Crystal Growth in the SUBSA furnace at the International Space Station (ISS)

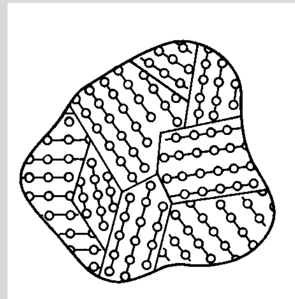
A.G. Ostrogorsky, Illinois Institute of Technology, Chicago, IL
Martin Volz, , NASA MSFC EM31, Huntsville, AL35812
Arne Croell , University of Alabama, Huntsville, AL35812

1. Introduction: Why Single Crystals ? Growth techniques.
2. *Melt flow, heat and* mass transfer
3. Using the baffle on Earth and at the IS.
4. What have we learned ? Future experiments at ISS

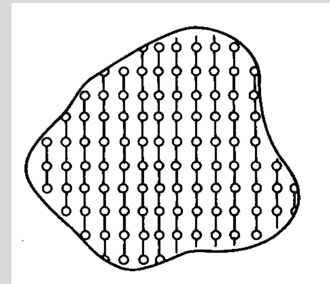
7th Annual International Conference on Mechanical Engineering, 17-20 July 2023, Athens, Greece

Why Single Crystals ?

Features:
- Uniform on micro-scale
- Beauty, rarity



Poly



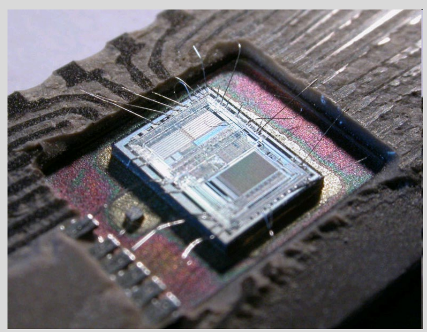
Single

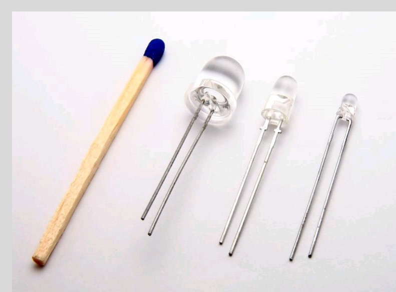
Research :
- metals,
- semiconductors,
- superconductors,
- protein crystals..

Applications:

electronic/opto-electronic devices

VLSI, LED, lasers, ..
electromechanical transducers…
detectors

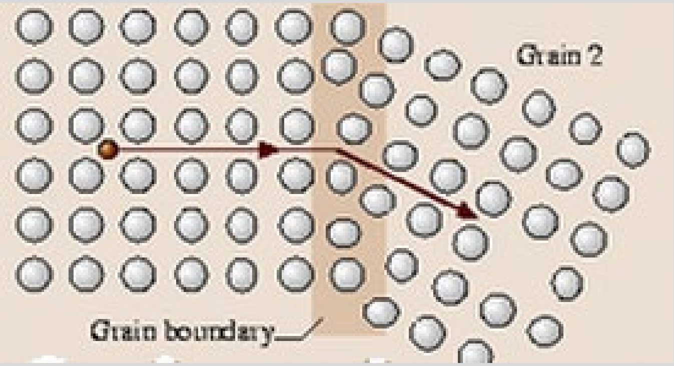


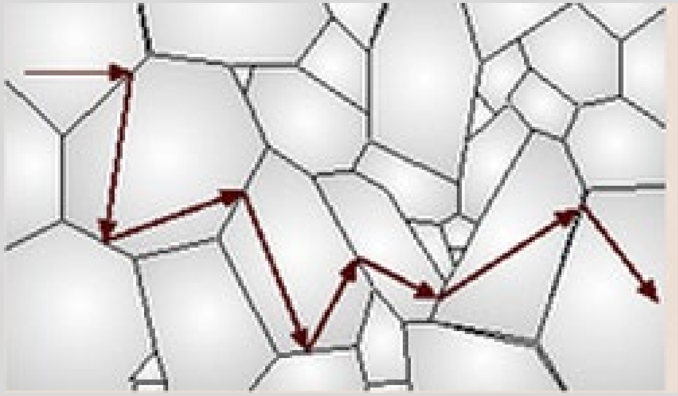


Rolls-Royce, single-crystal, nickel-superalloy

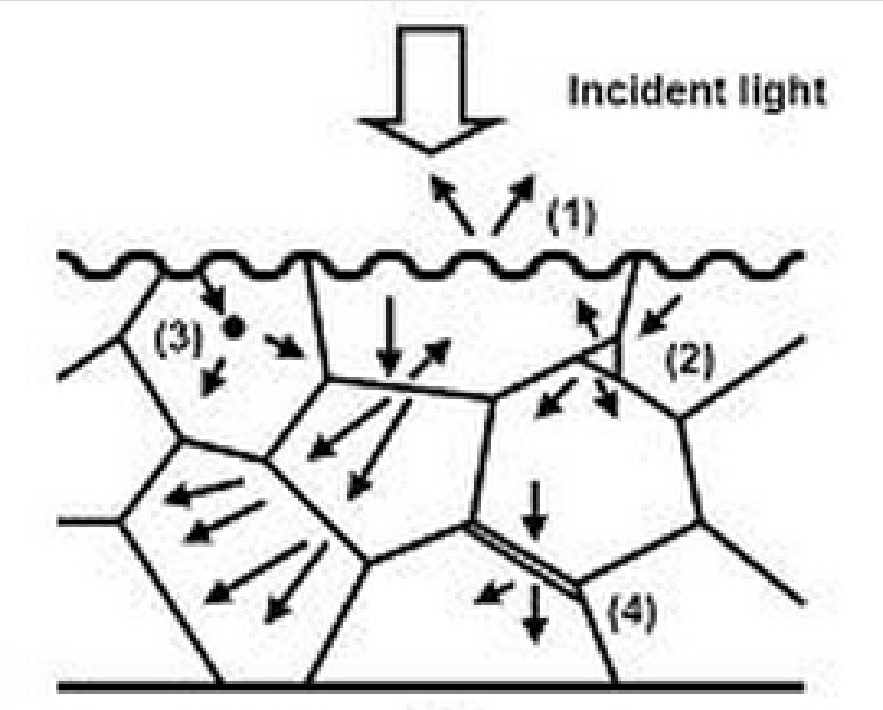
HPGe

Scattering of electrons and light



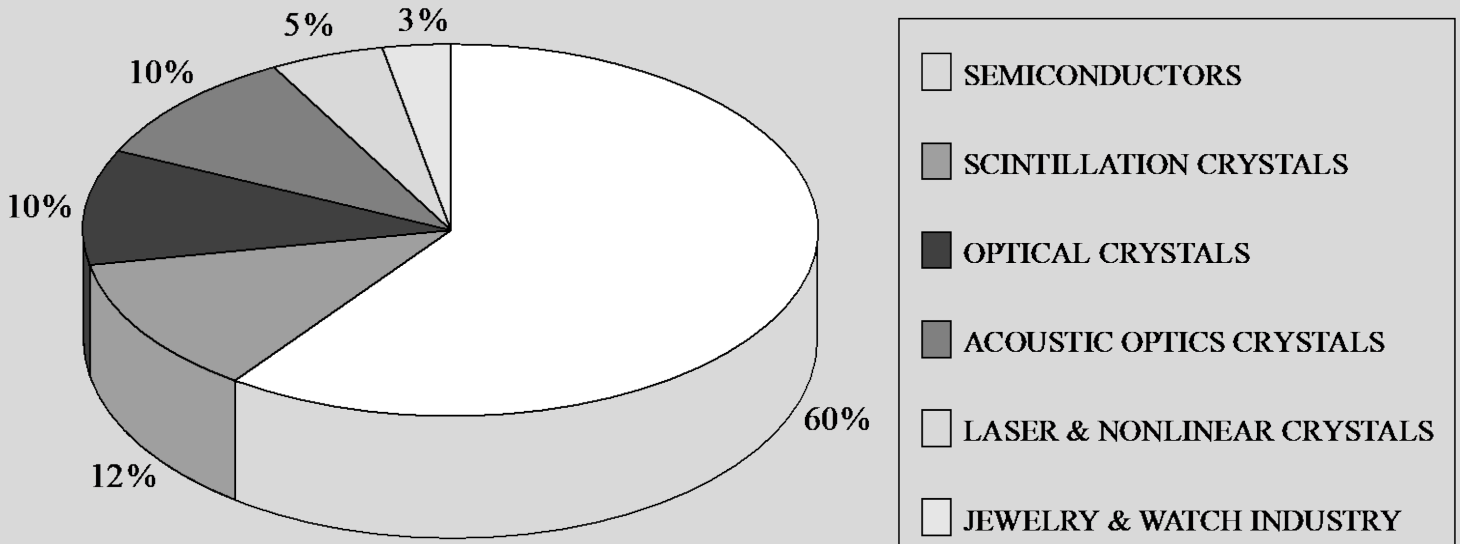


- grain boundaries



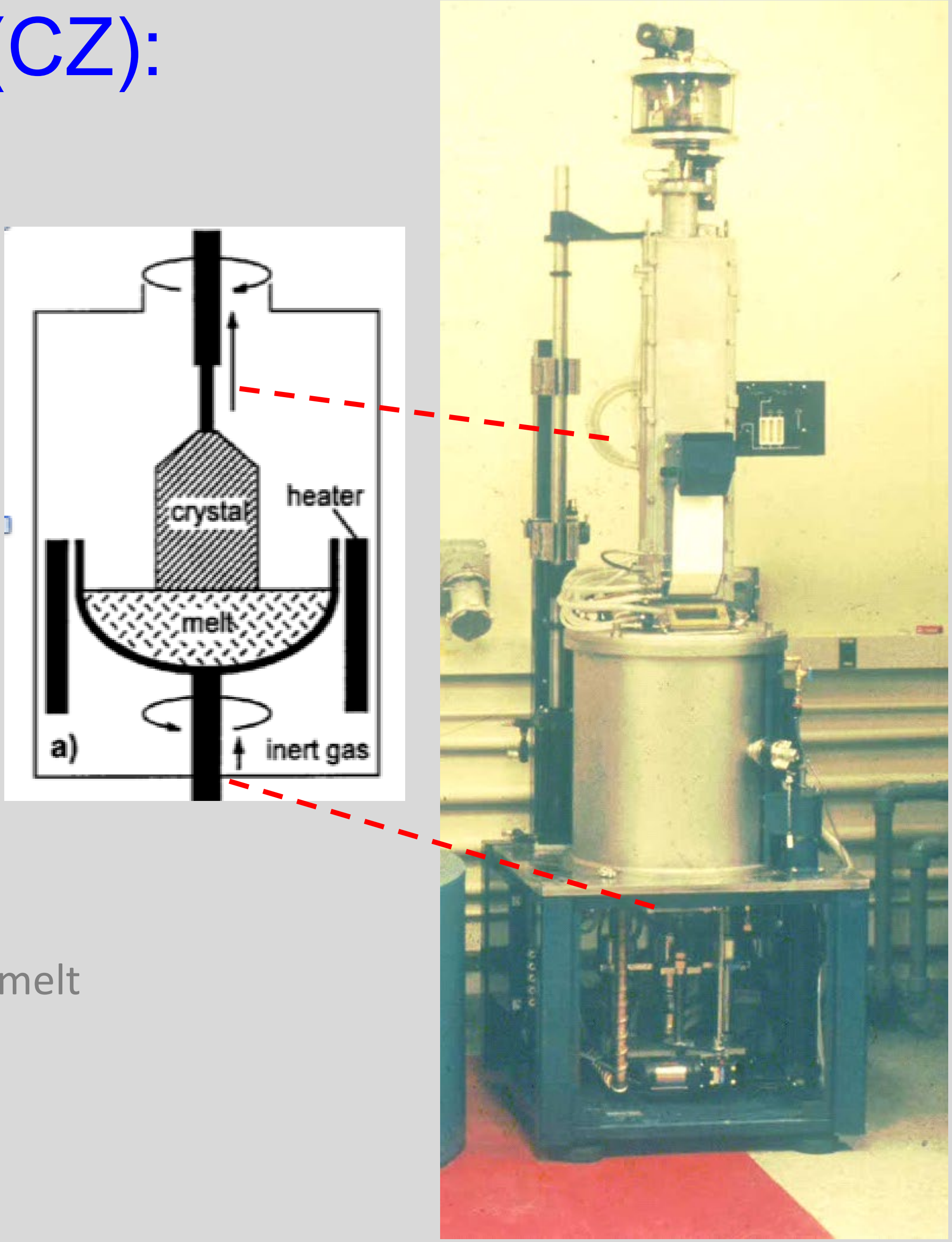
Defects/impurities:
1. Diffuse scattering
2. Pores,
3. Precipitates, etc.

Single Crystals-World Production: 20,000 tons/year



- ~60% are semiconductors silicon, GaAs, InP used for:
- **Electronics**
- **Optoelectronic** devices: emit, detect and control light (includes gamma rays, X-rays, ultraviolet and infrared

Czochralski Method (CZ):



1.Charge is melted

2. Seed is dipped into the melt

3. Crystal grows as atoms from the melt adhere themselves to the seed.

Governing Equations for fluid flow, heat and mass transfer

FM
$$\begin{cases} \nabla \cdot \vec{V} = 0 \\ \dfrac{\partial \vec{V}}{\partial t} + \left(\vec{V} \cdot \nabla\right)\vec{V} = -\nabla p + \nabla^2 \vec{V} + Gr\left(T_0 - T\right)\vec{i}_g \end{cases}$$

$$\mathrm{Re} = \frac{V\,L}{\nu}$$

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

Heat
$$\frac{\partial T}{\partial t} + \left(\vec{V} \cdot \nabla\right)T = \frac{1}{\mathrm{Pr}}\nabla^2 T$$

Mass
$$\frac{\partial C}{\partial t} + \left(\vec{V} \cdot \nabla\right)C = \frac{1}{Sc}\nabla^2 C$$

$$\frac{Gr}{Re^2} \sim \frac{\text{strength of natural convective flow}}{\text{strength of forced convective flow}}$$

Natural convection (NC) is:

1. *dominating*, *for* $\sqrt{Gr} >> Re$ — Bridgman
2. *significant*, *for* $\sqrt{Gr} \sim Re$ — CZ
3. *negligible*, *for* $\sqrt{Gr} << Re$ — Ideal (?)

Options to control melt flow:

a) Reduce natural convection:

- Magnetic fields
- Reduced gravity (μg)
- Use a **baffle** in the melt

b) Impose forced convection

- Crystal/crucible rotation (CZ)
- Accelerated Crucible Rotation
- Coupled Vibrational Stirring
- Traveling Magnetic Fields

MIT, 1986

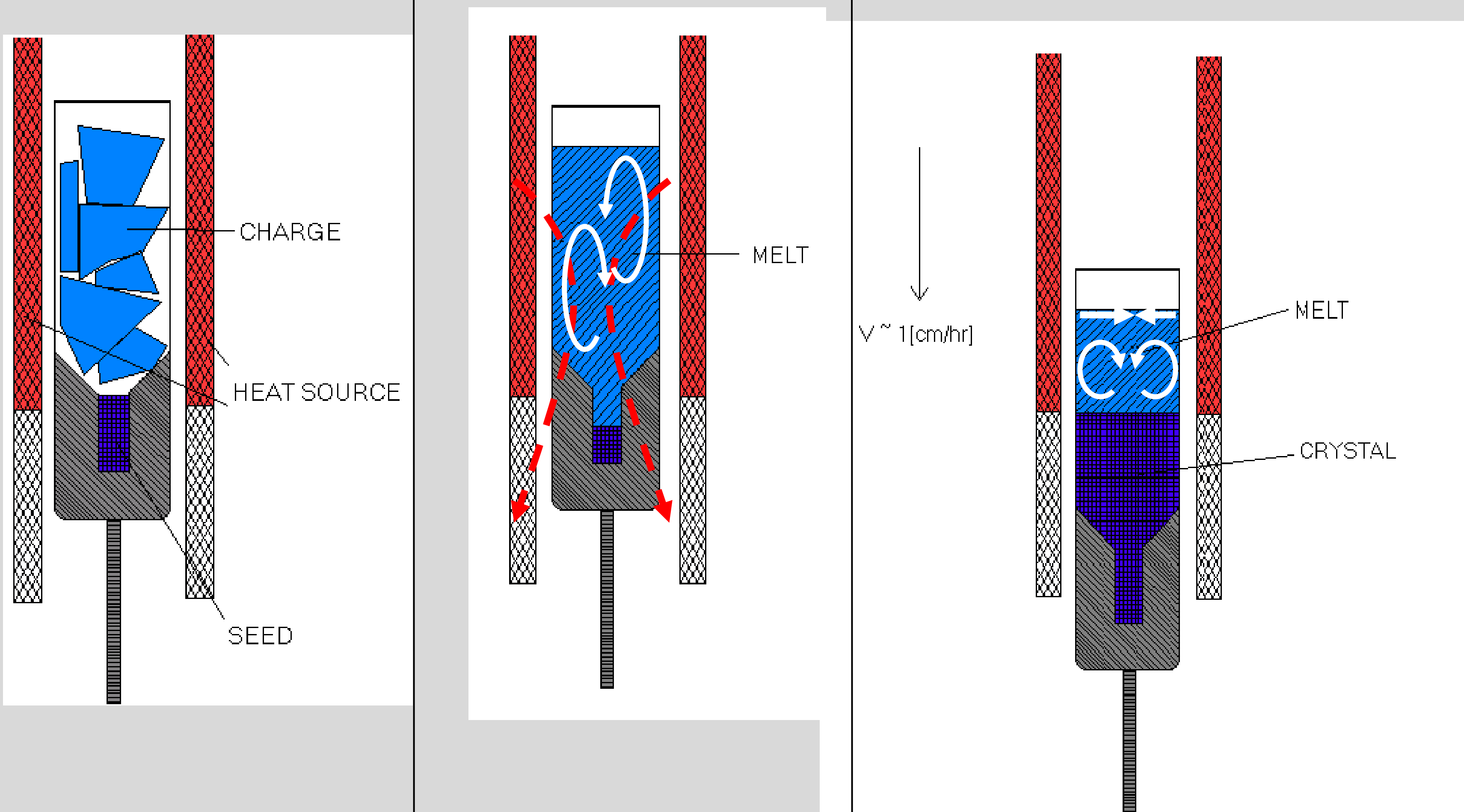
Directional solidification (Bridgman)

1. Melting,
2. Seeding

4. Growth: Interface is advanced by moving the container or the gradient

HOT

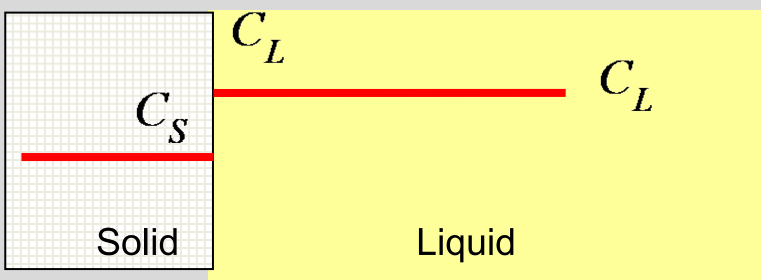
COLD



2 Distribution of impurities in the crystal

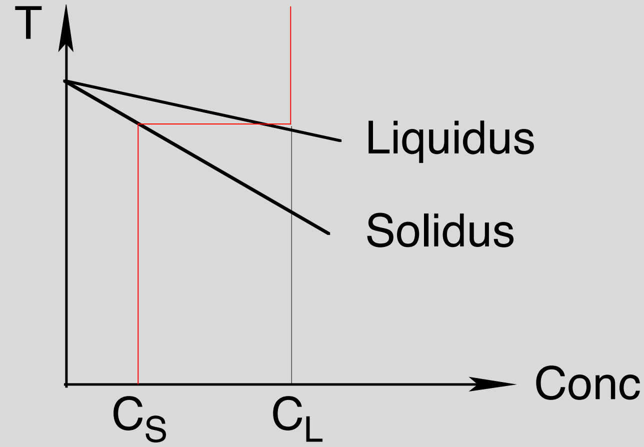
Solute partitioning at the S/L Interface

Equilibrium



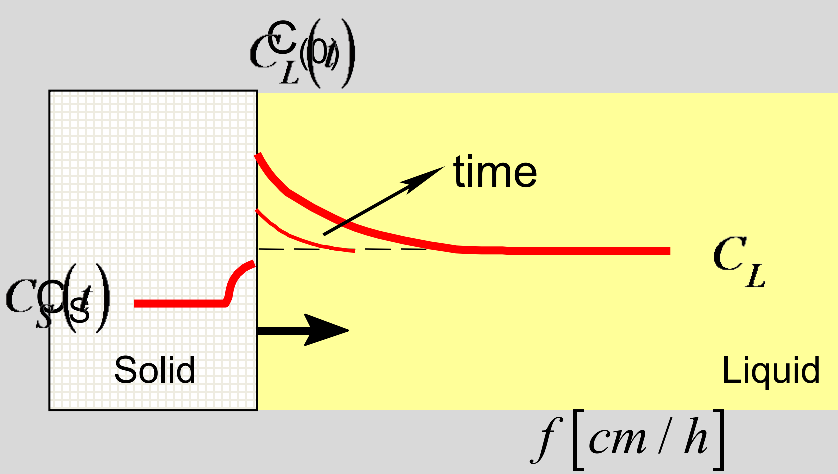
Solid

$$\frac{C_S}{C_L} = k_0$$

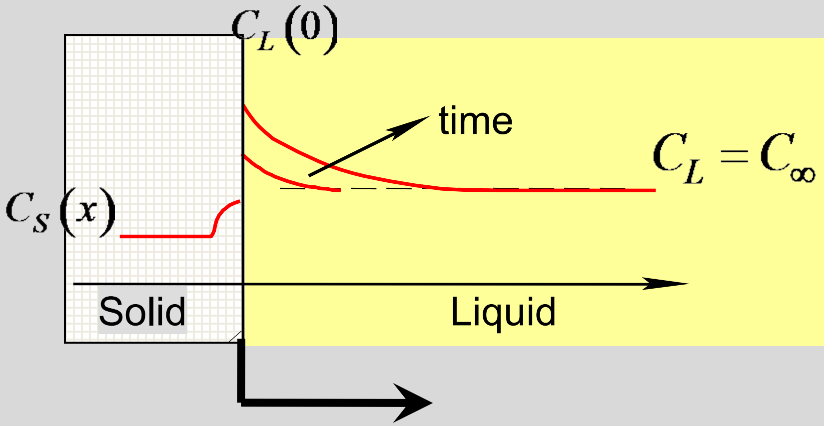


k_0 is a fundamental property; it appears in equations involving redistribution of the solute.

Beginning of motion



OPTION I: *"Ideal Diffusion-Controlled Solidification"* ***(g=0)***

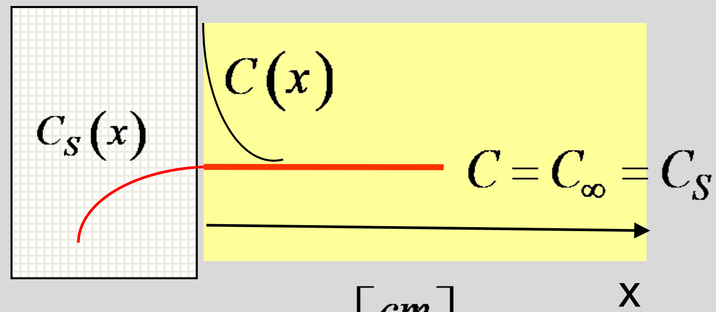


$$f\left[\frac{cm}{hr}\right] = const. = 5\,mm/h$$

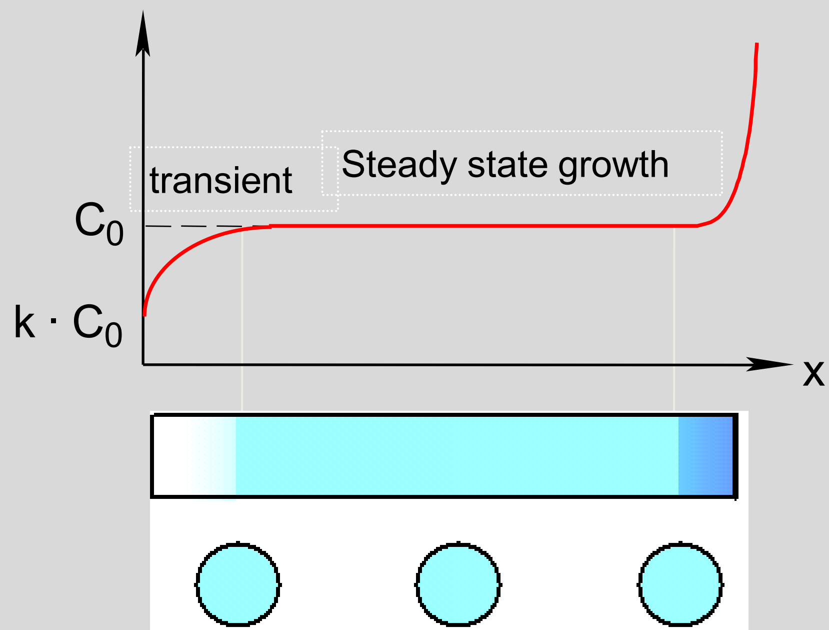
$$Gr = \frac{g\beta\Delta T L^3}{\nu^2} = \left(\frac{\beta}{\nu^2}\right)\left(g\Delta T L^3\right)$$

$$g \to 0$$

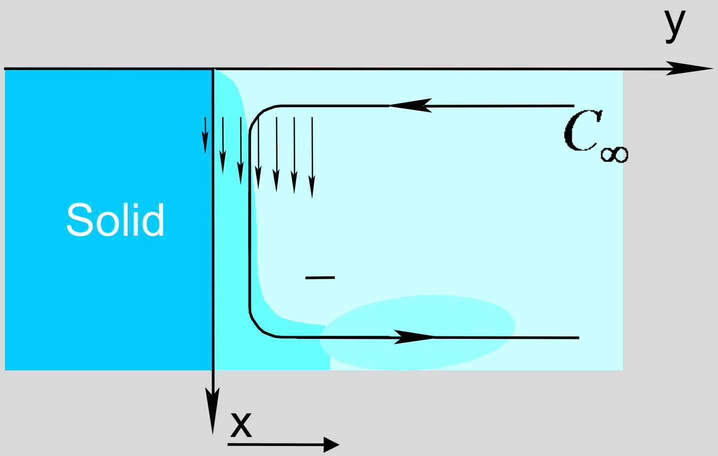
Steady-state



$$f\left[\frac{cm}{hr}\right] = const.$$

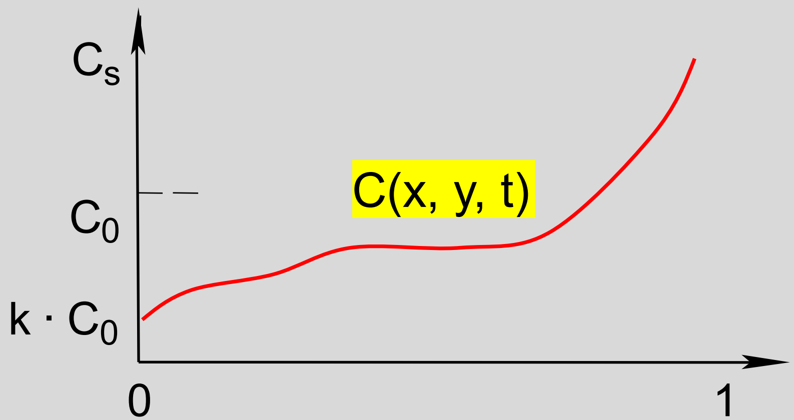


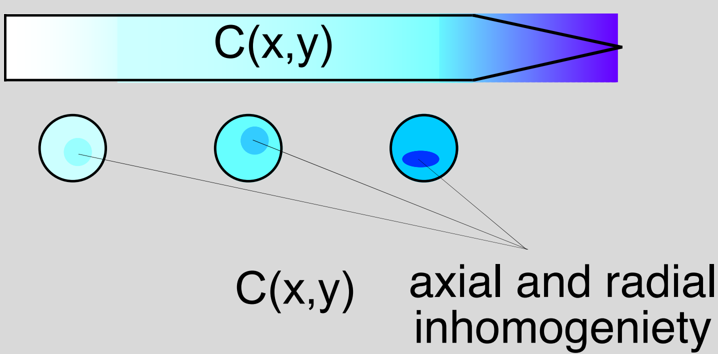
OPTION II: *On Earth flow-controlled T and C in the melt*



V(t), T(t), C(t)

no steady state





Continuity

$$\nabla \cdot \vec{V} = 0$$

N-S

$$\frac{\partial \vec{V}}{\partial t} + \left(\vec{V} \cdot \nabla\right)\vec{V} = -\frac{1}{\rho}\nabla p + \nu \nabla^2 \vec{V} + \frac{\vec{F}}{\rho}$$

Energy

$$\frac{\partial T}{\partial t} + \left(\vec{V} \cdot \nabla\right) T = \alpha \nabla^2 T$$

Species

$$\frac{\partial C}{\partial t} + \left(\vec{V} \cdot \nabla\right) C = D \nabla^2 C$$

Melt flow is unavoidable

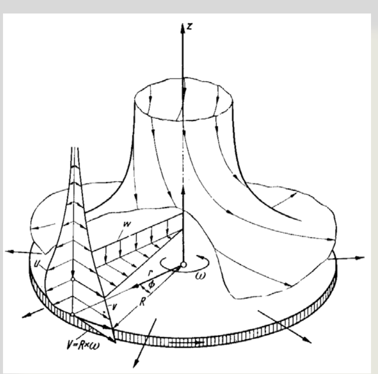
OPTION III: *Perfect mixing (i.e. homogeneous melt)*

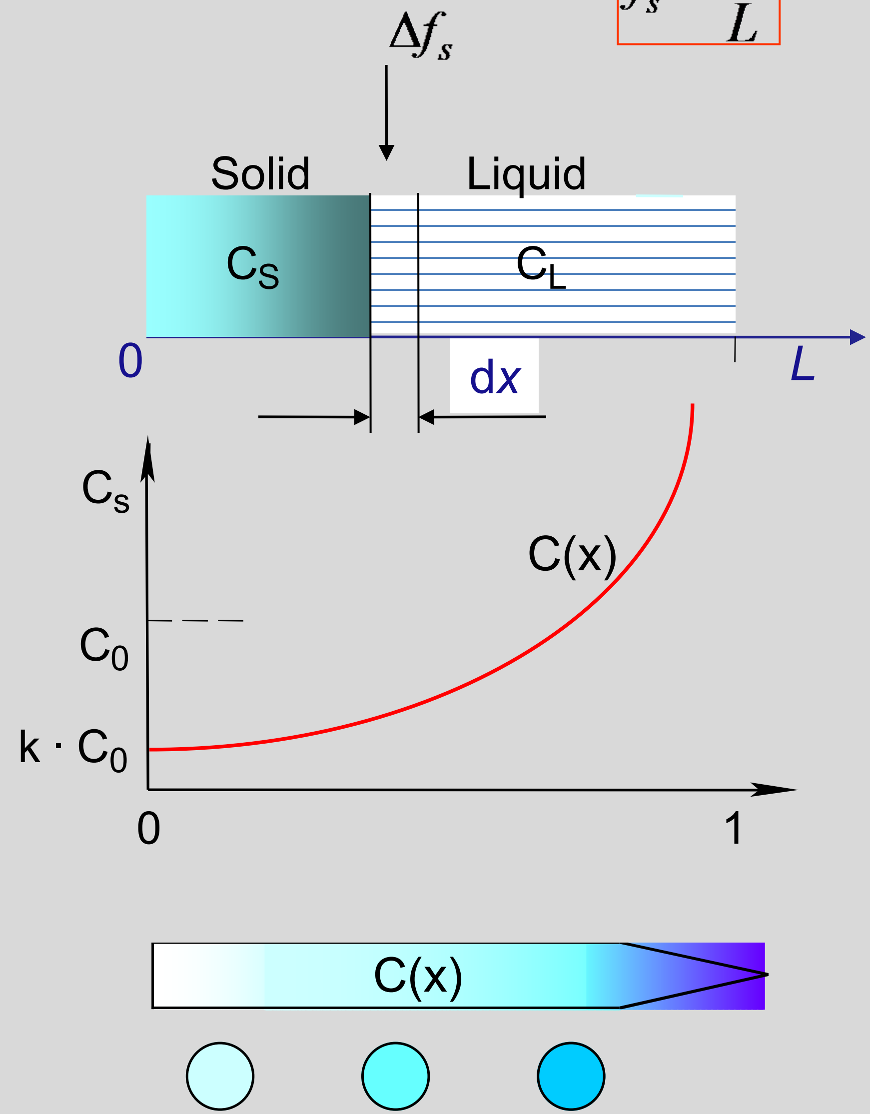
$$f_s \equiv \frac{x}{L}.$$

G. Gulliver (1921) and E. Scheil (1942) assumed:

- homogeneous melt
- No diffusion in solid
- Local equilibrium at S/L interface

$$C_S(x) = C_0 \cdot k\left(1 - \frac{x}{L}\right)^{(k-1)}$$





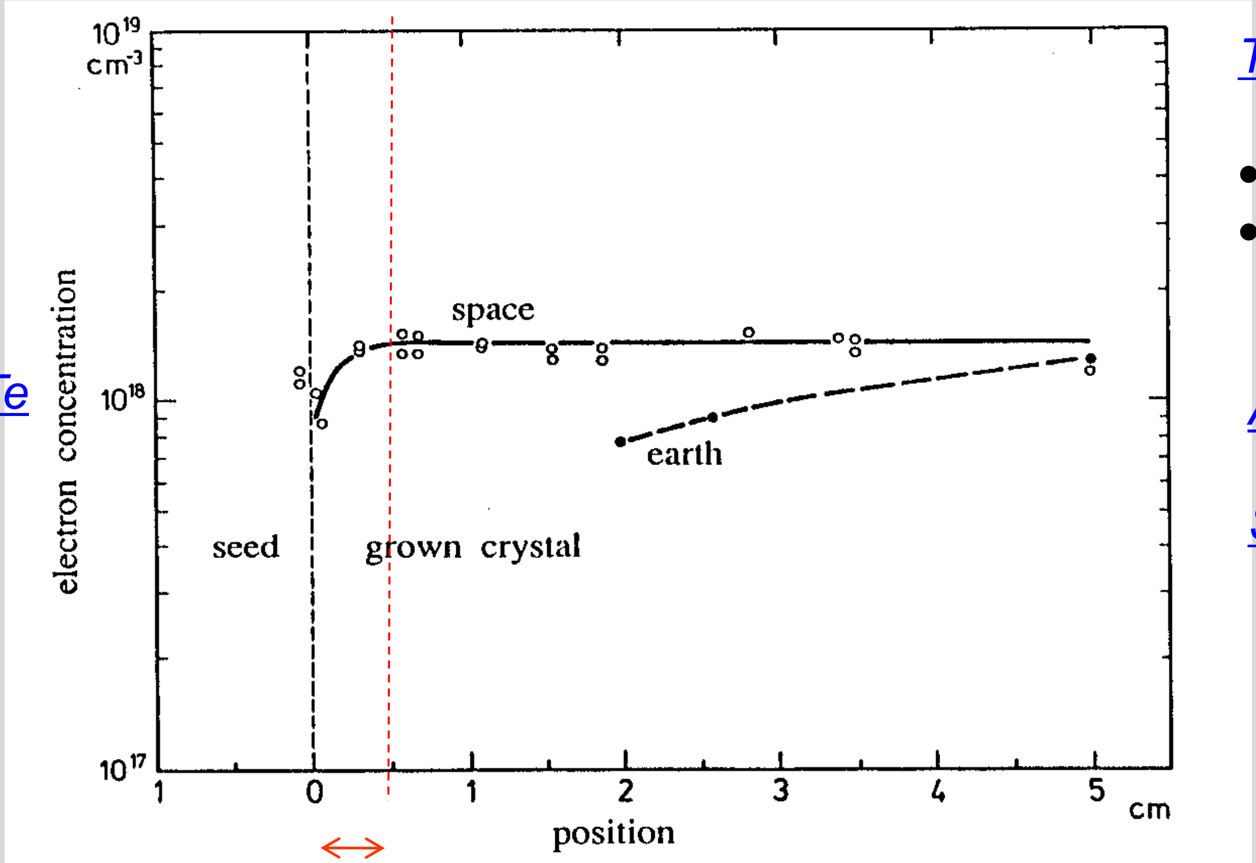
Axial inhomogeneity, C(x)

Witt et al. 1975, Skylab III Mission in near-earth orbit

"ideal, diffusion controlled steady state-segregation, never accomplished on earth, was achieved …" .

A.F. Witt et. Al., J. Electrochem. Soc.122 (1975) 276.

Te



L transient

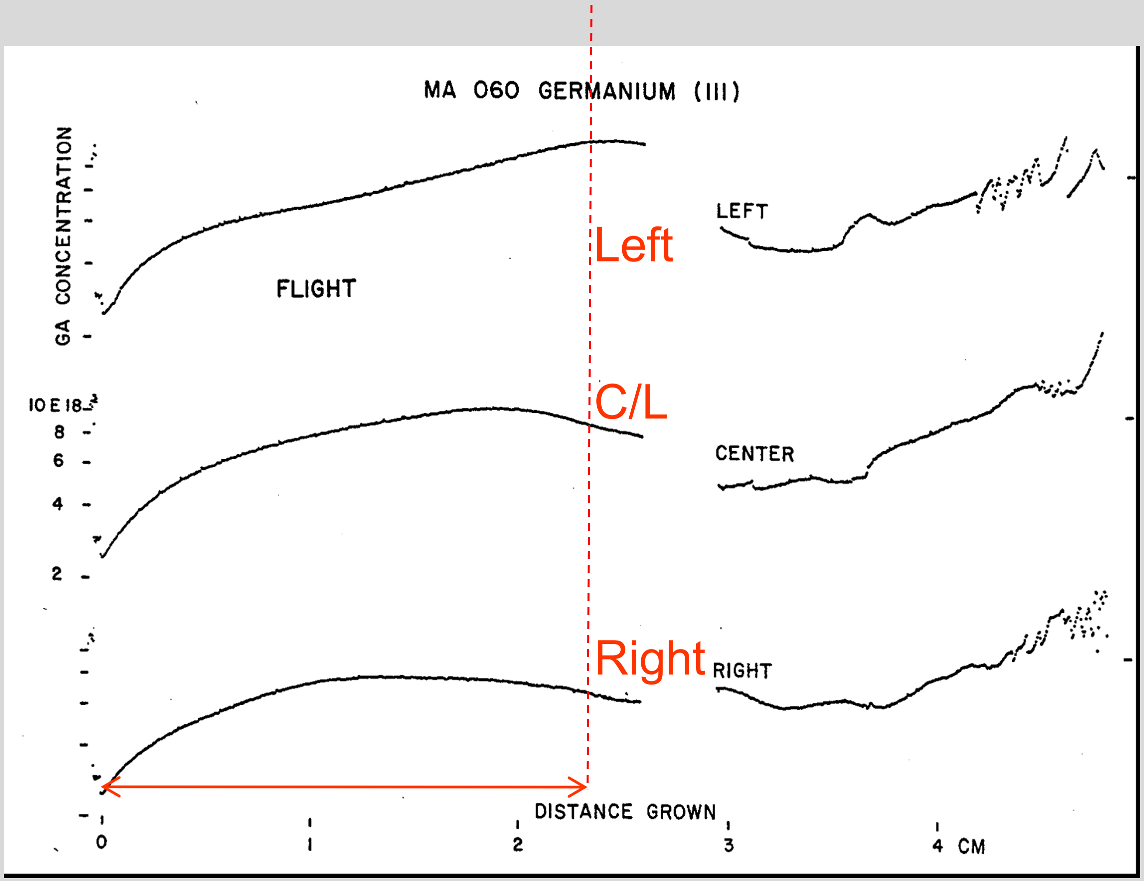
Te-doped InSb (k_0 =0.5)

- Initial transient 0.5 cm
- Steady state

ALI

Sn doped InSb (k_0~0.01)

Apollo-Soyuz 1978, Witt et al.: Ga-doped Ge (k=0.087)



"Existing gap between theory and experiment ….is largely attributed to gravity-induced convection effects.."

- k_0~0.087;
- 3 cm/h
- Initial transient ~3 cm
- no Steady state

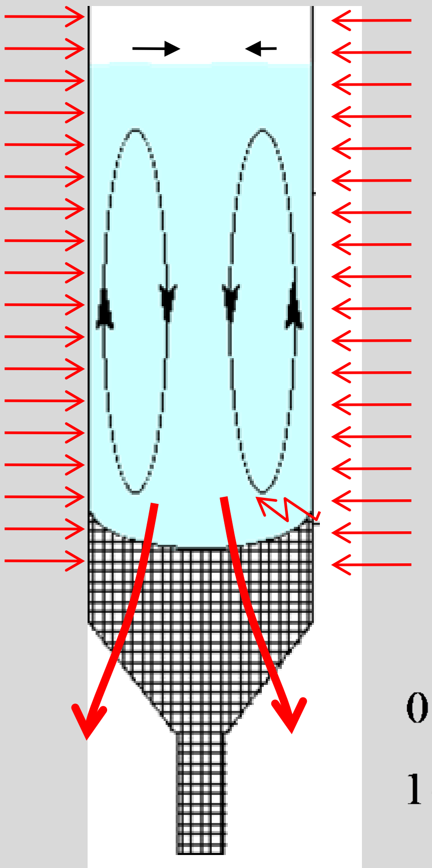
$L_{transient}$~ 3 cm

$$Gr = \frac{g\beta\Delta T\ L^3}{\nu^2}; \quad g \sim 10^{-4} g_0$$

3. Using the baffle on Earth and ISS (SUBSA investigations).

Crystal Growth using a Baffle in Bridgman furnace (1990-)

A.G. Ostrogorsky,
US Patent #5,047,113, (1991)
J. Crystal Growth 104, (1990), 233-238.
J. Crystal Growth 110, (1990) 950-954

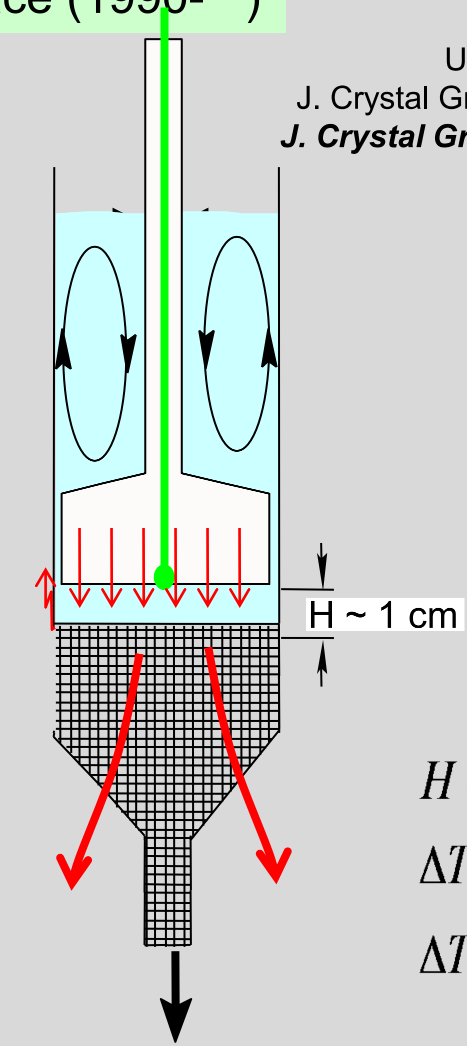


$T(t)$

Convex interface

$0 < H(t) < 10\ cm$

$1 < \Delta T(t) < 10\ C$



$H \sim 1\ cm \sim const.$

$\Delta T_{radial} < 1\ C$

$\Delta T_{axial} \sim 20\ C \sim const.$

$$Gr = \frac{g \cdot \beta \cdot \Delta T \cdot H^3}{\nu^2} \sim g \cdot \Delta T \cdot H^3$$

$\Delta T_{radial} \sim 10\times\ reduced$

$H^3 \sim 1000\times\ reduced$

Ga-doped Ge, **k=0.087**

Bridgman

$10^{-5} g_0$

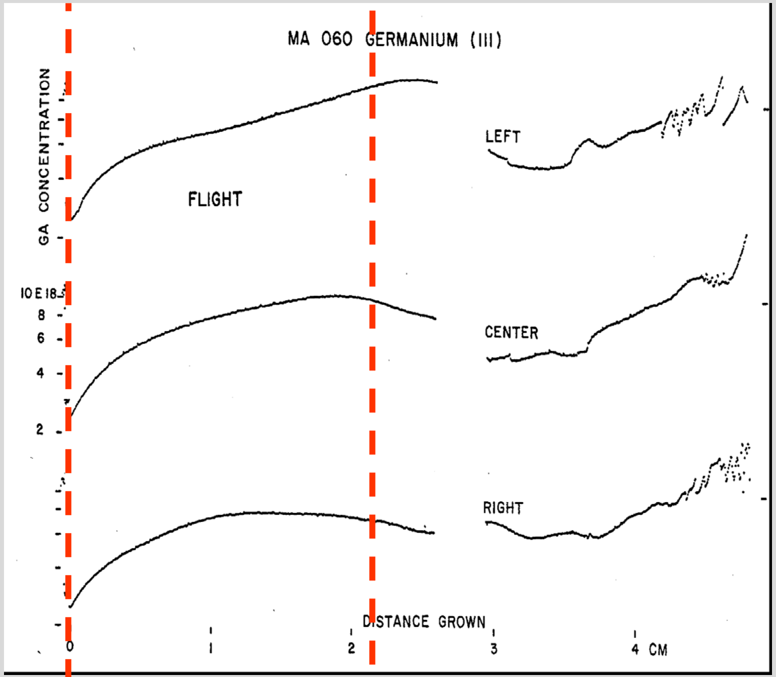
Apollo-Soyuz 1978

Witt et al.

Ge:Ga;

V_R=30mm/h

D=1.7 x10^{-4} cm^2/s



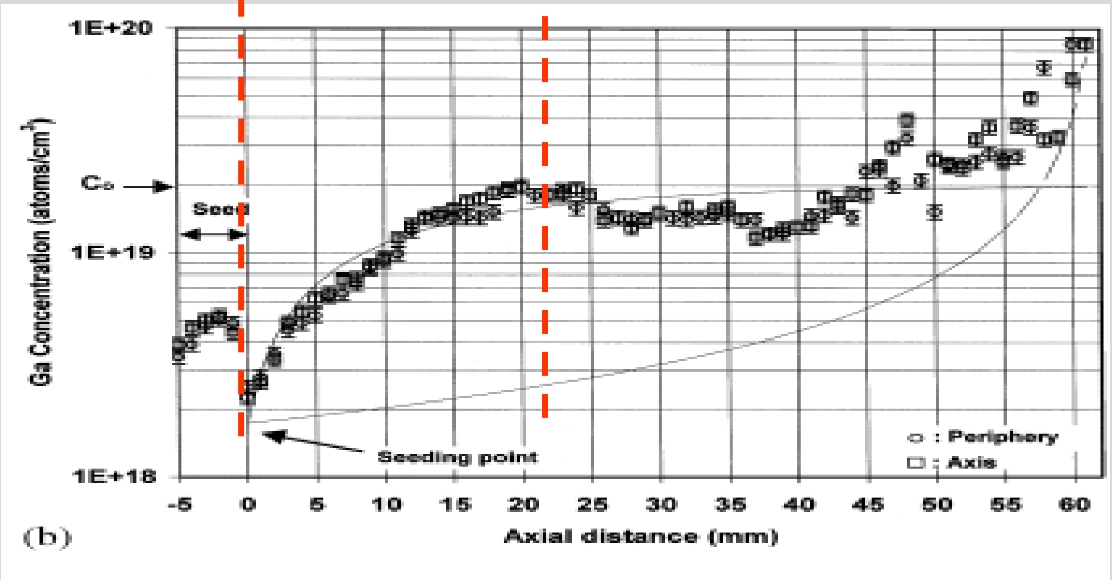
Bridgman (baffle)

g_0

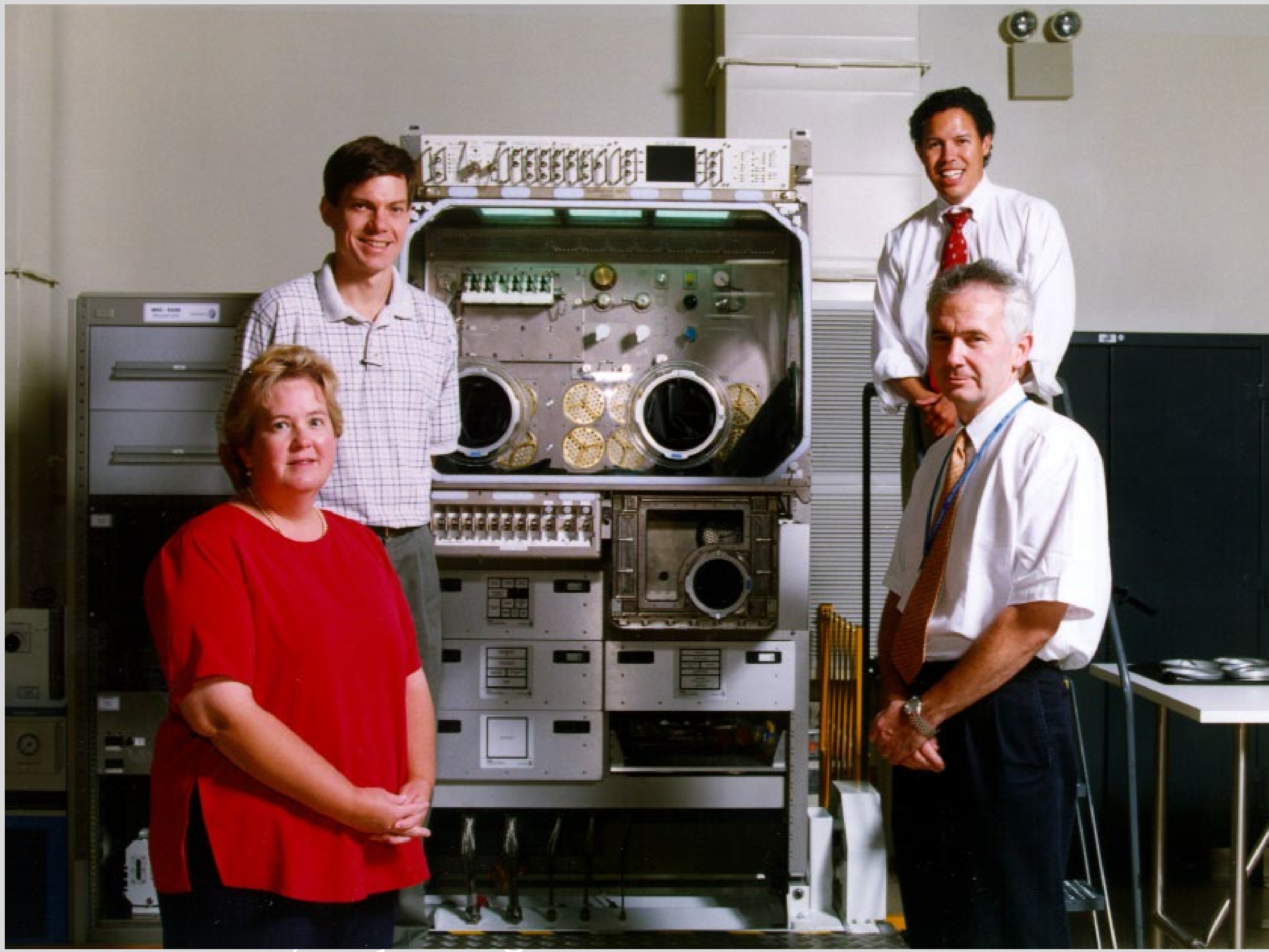
Dutta and Ostrogorsky, ***J. Crystal Growth 217*** (2000) 360-365.

V_R=30mm/h

Grown with the baffle at 1 g_0

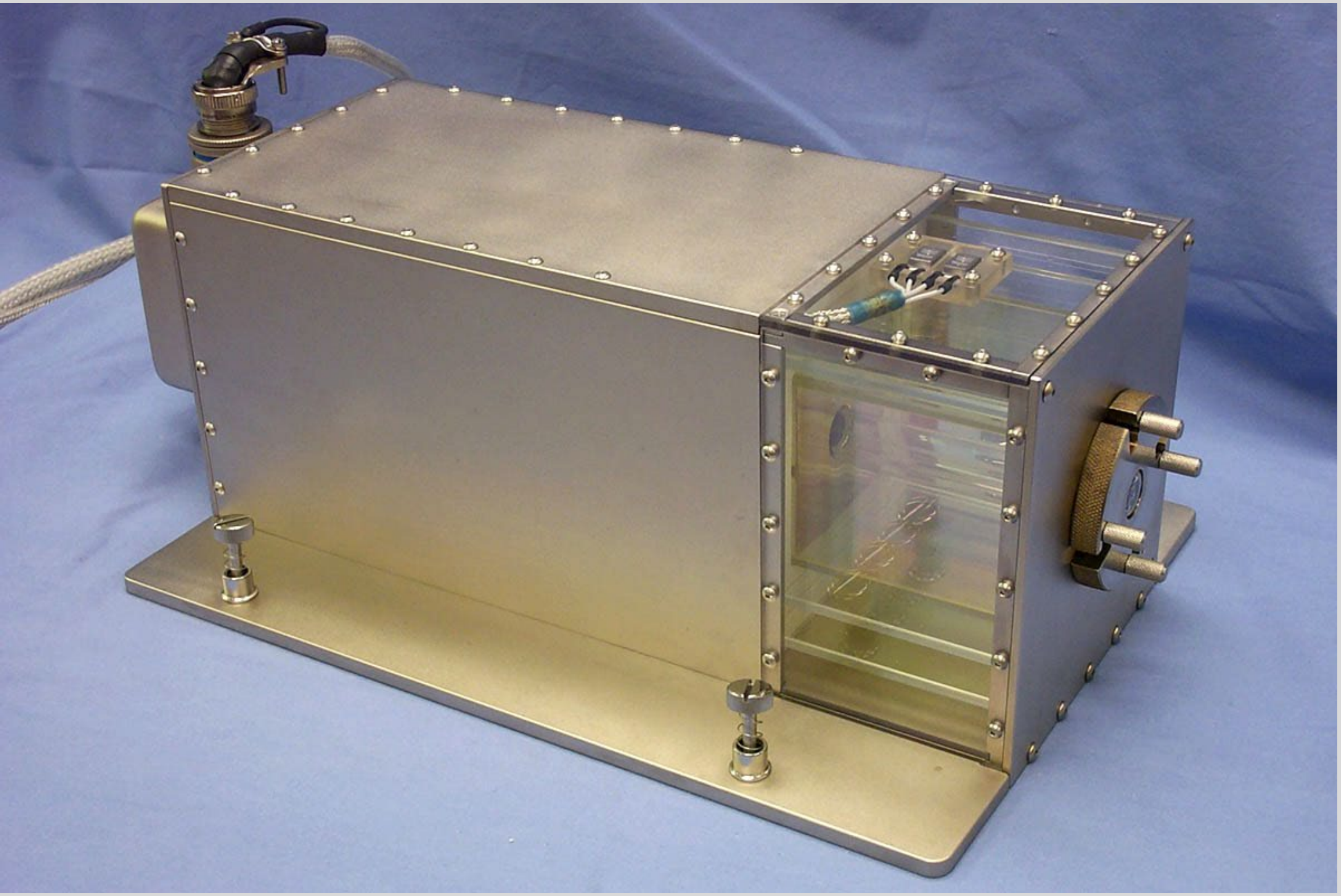


1. SUBSA 1: Solidification Using a **Baffle** in Sealed Ampoules **(InSb)**	1993-2004
2. Detached Melt and Vapor Growth of InI in **SUBSA** Hardware **(InI)**	2016-present
3. Diffusion Coefficients of Dopants in molten **Ge** and **Si**	2020-2025



- A.G. Ostrogorsky, PI, Rensselaer Polytechnic Institute (RPI)

SUBSA Hardware

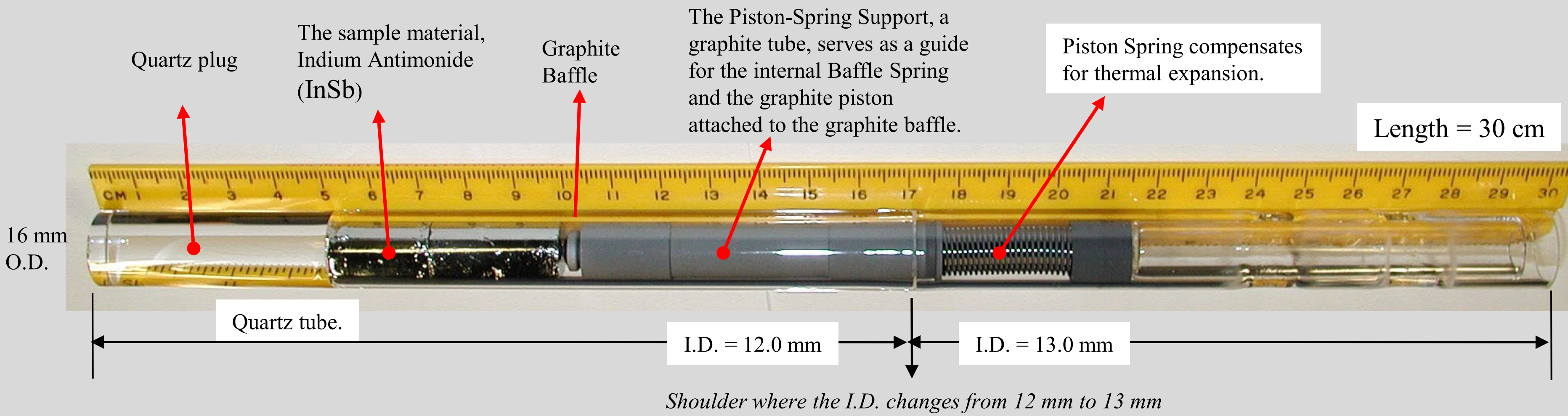


1 DaqPad

1 Process Control Module

It's a Boy !
Born May 8, 2001 at 10:35 p.m.
Weight: 14 lbs, 9 oz; Length: 15 inches

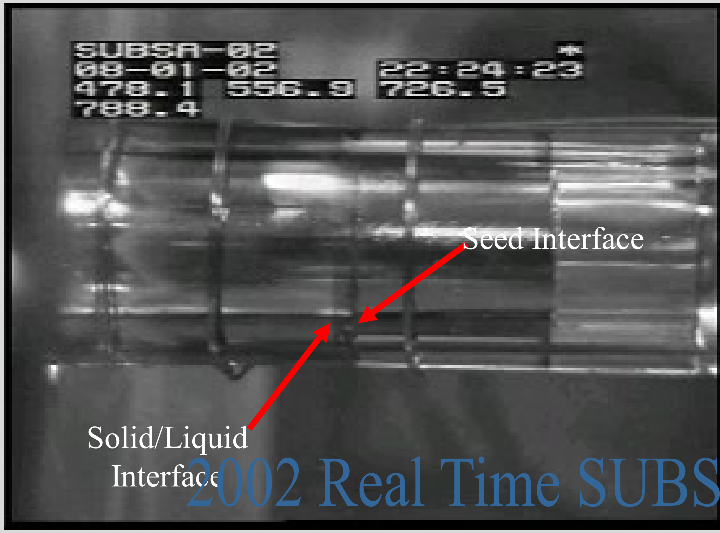
SUBSA Sample Ampoule (Baffle Assembly)

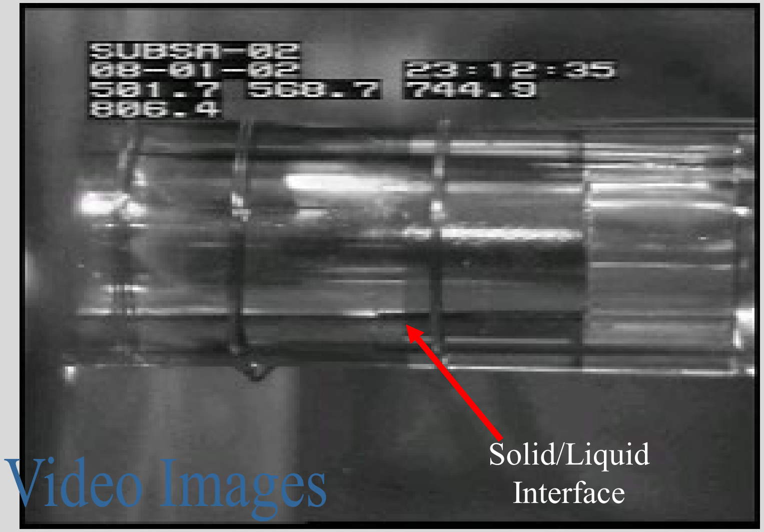


- Prepared on the ground before flight by loading the processing materials (up to 50g InSb doped with up to 50mg of Cd, Te, Ga, Zn, Ca, or As) into the ampoules. Some of the ampoules may also have up to 2g of a LiCl-KCl liquid encapsulant.

- The ampoules will be sealed under a 10E-3 torr or better vacuum. A cartridge head and four (4) external thermocouples will then be added to finish the Sample Ampoule Assembly (SAA).

Solidification Using a Baffle in Sealed Ampoules
2002 Space Shuttle Endeavour MSG, ISS



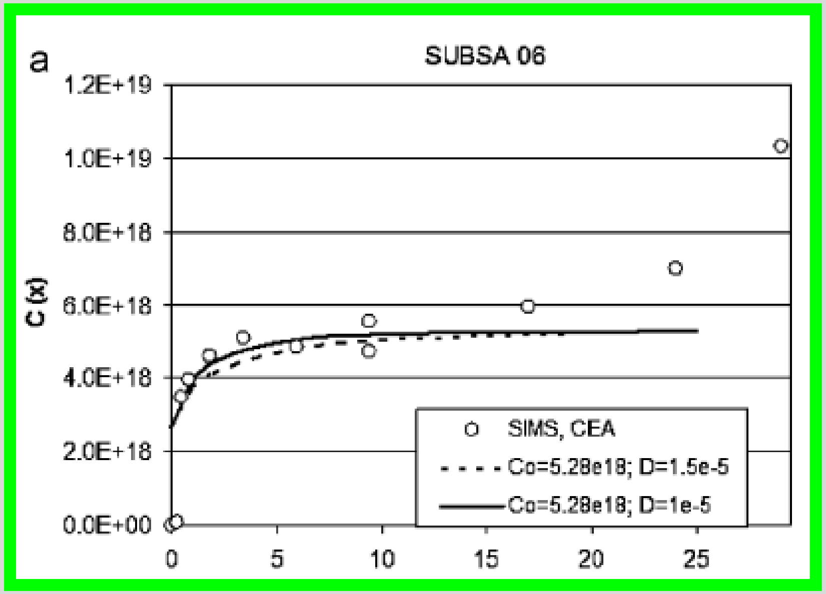


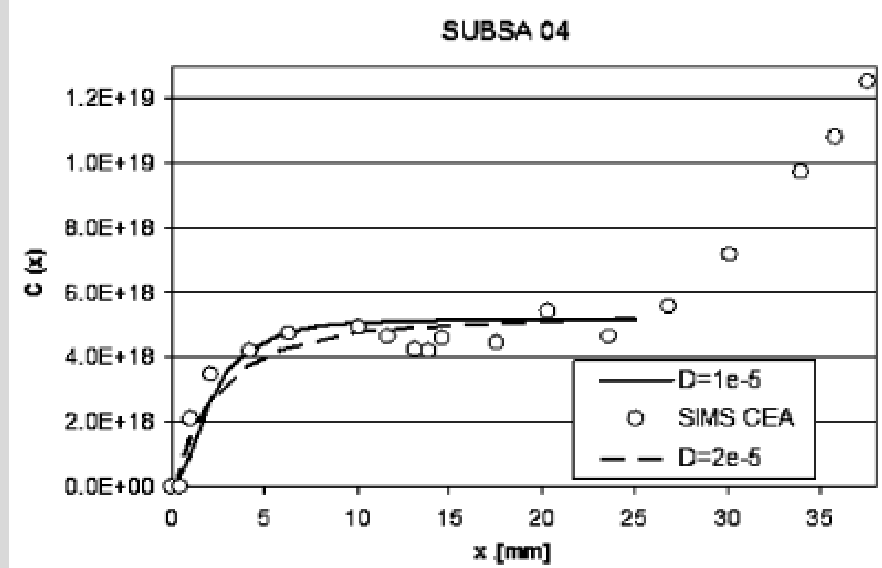
2002 Real Time SUBSA Video Images

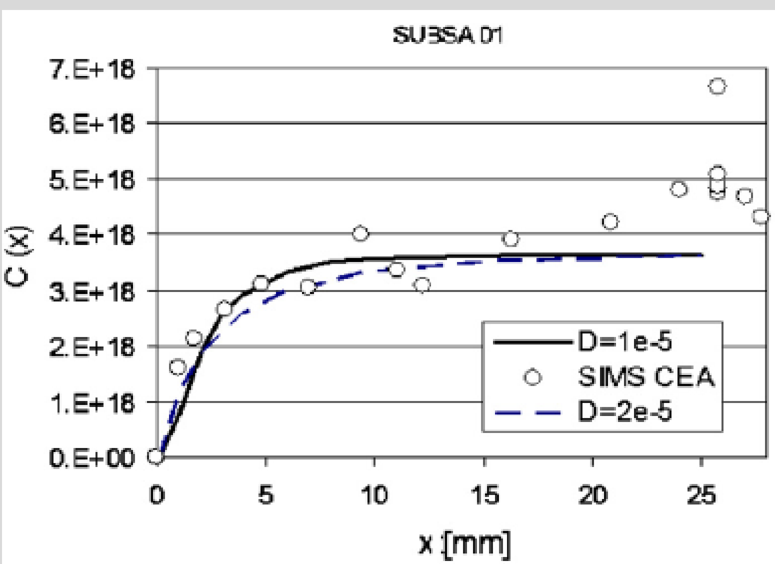
ISS, July 6, 2002, Peggy Whitson
1st experiment in MSG

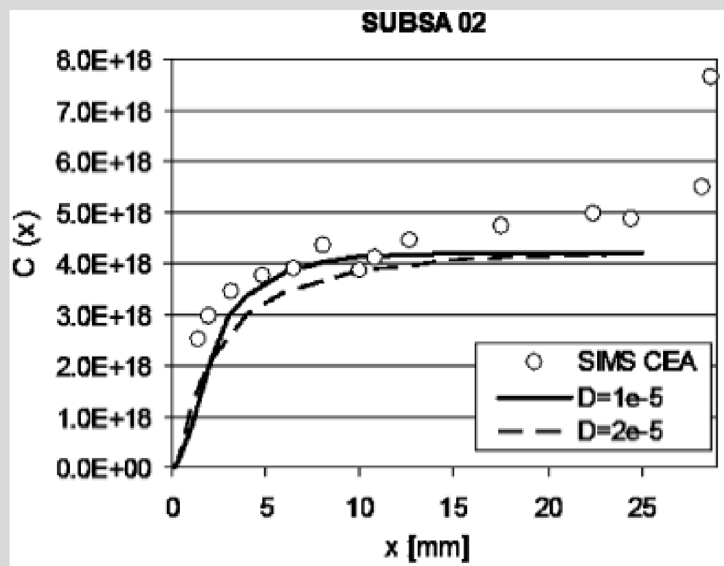
Monitoring room at RPI

SUBSA Te-doped InSb



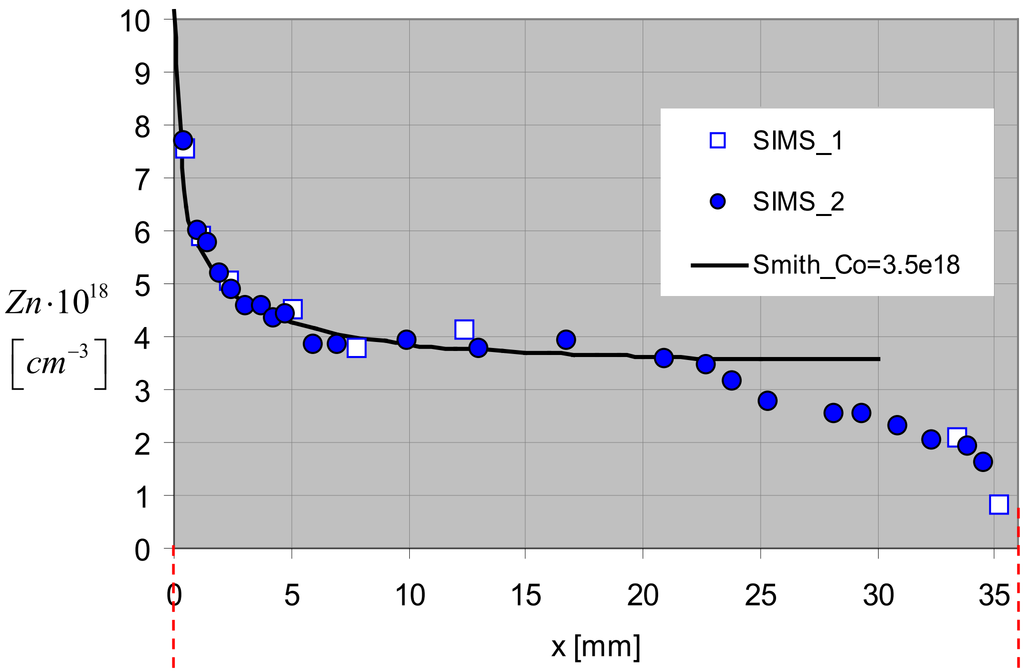


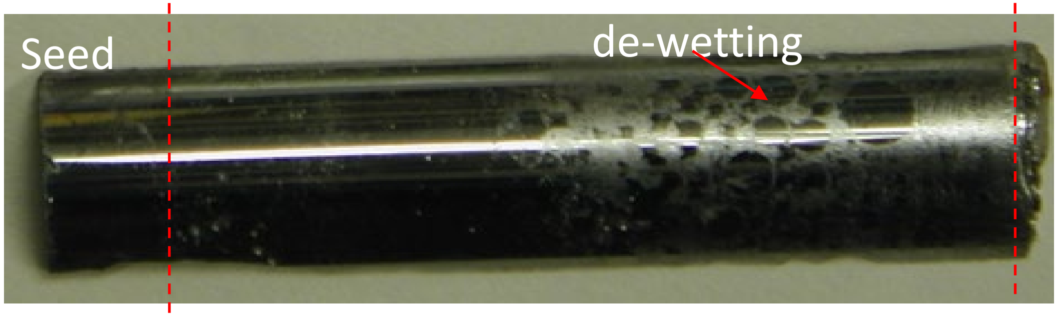




$$D = 1 \cdot 10^{-5} \left[\frac{cm^2}{s} \right]$$

SUBSA 10: Zn-doped; with baffle





Zn-doped => k=2.9
Te-doped =>. k=0.5

k_0 >1 is proffered for growth in microgravity.

D =1.2 x 10^{-5} cm^2/s

k>1 is shortening the initial transient in microgravity

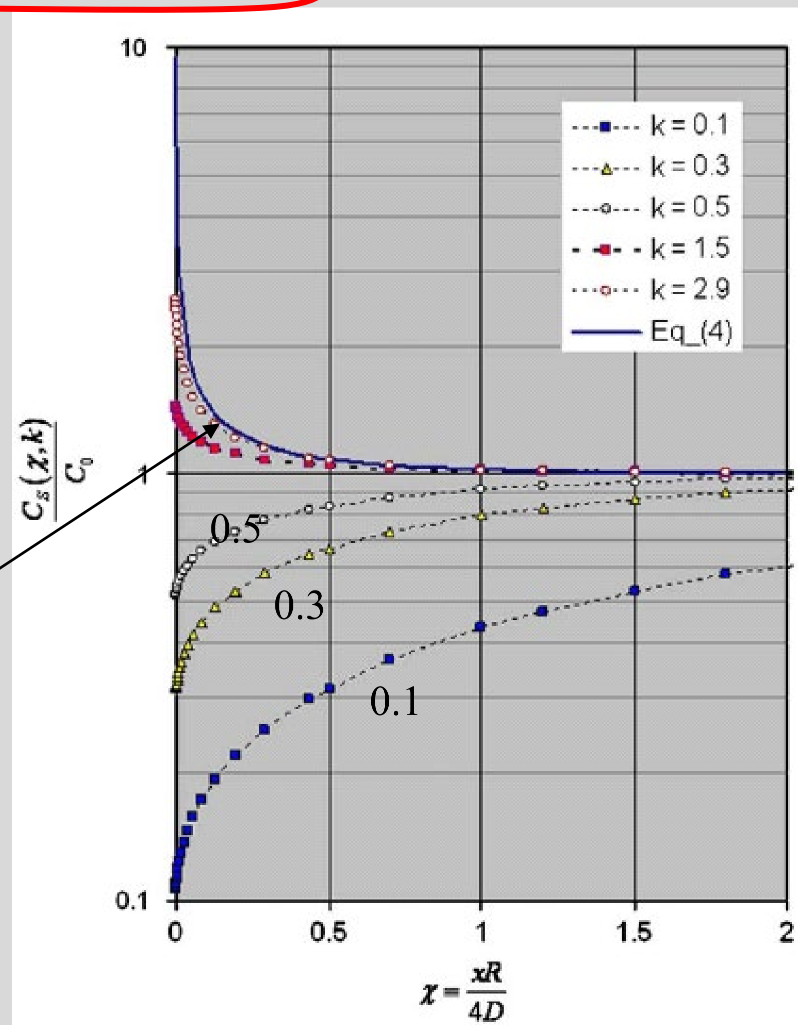
A.G. Ostrogorsky, C. Marin, M. Volz, T. Duffar, ***J. Crystal Growth*** (2009)

$$\frac{C_S(\chi,k)}{C_0} = \frac{1}{2}\left\{1+erf\sqrt{\chi}+(2k-1)\,\mathrm{e}^{-4k(1-k)\chi}\,erfc\left[(2k-1)\sqrt{\chi}\right]\right\}$$

$$\chi = \frac{xf}{4D}$$

$$\frac{C_S(\chi)}{C_0} = \phi(\chi) + F(k,\chi)$$

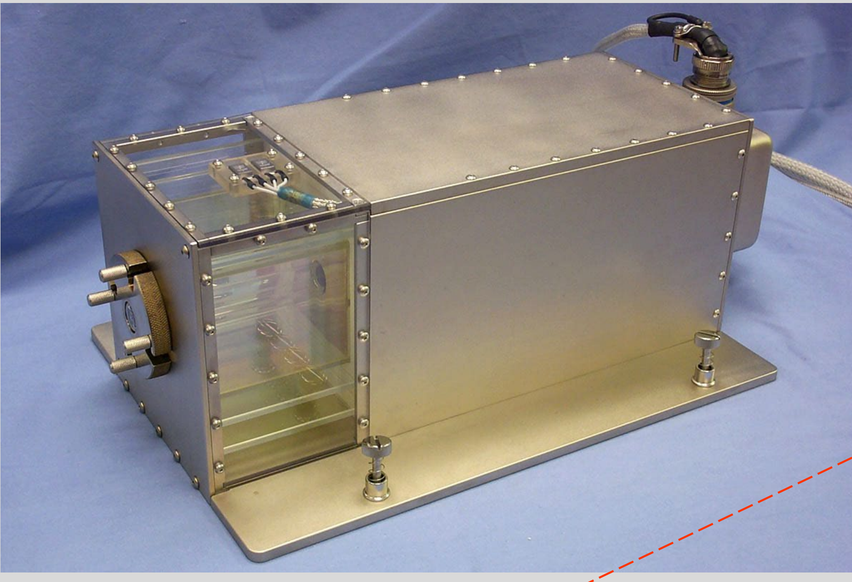
- $0 < k < 0.5$, **F** is negative, prolonging the transient.
- $k > 0.5$, F is positive, shortening the transients.

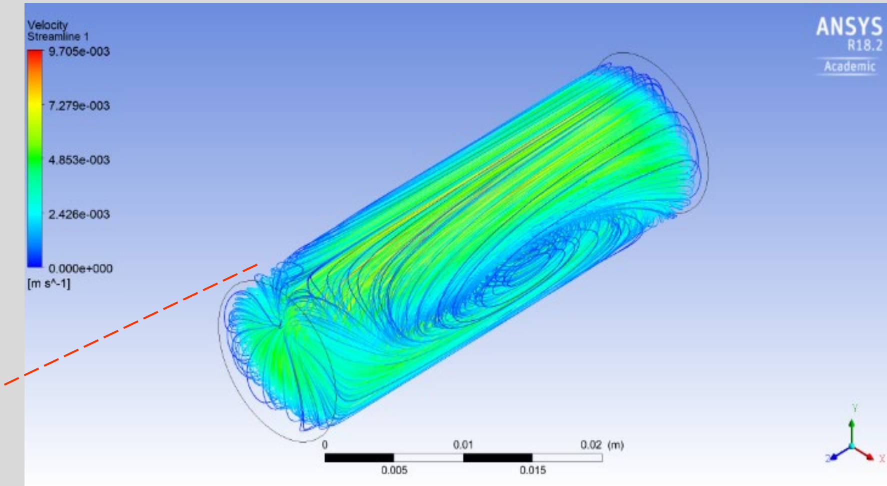


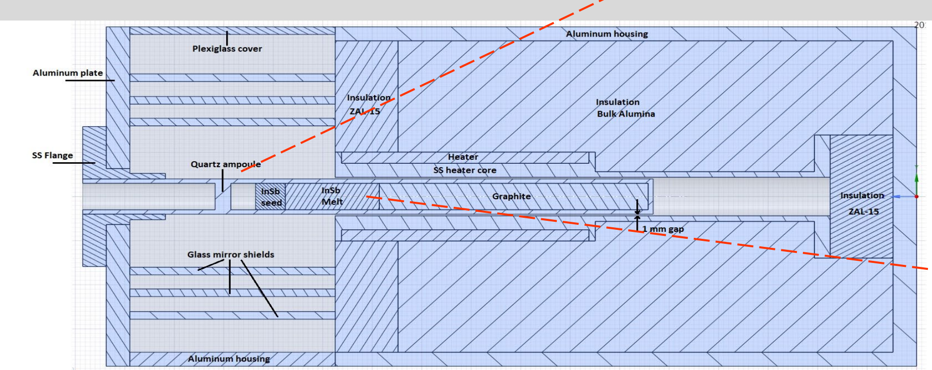
A.G. Ostrogorsky, et al., J. Crystal Growth (2009)

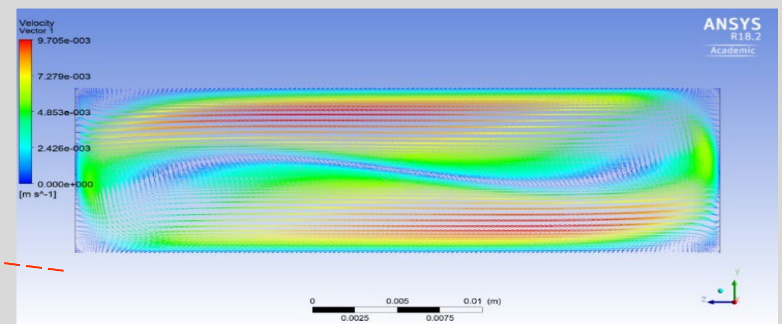
$$\frac{C_S(\chi)}{C_0} = \frac{1}{2}\left\{1+erf\sqrt{\chi}+\frac{e^{-\chi}}{\sqrt{\pi\chi}}\right\} \quad (4)$$

Present work: detailed ANSYS model of the SUBSA furnace









μg

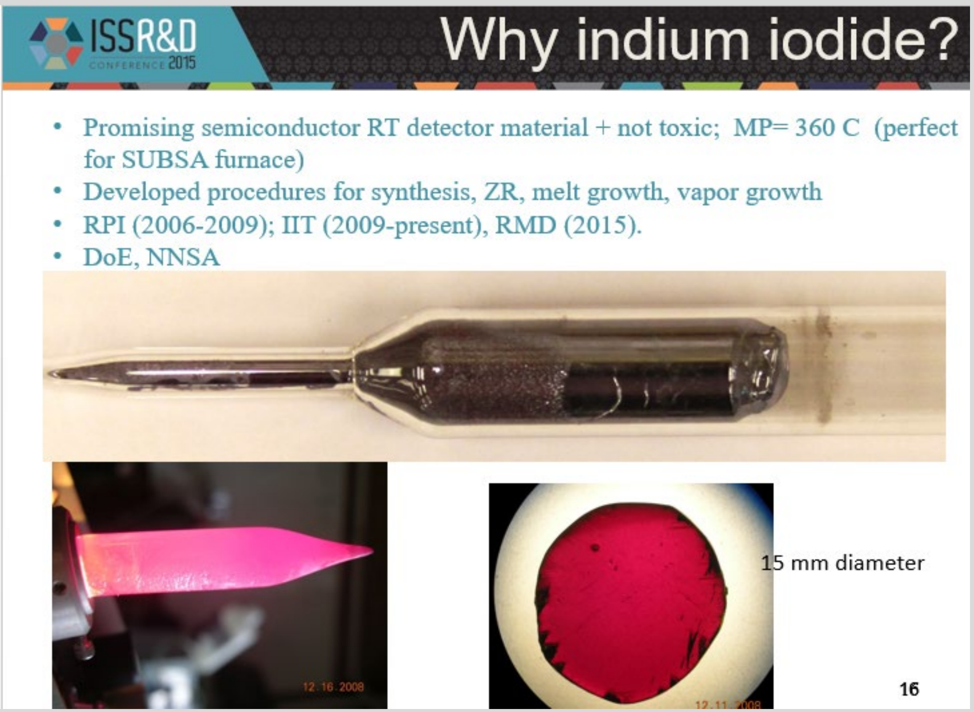
Reproduce the SUBSA experiments

- InSb (k~10 W/m-K)
- InI (k~0.5 W/m-K)
- On Earth and at ISS
- Useful for future investigations in SUBSA facility

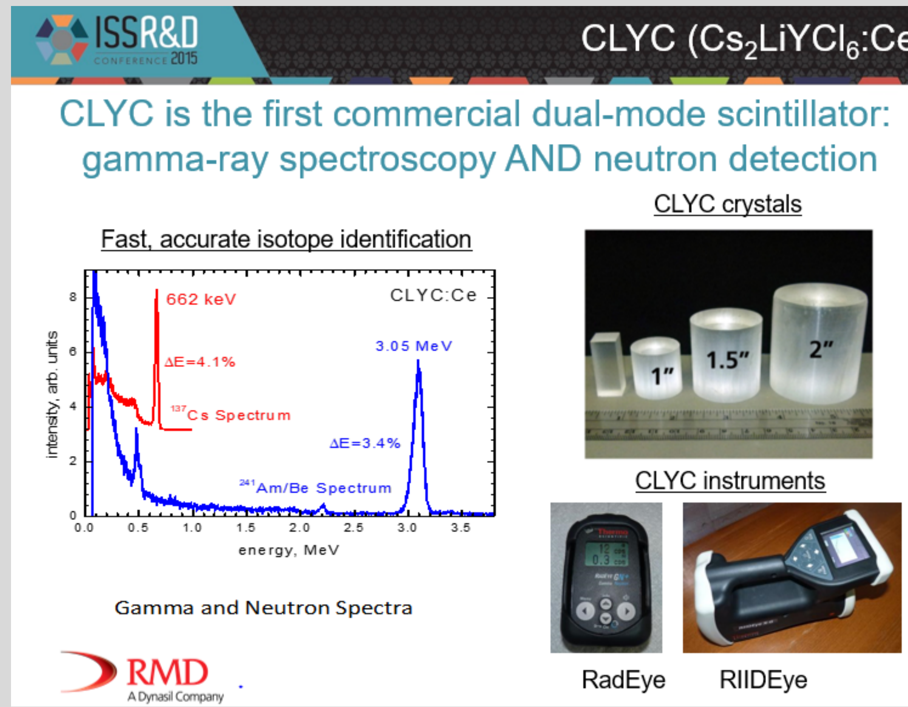
II-SUBSA 2015-present

The **refurbished SUBSA** flight unit was launched in the Fall of 2017

Detached Melt and Vapor Growth of **InI** in SUBSA Hardware (IIT, Ostrogorsky)



Crystal growth of **CLYC (Cs2LiYCl6:Ce)** in Microgravity (RMD, A. Churilov, J. P. Tower)



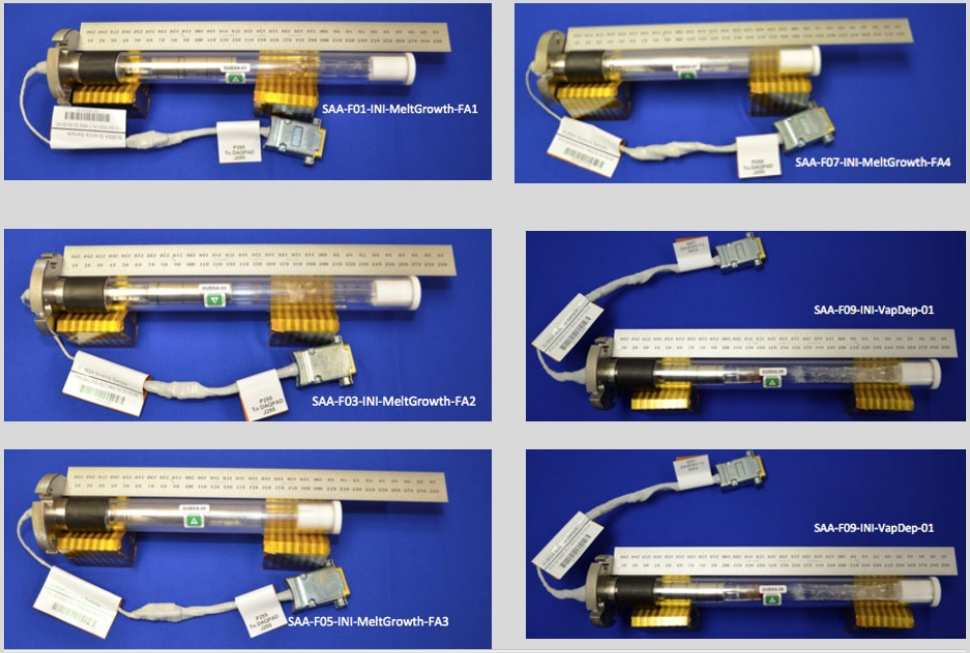
Properties not known

- 18 April, 2017 Launched Orbital ATK OA-7 Cygnus mission to ISS
- Four crystal growth experiments conducted in March-April 2019
- 4^{th} melt growth experiment was conducted on January 4, 2021
- 2 vapor growth experiments were completed

David St Jacque March 2019

Detached Melt and Vapor Growth of InI in SUBSA Hardware

SUBSA 2 InI Sample Ampoule Assembly



Note:
Major difference in properties between InSb and InI

III Diffusion Coefficients of Dopants in molten Ge and Si
2020- present

Numerical simulations require precise values of ***D.***

FM

$$\begin{cases} \nabla \cdot \vec{V} = 0 \\ \dfrac{\partial \vec{V}}{\partial t} + \left(\vec{V} \cdot \nabla\right)\vec{V} = -\nabla p + \nabla^2 \vec{V} + Gr\left(T_0 - T\right)\vec{i}_g \end{cases}$$

Heat

$$\frac{\partial T}{\partial t} + \left(\vec{V} \cdot \nabla\right) T = \frac{1}{\Pr} \nabla^2 T$$

Mass

$$\frac{\partial C}{\partial t} + \left(\vec{V} \cdot \nabla\right) C = \frac{1}{Sc} \nabla^2 C$$

Boundary Condition (BC) at S/L interface:

$$-\left.\frac{\partial C}{\partial x^*}\right|_{x=0} = Pe\left(1 - k_0\right)C_0 = Nu\left(C_0 - C_L\right)$$

Solidification and Quenching Low Gradient Furnace (LGF)

FC	NC	HT	MT
$Re = \frac{V \cdot L}{\nu}$	$Gr = \frac{g \beta \Delta T L^3}{\nu^2}$	$\Pr = \frac{\nu}{\alpha}$	$Sc = \frac{\nu}{D}$

$$k_0 = \frac{C_S}{C_0} \qquad Pe \equiv \frac{f \cdot L}{D} \qquad Nu \equiv \frac{h \cdot L}{D}$$

ACKNOWLEDGEMENTS

NASA MSFC

Dr. Martin P. Volz, Project Scientist, co-investigator

Dr. Fernando Reyes Tirado, Paul Luz, Linda Jetter

Prof. Dr. Arne Cröll, U. Freiburg, UAH.

Dr. Lodewijk van den Berg, Constellation Technology

Largo Florida.

Postdocs: Dr. Partha Duta, Dr. Carlos Marin,

PhD Students: A.V. Churilov (2005), V. Riabov (2023)

MS Students: S. Meyer (MS 1997), M. Vogel, RPI (1999)

Support by NASA and CASIS, 1993 – 2023.