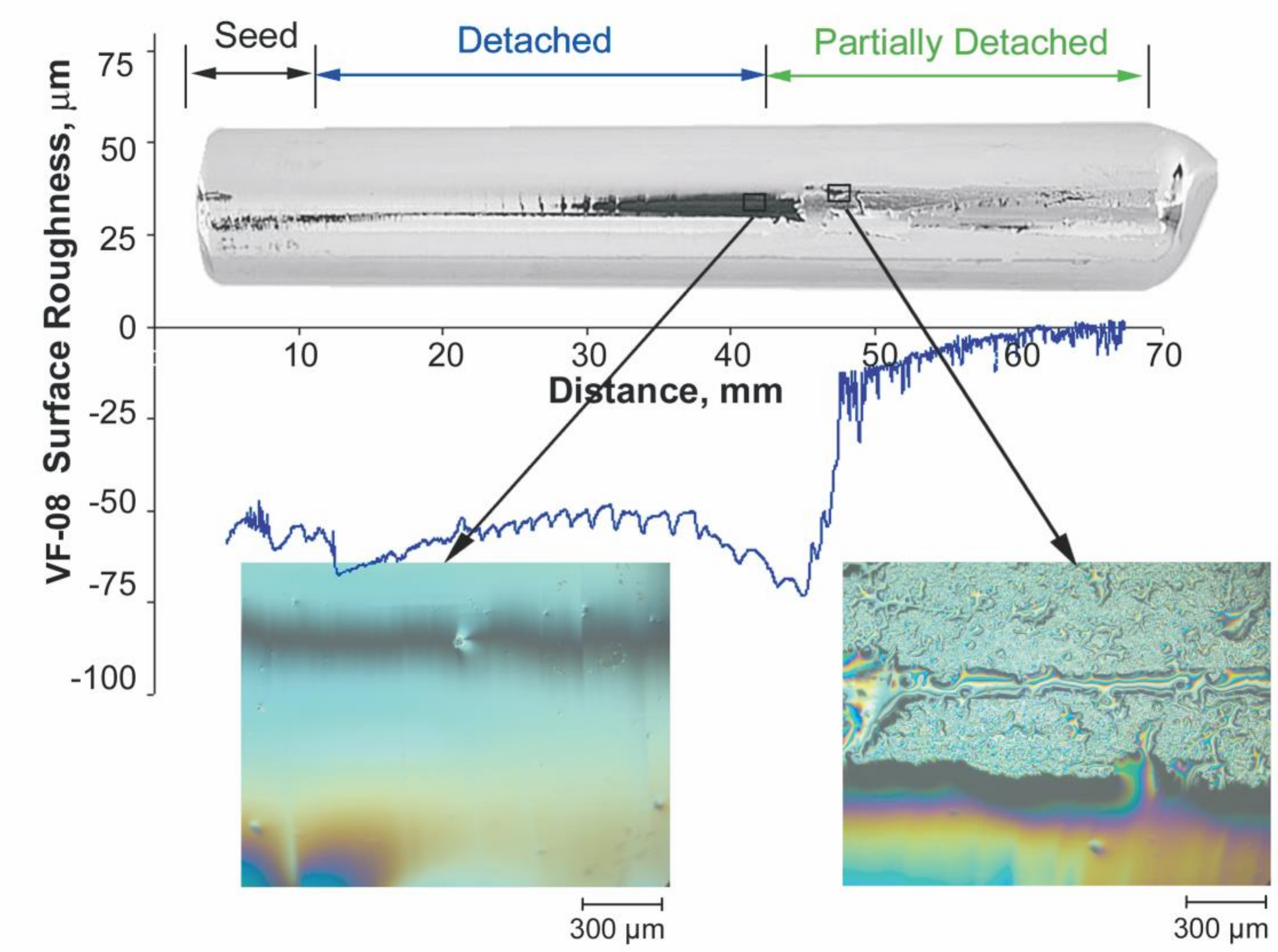


Partially Attached GeSi



M. P. Volz, M. Schweizer, N. Kaiser, S. D. Cobb, L. Vujisic, S. Motakef, F. R. Szofran, *JCG* 237-239 (2002) 1844-1848

Detached Ge in pBN Ampoule



Etch Pit Densities in Detached/Attached Crystals

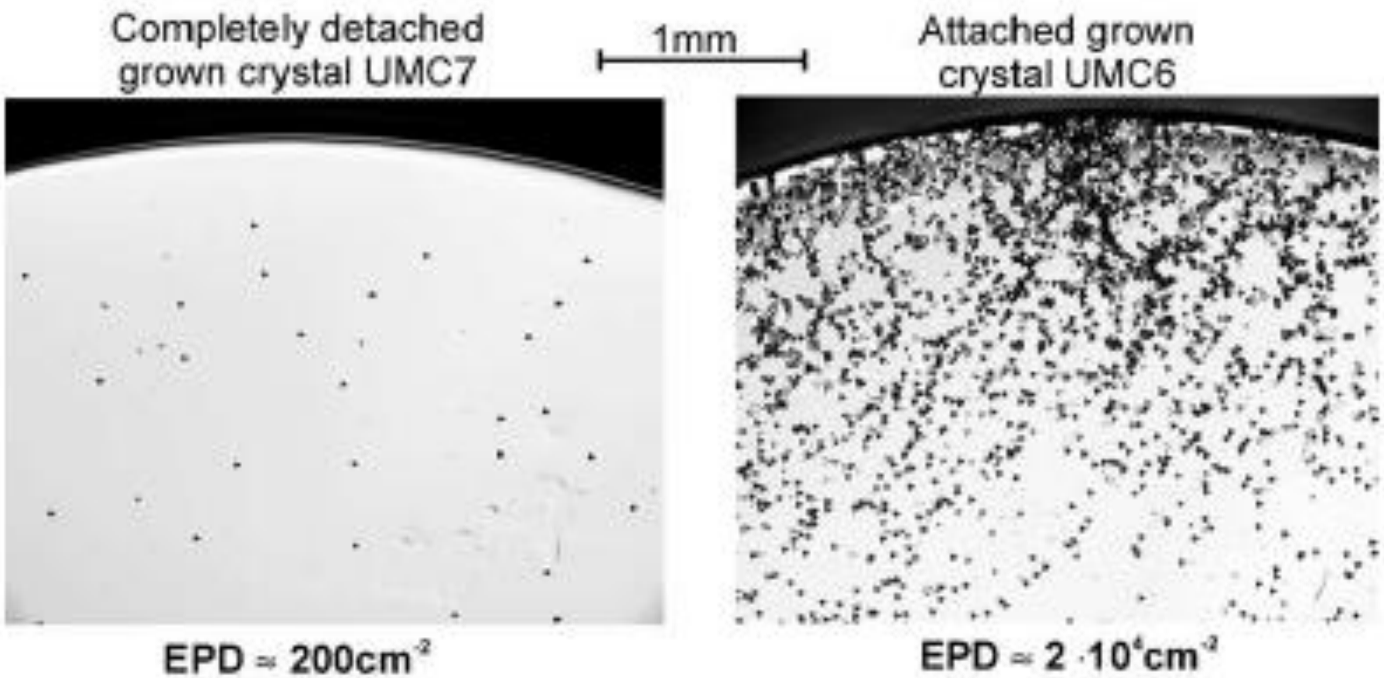


Fig. 5. Micrograph from the detached-grown sample UMC7 and from the attached-grown sample UMC6.

M. Schweizer, S. D. Cobb, M. P. Volz, J. Szoke, F. R. Szofran, JCG 235 (2002) 161-166

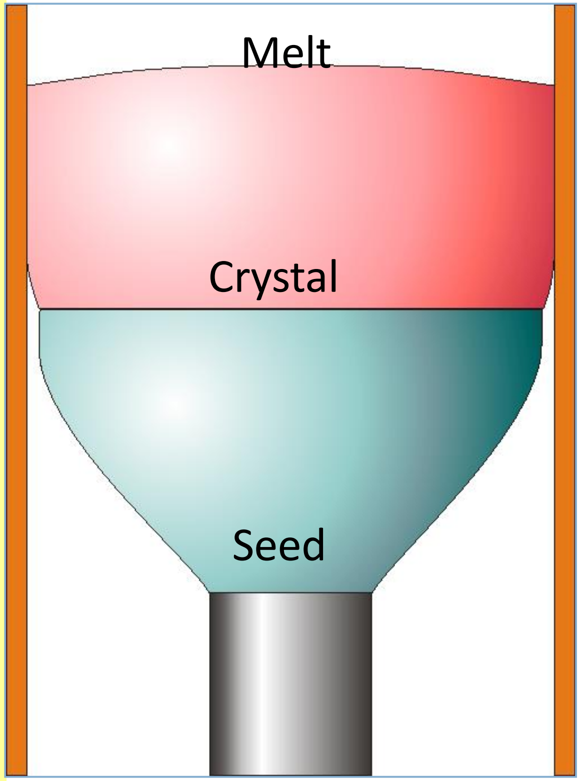
Serendipitous Observations of Detached Growth in Microgravity

- **Microgravity experiments have yielded detached ingots that have one or more of the following characteristics (Regel and Wilcox, Microgravity Science and Technology, 1999):**
  - Free movement in container after growth
  - Isolated surface voids or bubbles
  - Surface ridges and lines
  - Contact only at peaks of grooved ampoules
  - Gap of 1-60 µm between ingot and wall after accounting for thermal contraction
  - Large gap (>1 mm) with a wavy surface or hourglass-shaped neck next to seed
- **Occurrence of detachment is unpredictable (Regel and Wilcox, Microgravity Science and Technology, 1999):**
  - Predominately observed in semi-conductors but also in metals and alloys
  - Occurs at fast and slow growth rates
  - Independent of dopant
  - Features of detachment not reproducible
  - Occurrence of detachment not reproducible
  - Independent of oxygen presence

Motivation for Flight Experiments

ICEAGE seeks a better understanding of detachment by conducting a series of microgravity experiments in which the relevant parameters are varied

- What are the conditions for detachment in microgravity and how do they depend on the governing parameters?
  - Growth angle
  - Contact angle
  - Pressure differential
  - Bond number (ratio of gravity to capillarity)
- Which detached growth solutions are dynamically stable?
- How does an initial crystal radius evolve to one of the following states?
  - Stable detached gap
  - Attachment to the crucible wall
  - Meniscus collapse



Microgravity Effects

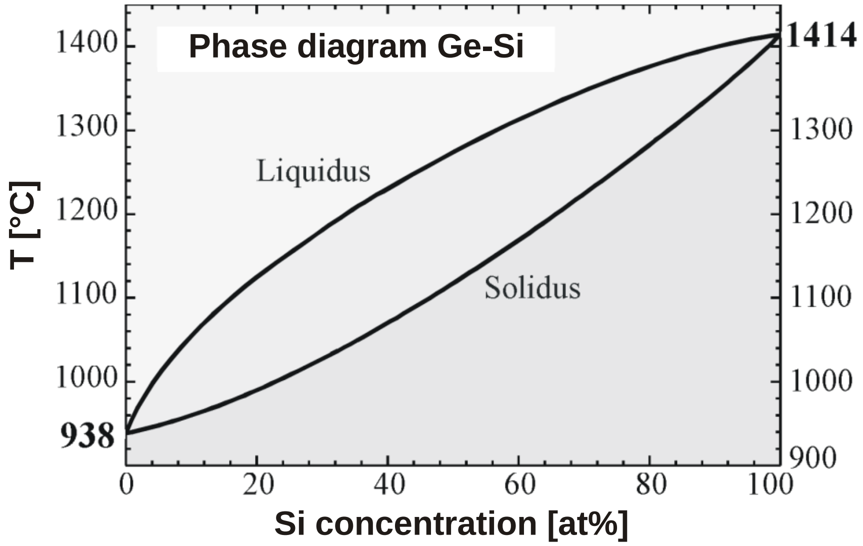
- Microgravity reduces the pressure head (ρgh) resulting from the weight of the melt.
  - Detached growth requires that capillary forces dominate over gravitational forces.
  - On Earth, gravity complicates a comparison of detached growth theory and experiment: the pressure head continuously decreases as the melt solidifies and the pressure varies along the height of the meniscus.
- Microgravity allows a larger value of the gap width.
  - On Earth, when the gap width becomes too large, gravity overcomes surface tension, a stable meniscus cannot be maintained, and the melt will flow down between the crystal and ampoule wall.
  - A large initial gap width will allow measurement of anisotropy in the growth angle.
- Microgravity enables a study of the dynamic stability of crystallization independent of thermal effects.

Why Study Germanium-Silicon Alloys?

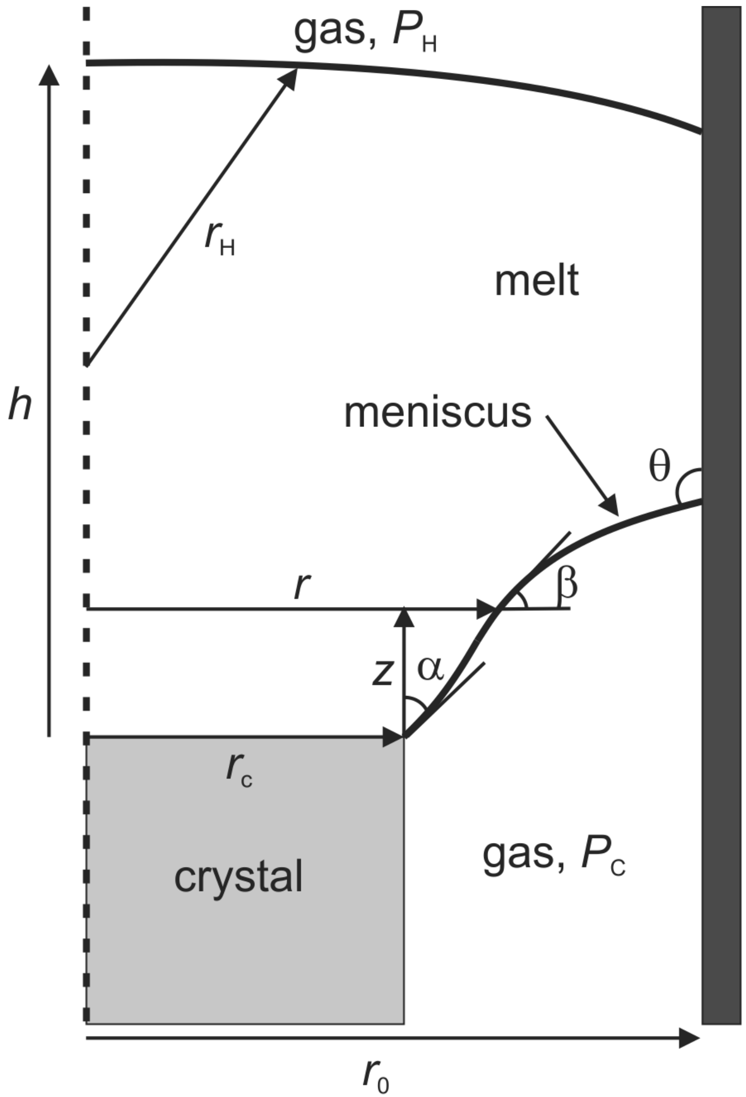
- Technological applications
  - X-ray and neutron optics (gradient crystals)
  - High-efficiency solar cell material
  - Thermoelectric converters
  - Increased carrier mobility compared to silicon, but can still be integrated into Si technology
- Characterization methods for silicon and germanium are well-established and are applicable to the alloy crystals.
- Relatively well known material properties and material parameters
- The vapor pressure of silicon and germanium melts can be neglected; they are non-toxic materials.

Technological Challenges of $Ge_{1-x}Si_x$

- Large separation of solidus and liquidus curves leads to strong segregation
- Lattice mismatch (4%) leads to increased stress, cracks, high dislocation densities, polycrystalline growth
- The reactivity of liquid silicon leads to a reaction with crucible materials (sticking) as well as contamination of the melt and the crystals



Schematic Diagram of Detached Solidification



M. P. Volz, K. Mazuruk, *Journal of Crystal Growth* 321 (2011) 29-35

Calculation of Meniscus Shapes

$$\frac{\frac{d^2z}{dr^2}}{\left(1+\left(\frac{dz}{dr}\right)^2\right)^{3/2}}+\frac{\frac{dz}{dr}}{r\left(1+\left(\frac{dz}{dr}\right)^2\right)^{1/2}}=\Delta P-Bz(r)$$

Young-Laplace Equation

$$\Delta P=\frac{\Delta P_m r_0}{\sigma},\quad \Delta P_m=P_H-P_C+\rho g h+2\frac{\sigma}{r_H}$$

ΔP : Dimensionless pressure differential across the meniscus

$$B=\frac{\rho g_0 r_0^2}{\sigma}$$

B = 3.248; Ge, r_0 = 6 mm

B = 4.651; InSb, r_0 = 5.5 mm

B : Bond number; ratio of gravity force to surface tension force

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$$\frac{\partial r}{\partial s}=\cos\beta,\quad \frac{\partial z}{\partial s}=\sin\beta,\quad \frac{\partial \beta}{\partial s}=-\frac{\sin\beta}{r}+\Delta P-Bz$$

Set of 3 coupled differential equations

Boundary Conditions

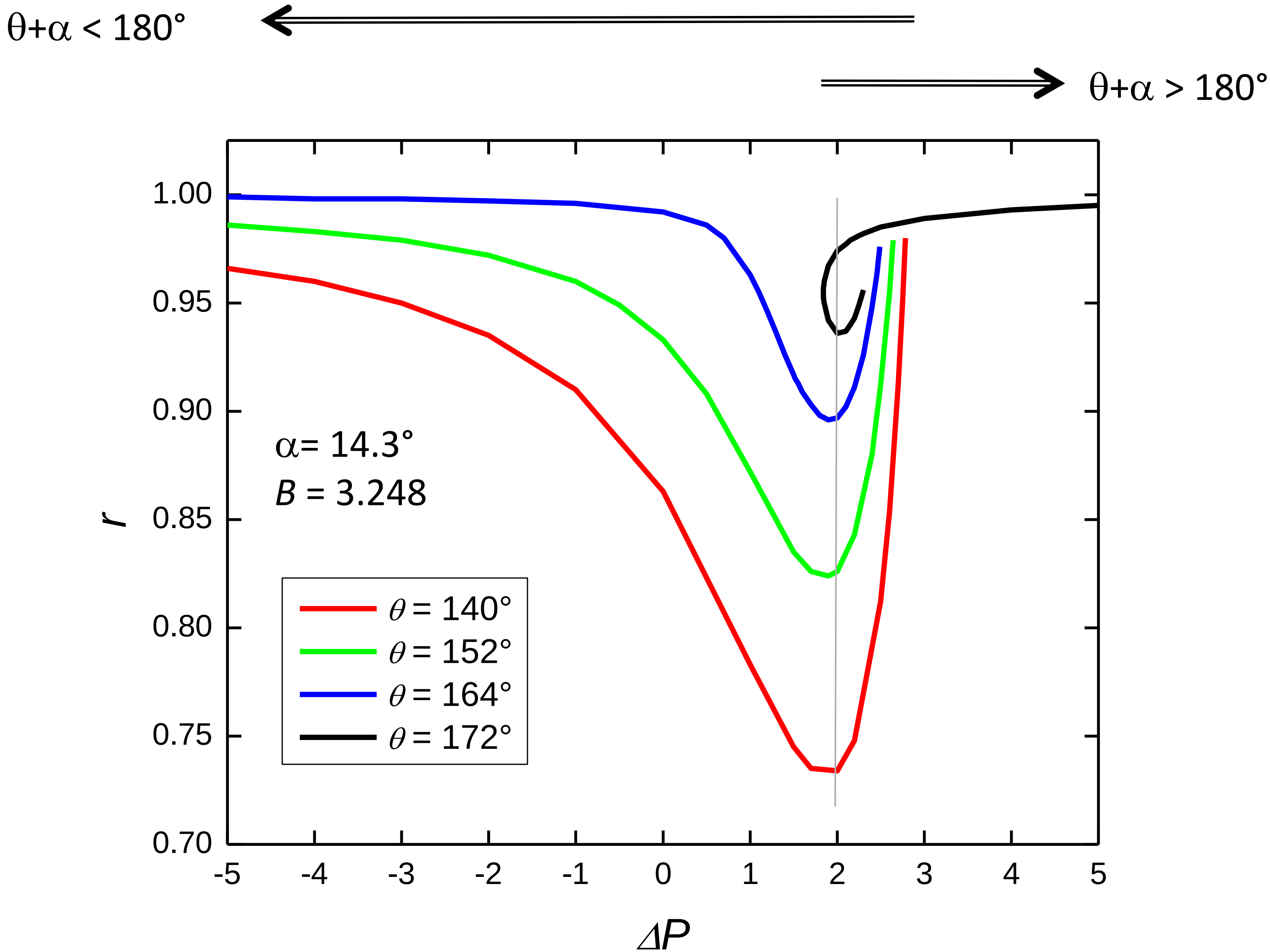
$z(0) = 0$; $\beta(0) = 90° - \alpha$;

$\beta(1) = \theta - 90°$; $r(1) = 1$

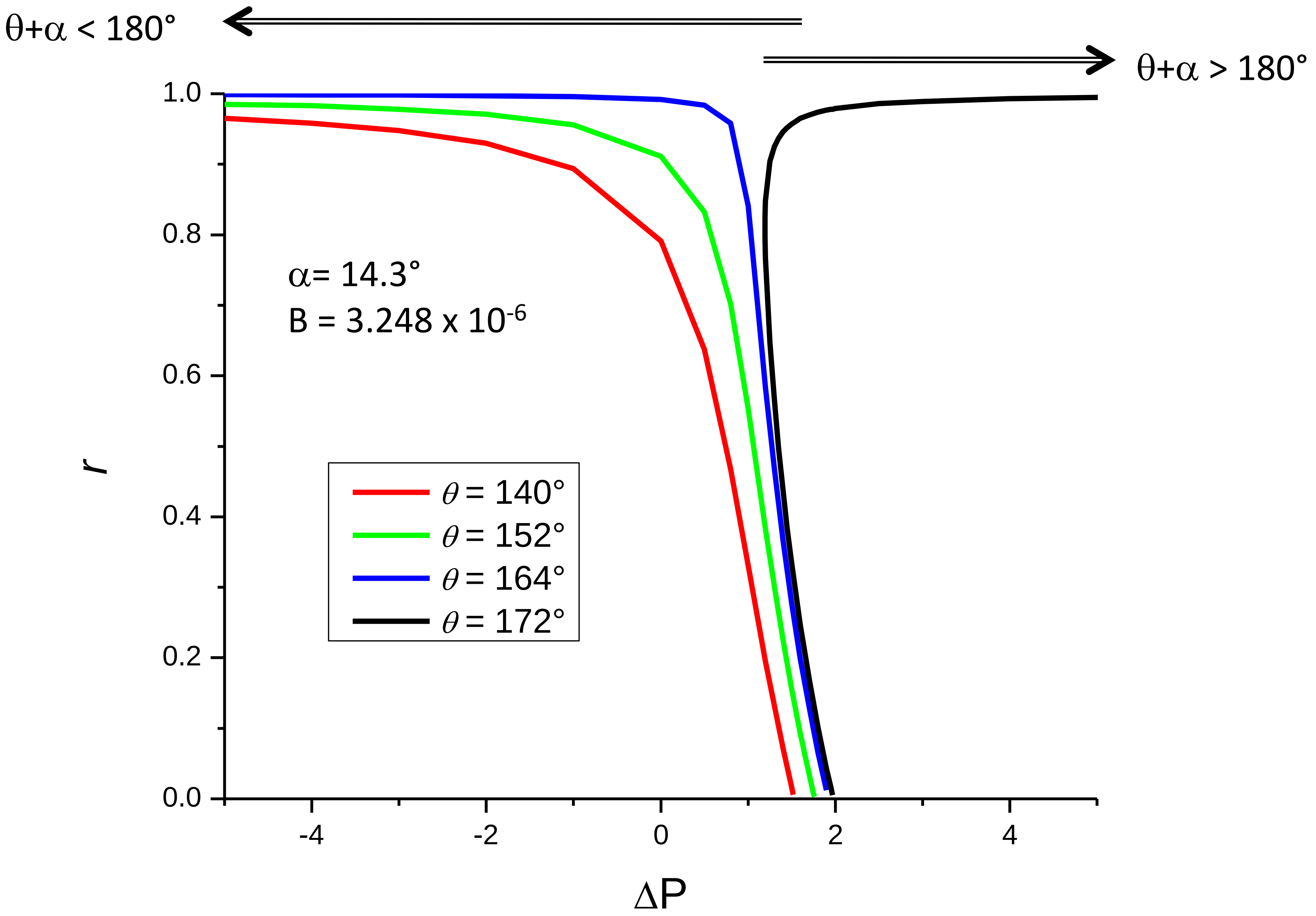
α: growth angle

θ: contact or wetting angle

Gap Width vs. Pressure Differential (Ge at 1*g*)



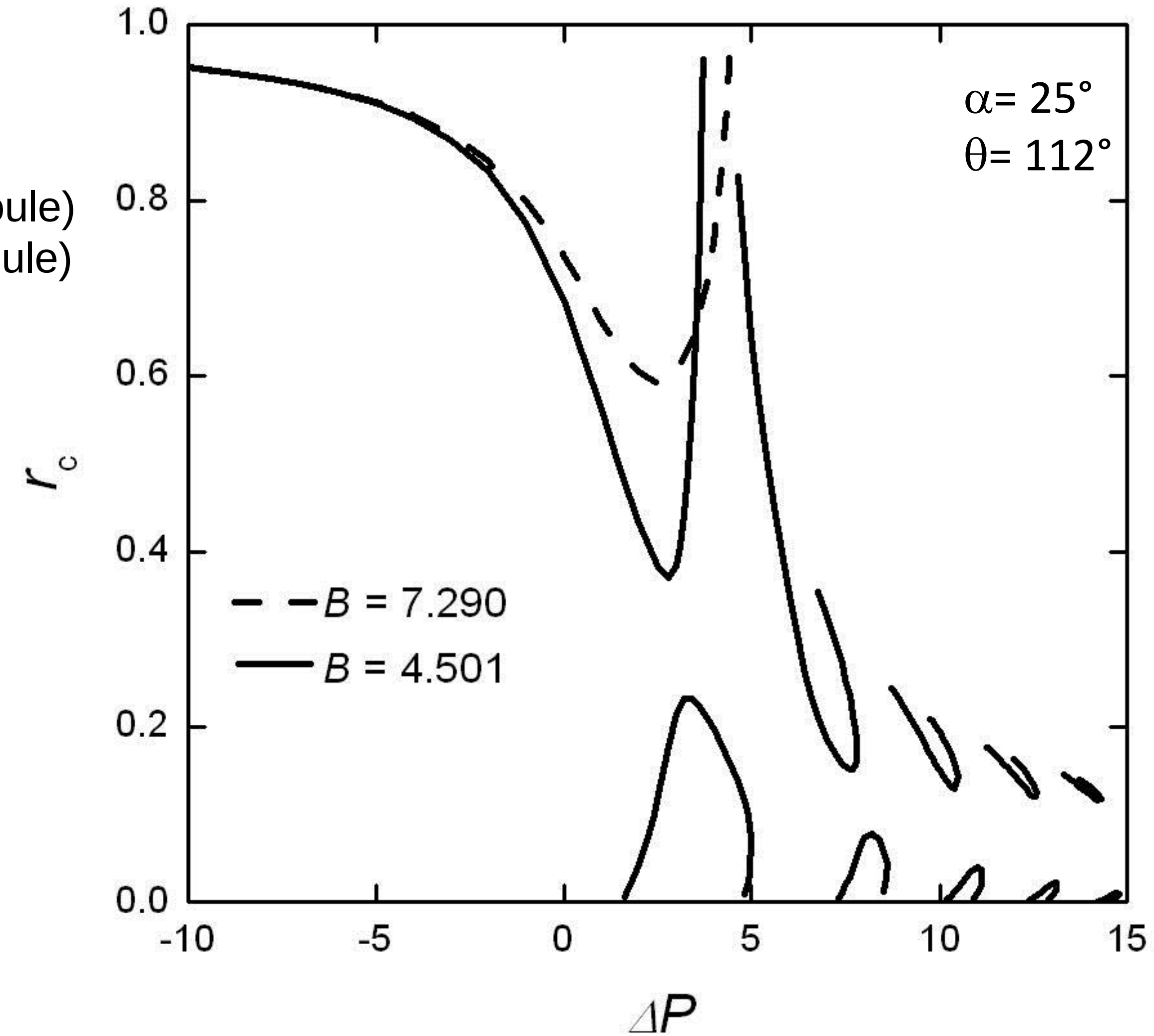
Gap Width vs. Pressure Differential (Ge at $10^{-6} \times g_0$)



Gap Width vs. Pressure Differential (InSb at 1*g*)

InSb at 1*g*

B = 7.209 (14 mm diam. ampoule)
B = 4.501 (11 mm diam. ampoule)



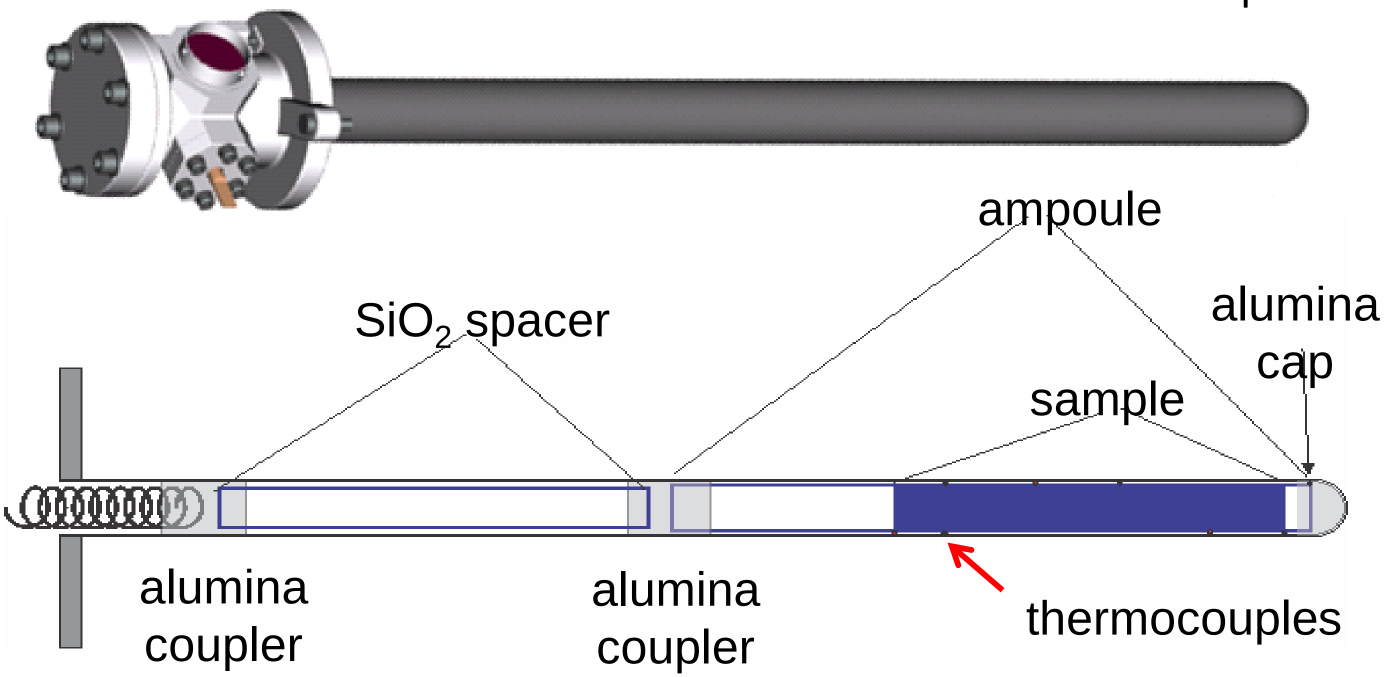
Equation nonlinearity creates isostates in the solution set

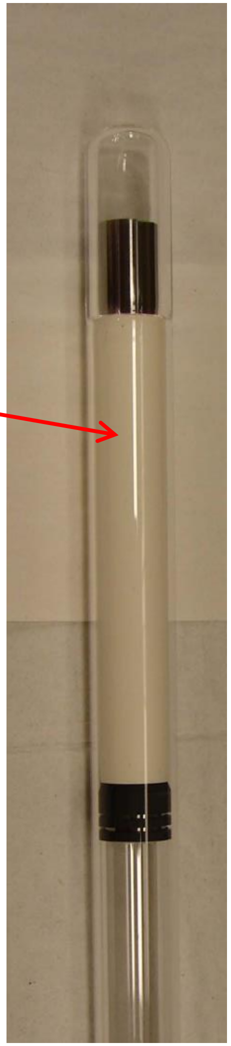
Flight Experiments

- A series of 10 GeSi and Ge:Ga samples will be processed on the ISS
- Processing parameters will be varied to asses their affect on detachment
  - Sample Material (GeSi, Ge:Ga)
    - ➢ Affects the growth angle
    - ➢ Comparison of semiconductor alloy and doped element
  - Inner Ampoule surface material (SiO_2, boron nitride)
    - ➢ Affects the contact angle
  - Pressure: positive, negative, or zero (vacuum) gas pressure below the meniscus

Ampoule and Cartridge Layout

- A $Ge_{1-x}Si_x$ ingot is placed inside a pyrolitic boron nitride (pBN) tube and sealed in a SiO_2 ampoule.
- The ampoule is placed inside a cartridge which is inserted into the furnace.
- Thermocouples in the cartridge provide for real-time monitoring of the thermal profile





Summary

- Crystals grown by the detached Bridgman method have greatly increased crystalline perfection, motivating a systematic study of the phenomenon
- A theory describing the conditions for detachment has been developed
- Only crystals where $\alpha + \theta > 180°$ are expected to achieve stable detached growth in microgravity
- Reproducible detached growth has been achieved in the laboratory under limited conditions
- Microgravity will allow the study of detachment over a range of parameters not possible to achieve on Earth
- A series of Ge and GeSi crystal growth experiments are being developed for processing on the ISS

Contributing Personnel

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