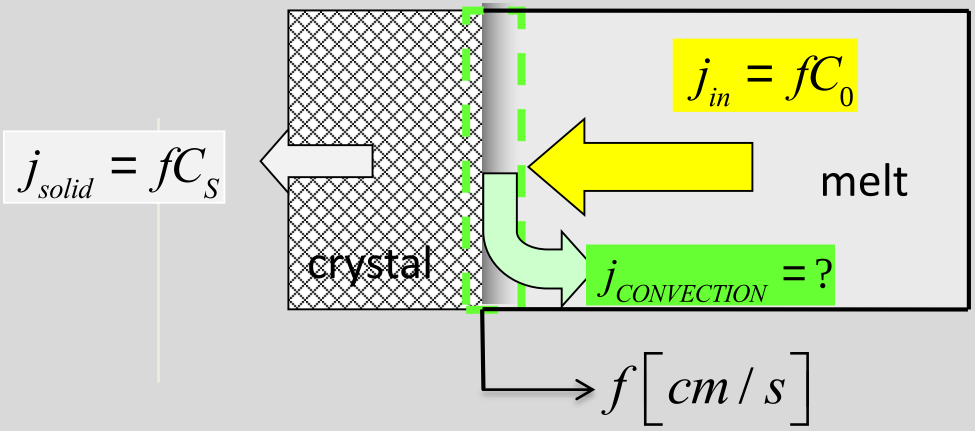
Measurement of Diffusion Coefficients of Dopants in Ge and Si melts

Aleksandar G. Ostrogorsky
Illinois Institute of Technology, Chicago, IL 60616,
Martin Volz
NASA Marshall Space Flight Center, Huntsville, AL35812
Arne Croell
U. Alabama Huntsville, Huntsville, AL35899 and
Crystallography, U. Freiburg, 79104 Freiburg, Germany

1. Introduction
2. Techniques used to measure D in Ge and Si melts
    a) Direct – C(x) in capillaries
    b) Indirect – $C_S(x)$ crystals
3. D values
4. Present/planned experiments: g_0 and μ
5. Conclusion

1. Introduction-Relevance to Single Crystal Growth:

Calculations and modeling are needed to optimize the process



Governing Equations:

FM

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

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

Heat

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

Mass

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

FC NC HT

MT

$$\mathrm{Re} = \frac{V \cdot L}{\nu} \qquad Gr = \frac{g\beta\Delta T L^3}{\nu^2} \qquad \Pr = \frac{\nu}{\alpha} \qquad Sc = \frac{\nu}{D}$$

Boundary Condition (BC) at S/L interface:

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

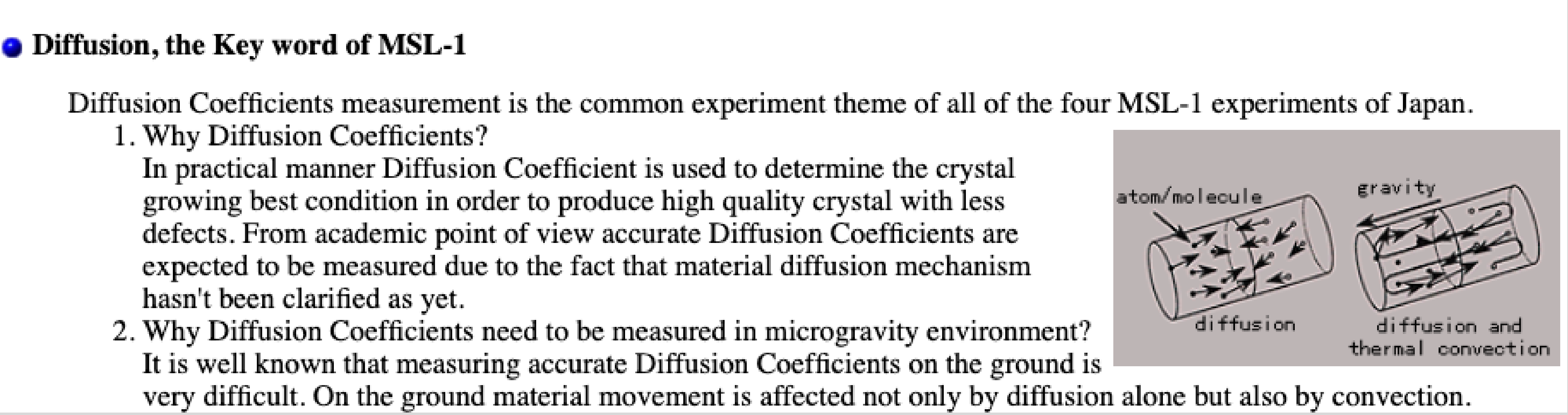
⇒

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

- It often becomes necessary to calculate the distribution of impurities in the melt and in the growing crystal.
- The calculations, require **D**.

Introduction-Relevance and MSL-1

http://iss.jaxa.jp/kibo/kibo-j/msl/index_e.html



Diffusion, the Key word of MSL-1

Diffusion Coefficients measurement is the common experiment theme of all of the four MSL-1 experiments of Japan.

1. Why Diffusion Coefficients?
   In practical manner Diffusion Coefficient is used to determine the crystal growing best condition in order to produce high quality crystal with less defects. From academic point of view accurate Diffusion Coefficients are expected to be measured due to the fact that material diffusion mechanism hasn't been clarified as yet.
2. Why Diffusion Coefficients need to be measured in microgravity environment?
   It is well known that measuring accurate Diffusion Coefficients on the ground is very difficult. On the ground material movement is affected not only by diffusion alone but also by convection.

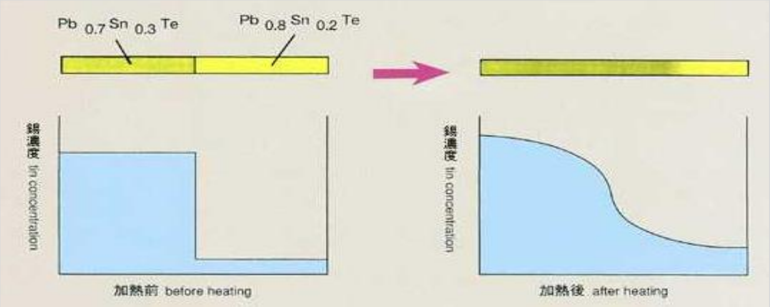
Experiment Themes and Principal Investigators (PIs) Using LIF

1. Diffusion of Liquid Metals and Alloys
   (Dr.Toshio Itami, Hokkaido University)
2. Diffusion of Liquid Lead-Tin-Telluride
   (Ms.Misako Uchida,Ishikawajima Heavy Industry Co.Ltd.)
3. High Accuracy Measurements of Impurity Diffusion Coefficients in Ionic Melts in Microgravity
   (Dr.Tsutomu Yamamura,Tohoku University)
4. Measurements of Diffusion Coefficients by Shear Cell Method
   (Dr.Shinichi Yoda, National Space Development Agency of Japan)
5. Liquid Phase Sintering
   (Dr.Randall German,Pennsylvania State University)
6. Diffusion Processing in Molten Semiconductors
   (Dr.David N.Mattiesen,Case Western Reserve University)

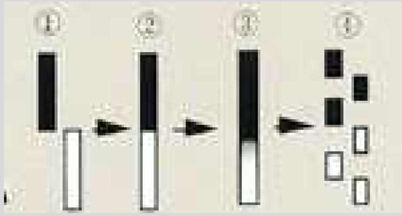
Techniques used to measure D

a) *Direct: diffusion in static capillary liquid columns*

D is determined by fitting the measured C(x)

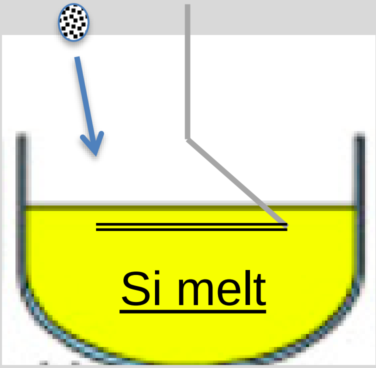


Long Capillaries (MSL-1: 1 and 2)
- a d=2 mm 60mm long rod of tin.
- Tin isotope tracer is placed on one end.



Shear Cell method (MSL-1: 4 and 6)

- At t=0, one doped and one undoped liquid columns are brought into contact
- At $t=t_{end}$, the liquid columns are sheared + solidified.



Reservoir-Capillary method

- A large reservoir is in contact with an undoped column.
- At t=0, reservoir is doped
- At $t=t_{end}$, the liquid column is frozen.

Shaskov and Gurevich (1968)

Techniques used to measure D, cont.

b) Indirect: diffusion in the solute layer “δ” at the interface of a growing single crystal

- D is determined by fitting $C_S(x)$, in the crystal.
- Natural convection (NC) has to be “eliminated”

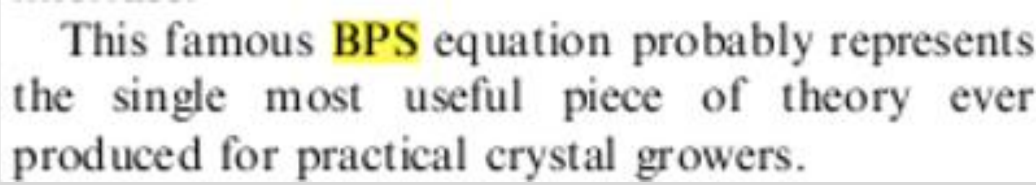
1993-2004

Bridgman process:

- Microgravity, US (Apollo-Soyuz Witt et al…) USSR..
- Magnets (Matthisen et al. , Szofran);
- Baffle on Earth (CGB), Ostrogorsky (1990 -)
- Solidification Using a Baffle in Seale Ampoules (SUBSA, 2002, 2019)

Czochralski process (CZ):

- Burton, Prim and Slichter **(BPS, 1953) - Ge**
- Turvivslkii (1962) - **Si**
- Kodera (1963) - **Si**

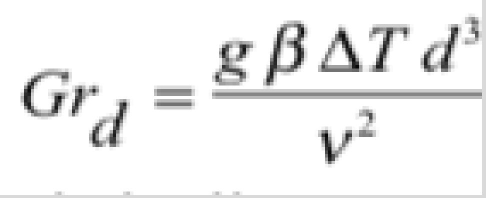


This famous BPS equation probably represents the single most useful piece of theory ever produced for practical crystal growers.

Sources of error:

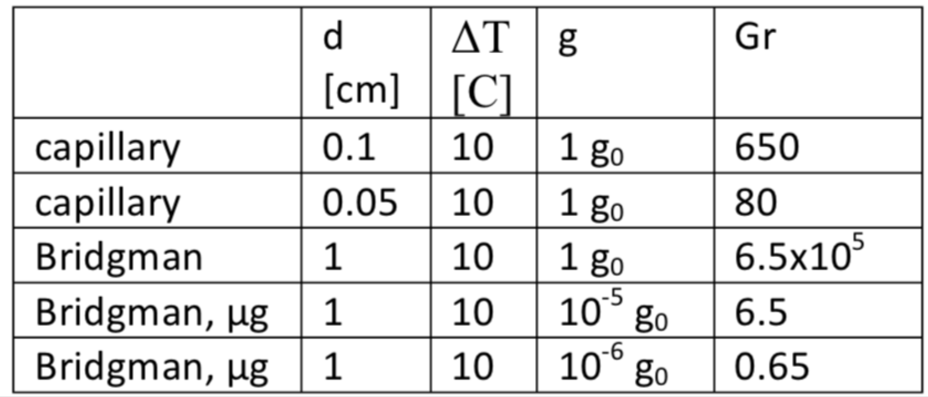
Capillaries: (i) "Forced" convection, driven by shearing. (ii) Natural convection (on Earth). (iii) T(x) ~ Tm + 20 C

Bridgman: (i) natural convection, (ii) Marangoni , (iii) bubbles.



$$Gr_d = \frac{g \beta \Delta T d^3}{\nu^2}$$

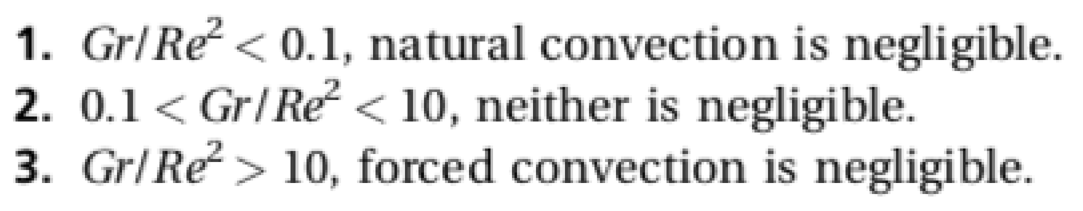
$$Baffle : \Delta T\, L^3$$



	d [cm]	ΔT [C]	g	Gr
capillary	0.1	10	1 g_0	650
capillary	0.05	10	1 g_0	80
Bridgman	1	10	1 g_0	$6.5\text{x}10^5$
Bridgman, μg	1	10	10^{-5} g_0	6.5
Bridgman, μg	1	10	10^{-6} g_0	0.65

Czochralski : (i) FC – Navier-stokes equations. (ii) NC

- Natural convection
- **Viscosity !!!**
- **BPS equation**
- **δ**



1. $Gr/Re^2 < 0.1$, natural convection is negligible.
2. $0.1 < Gr/Re^2 < 10$, neither is negligible.
3. $Gr/Re^2 > 10$, forced convection is negligible.

Sources of error: always natural convection

Capillaries:

(i) “Forced” convection, driven by shearing.

(ii) T(x) ~ Tm + 20 C

$$D = \frac{k_B T}{6\pi \eta r} \sim \frac{1}{\eta}$$

A. Witt: *“Existing gap between theory and experiment ….is largely attributed to gravity-induced convection effects..”*

Bridgman:

(i) Marangoni convection

(ii) bubbles.

(iii) Growth rate f[cm/hr]

$$Gr_d = \frac{g\,\beta\,\Delta T\,d^3}{\nu^2}$$

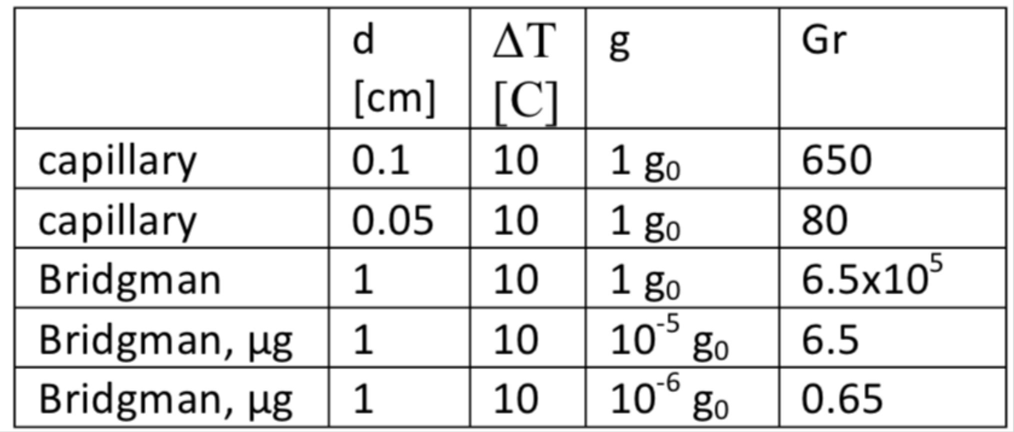
Czochralski : Bell Labs Technique

(i) Model used to fit the data, **BPS**

(ii) Viscosity !!!

$$\mathrm{Re} = \frac{\omega R^2}{\nu}$$

$$\frac{Gr}{\mathrm{Re}^2} << 1$$



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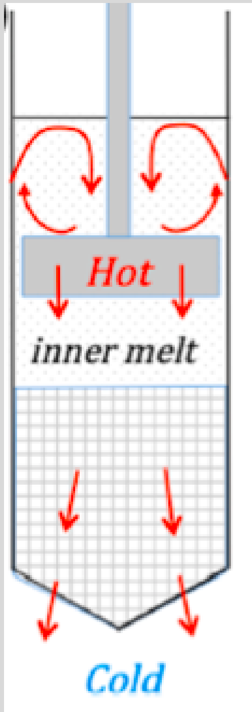
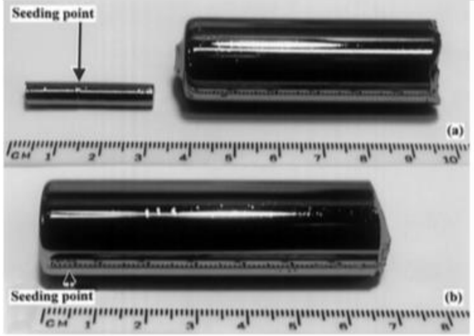
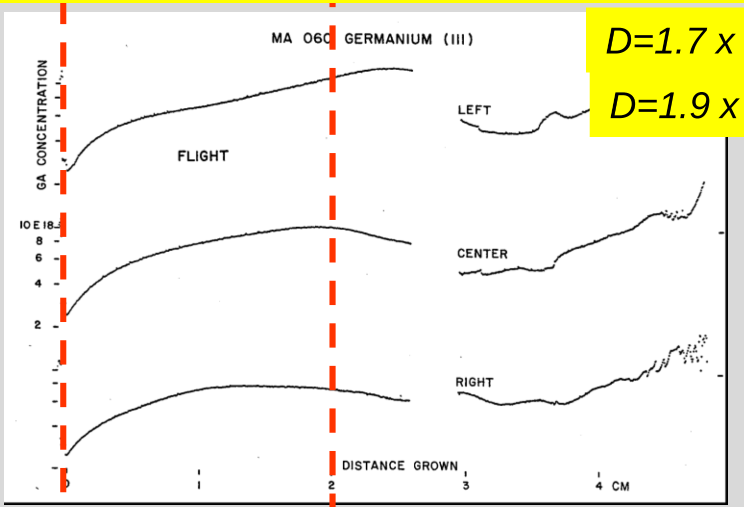
Ga-doped Ge

- Growth rate *f*= 3 cm/hr
- k_{eff}~0.65





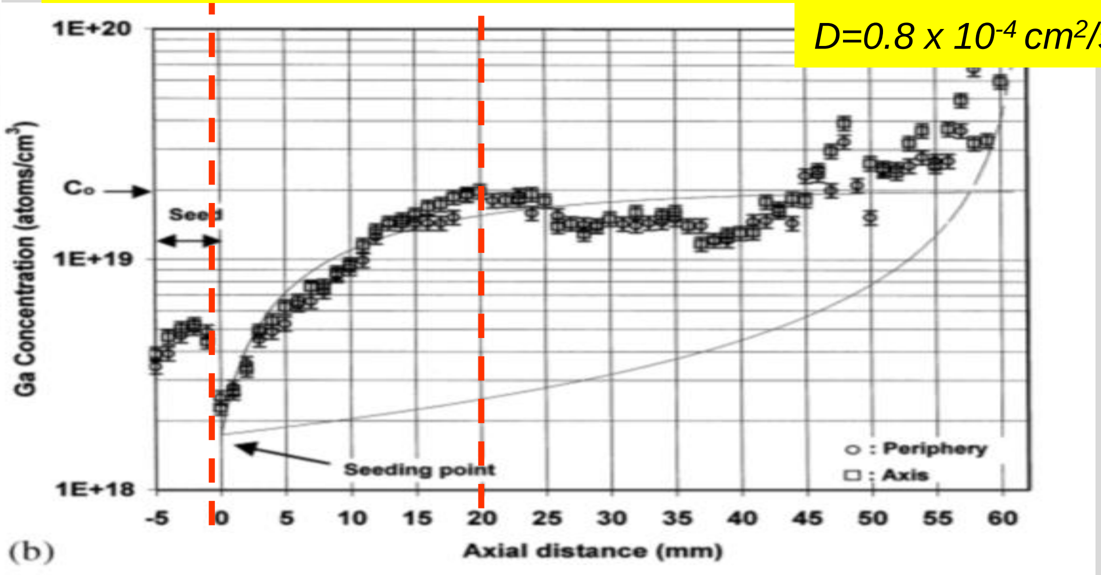
a) *Apollo-Soyuz 1978 mission, 10^{-5} g_0 . Witt et al.*



D=1.7 x 10^{-4} cm^2/s

D=1.9 x 10^{-4} cm^2/s

b) Vertical Bridgman with Baffle, Dutta &Ostrogorsky

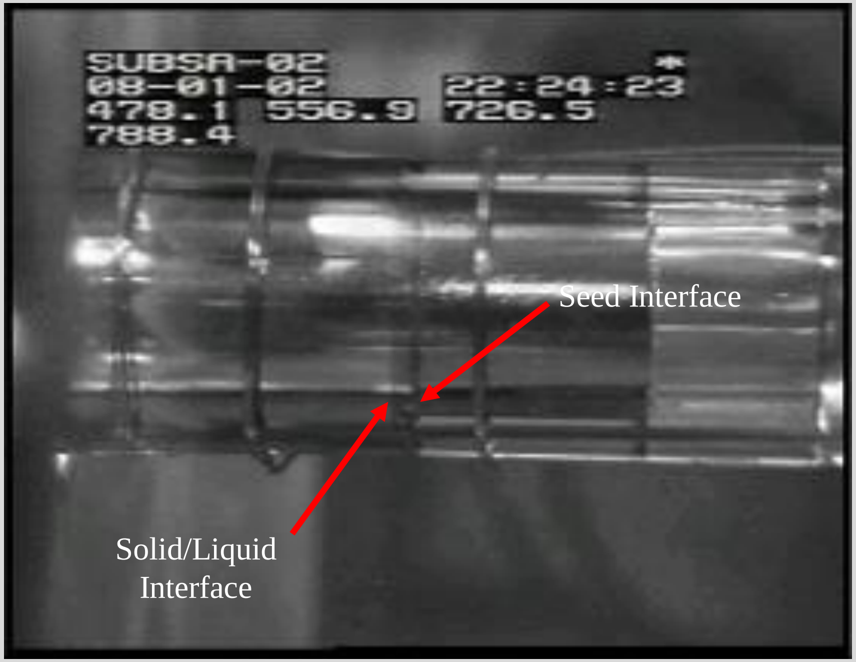


D=0.8 x 10^{-4} cm^2/s

Ga-doped Ge: D= 0.8×10^{-4} cm^2/s

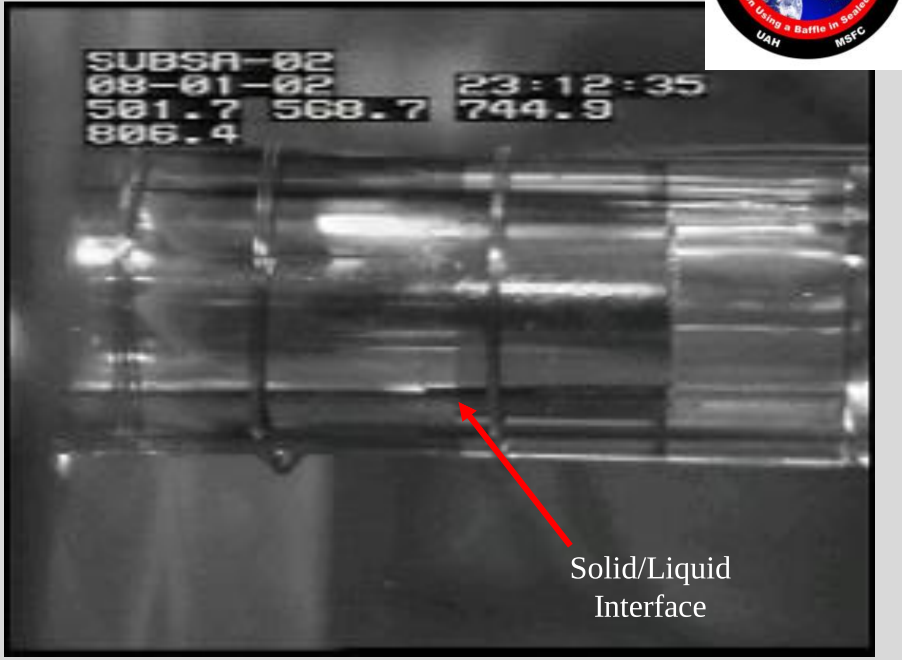
Dutta and Ostrogorsky, using a baffle as a flow restrictor, reducing NC and Gr. Bridgman growth in the17-zone Mellen furnace.

SUBSA (2002) Te and Zn-doped InSb

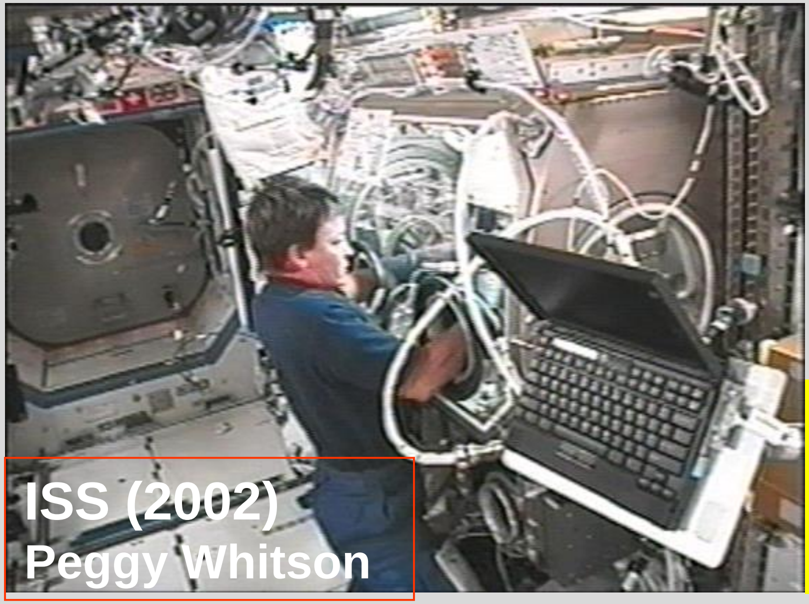


Seed Interface

Solid/Liquid Interface



Solid/Liquid Interface

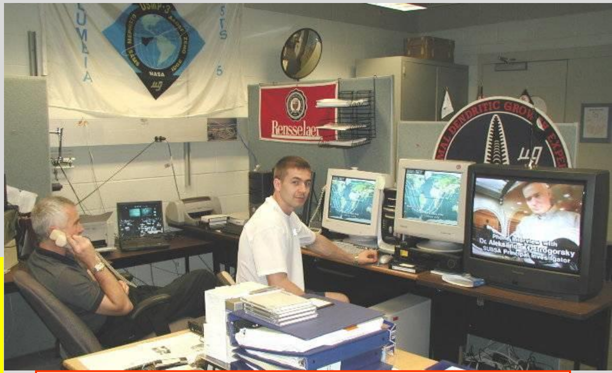


ISS (2002)
Peggy Whitson

- Precise seeding
- f = 0.5 cm/hr

$$D_{Te} = 1.0 \cdot 10^{-5} \left[\frac{cm^2}{s} \right]$$

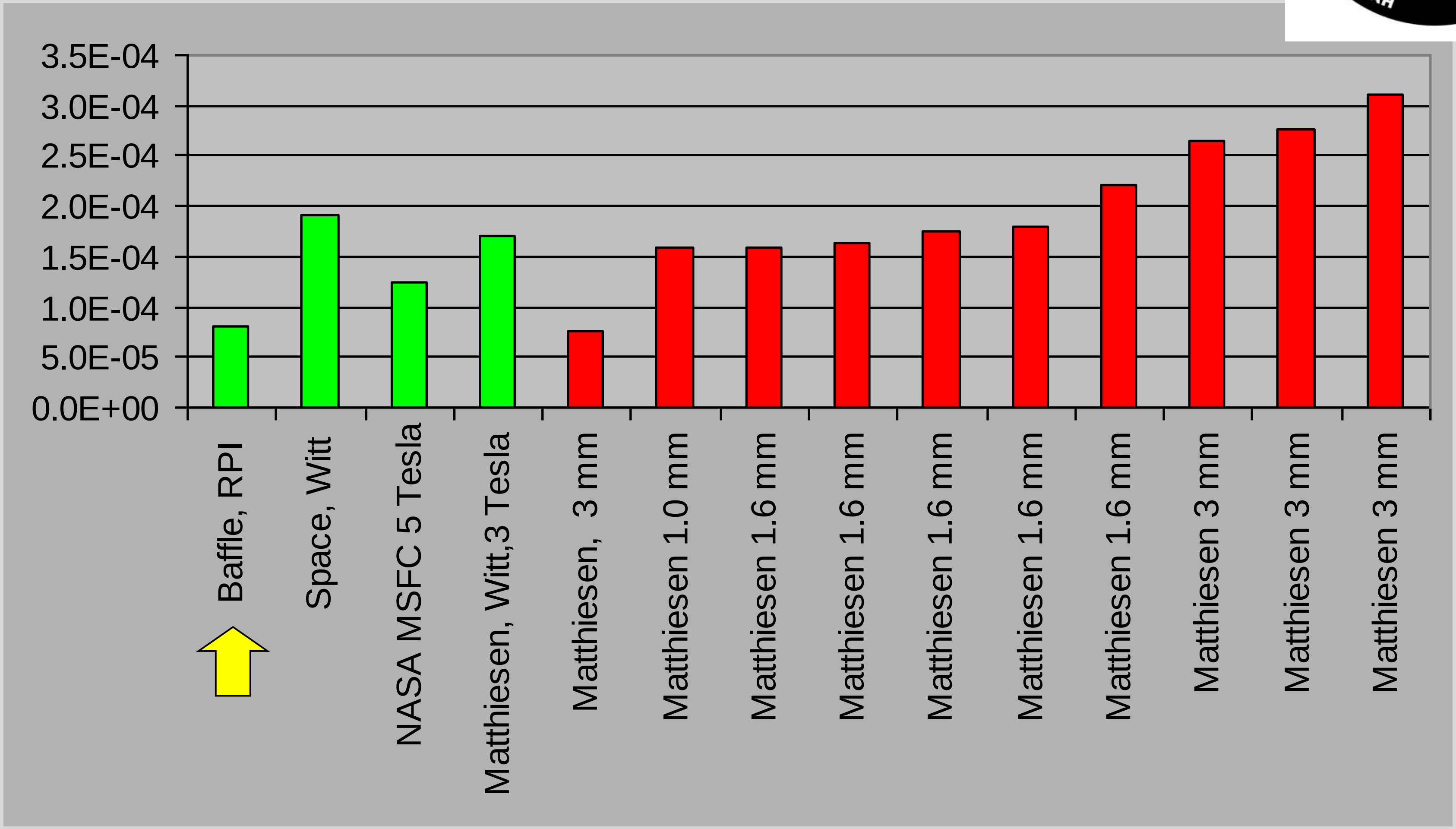
$$D_{Zn} = 1.2 \cdot 10^{-5} \left[\frac{cm^2}{s} \right]$$



Monitoring room at RPI

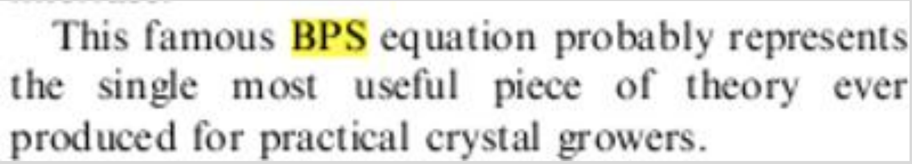
D [cm²/s] for Ga in molten Ge

Science Concept Review (SCR) for CGB – SUBSA (1998)



Bell labs.: CZ growth of Ga and Sb doped germanium CZ to validate the BPS model

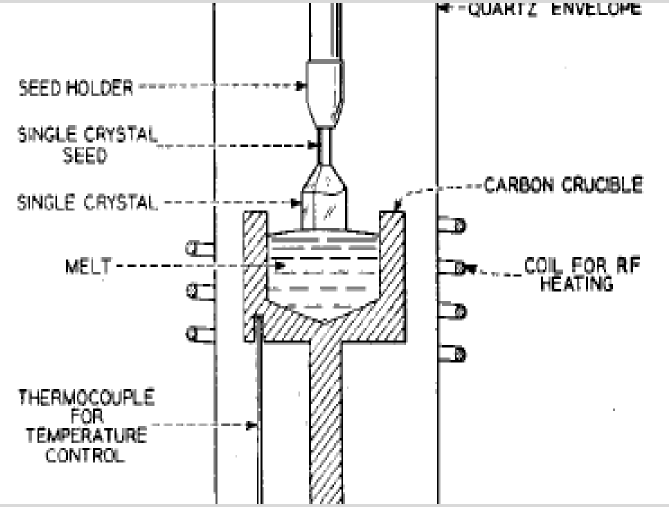
CZ : Ga and Sb doped Germanium



This famous **BPS** equation probably represents the single most useful piece of theory ever produced for practical crystal growers.

D. Hurle (editor HCG1)
P. Rudolph(editor HCG2):

29 cm/hr



d=2 cm

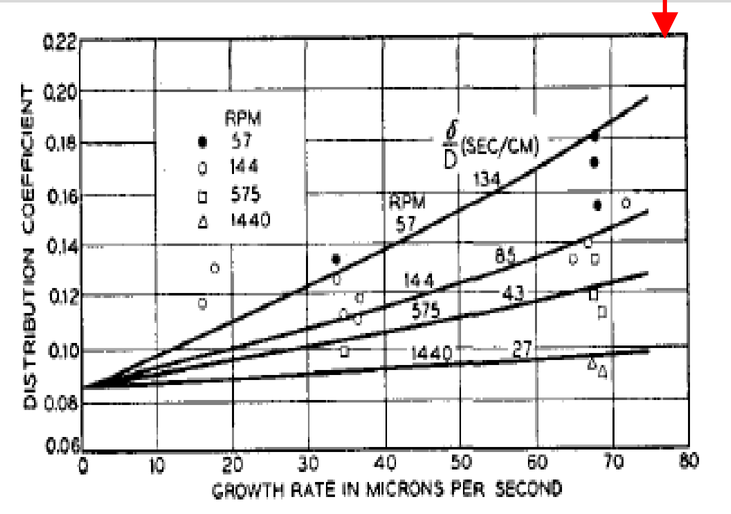


FIG. 4. Distrubition coefficient of gallium in germanium, as a function of cyrstal growth rate and rotation rate.

RPM	Re	Gr/Re^2
57	4.6E+03	~0.06
144	1.2E+04	~0.001
575	4.6E+04	0.0006
1440	1.2E+05	0.0001

BPS:

$$k_{eff} = \frac{C_S(x)}{C_0} = \frac{k}{k + (k-1)\exp\left[-f\left(\frac{\delta}{D}\right)\right]}$$

Levich:

$$\delta = 1.61 \cdot \left(\frac{D}{\nu}\right)^{1/3} \sqrt{\frac{\nu}{\omega}} = 1.61\ Sc^{-1/3} \sqrt{\frac{\nu}{\omega}}$$

$g,\ \Delta T,\ L^3$ *not in BPS*

$$D_{Ga} = 0.75 \times 10^{-4} \frac{\mathrm{cm}^2}{\mathrm{s}}$$

[1] J.A. Burton, R.C. Prim, W.P. Slichter, J. Chemical Physics 21 (1953) 1987.

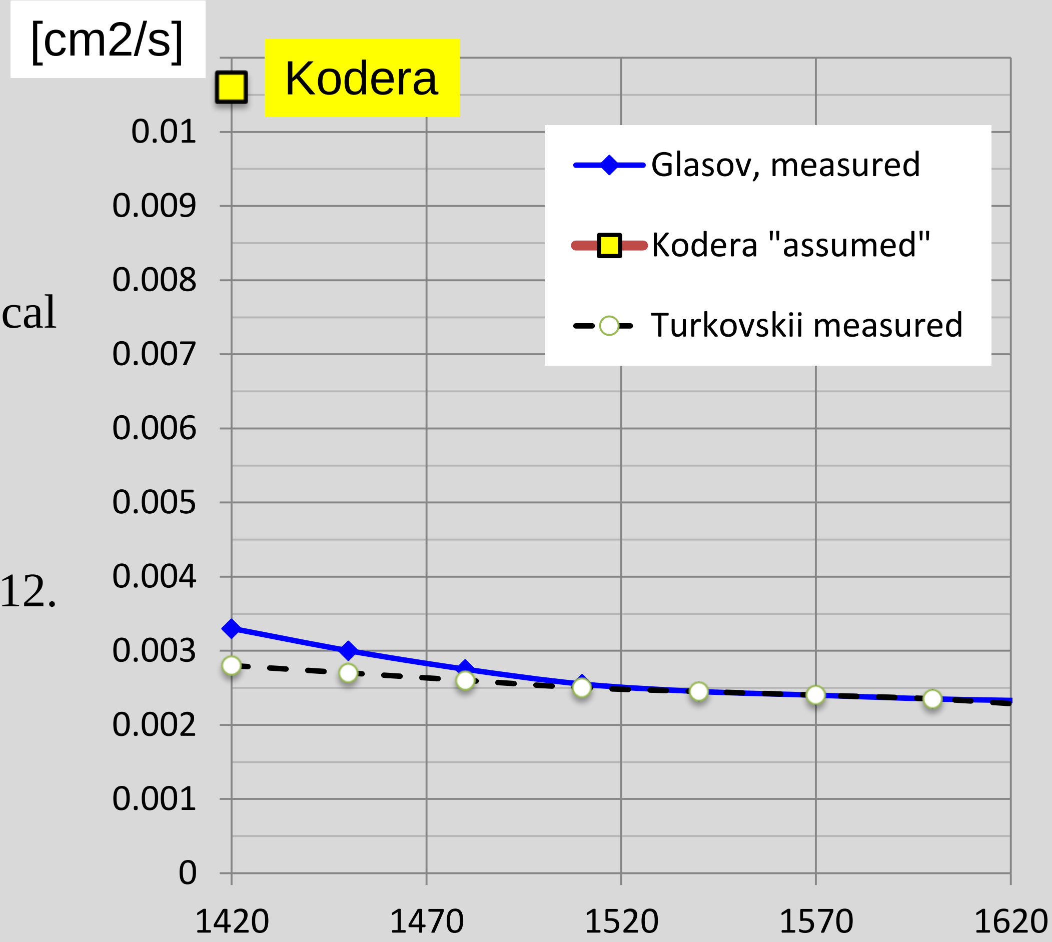
CZ Silicon

CZ Silicon 1:

B.M. Turovskii, Russian Journal of Physical Chem. 36, No.8 (1962) 983-985

CZ Silicon 2:

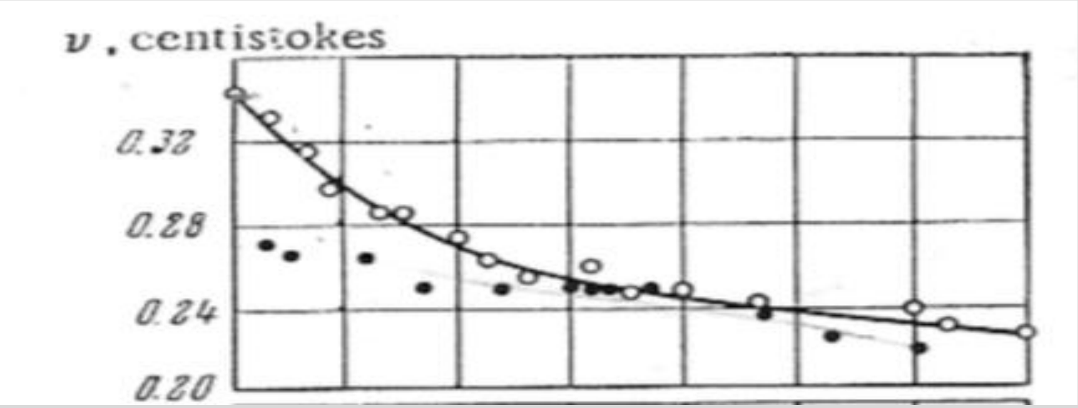
H. Kodera, Jpn. J. Appl. Phys. 2 (1963) 212.



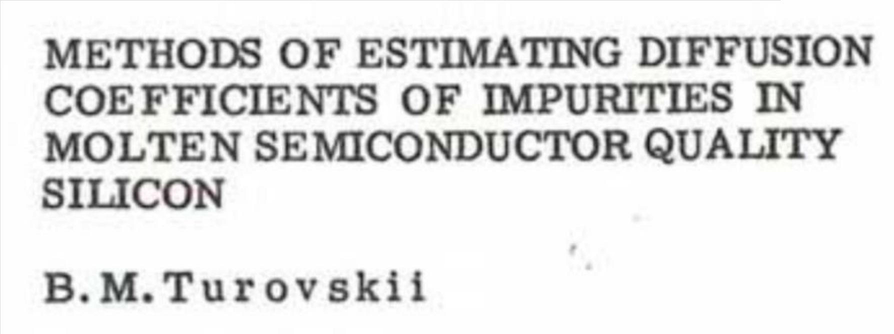
Error:

(i) "Normal" rpm and size: $\frac{Gr}{Re^2} \sim 1\,(?)$
NC not negligible

(ii) Kodera: Viscosity

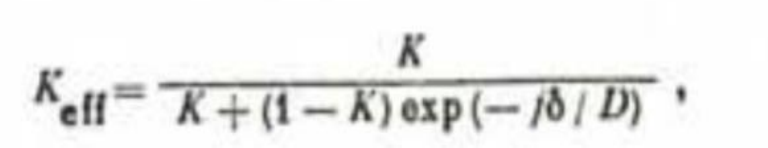


CZ Silicon 1:

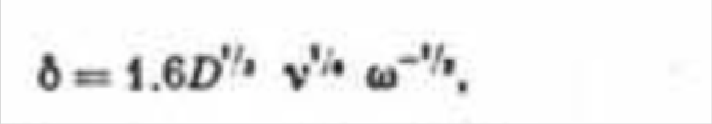


METHODS OF ESTIMATING DIFFUSION COEFFICIENTS OF IMPURITIES IN MOLTEN SEMICONDUCTOR QUALITY SILICON

B.M.Turovskii



$$K_{eff} = \frac{K}{K + (1 - K)\exp(-f\delta / D)},$$



$$\delta = 1.6D^{1/3}\ \nu^{1/6}\ \omega^{-1/2},$$

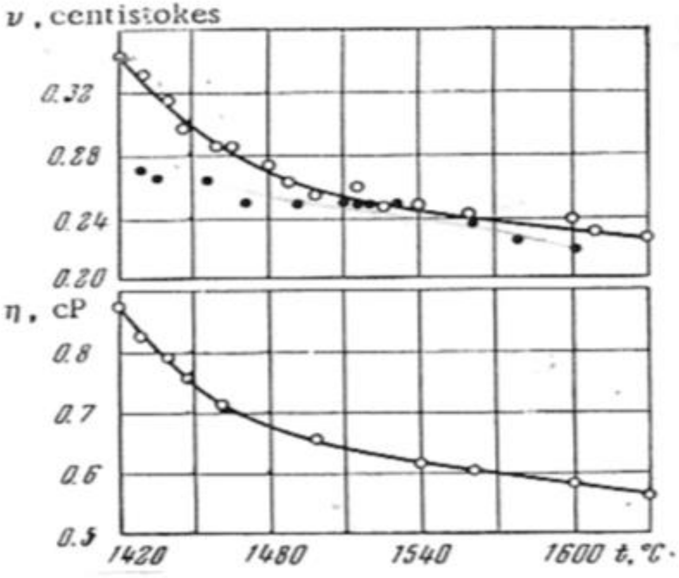


Fig. 17. Temperature dependences of the kinematic and dynamic viscosity of liquid silicon. ○) Results of the present authors; ●) Turovskii [147].

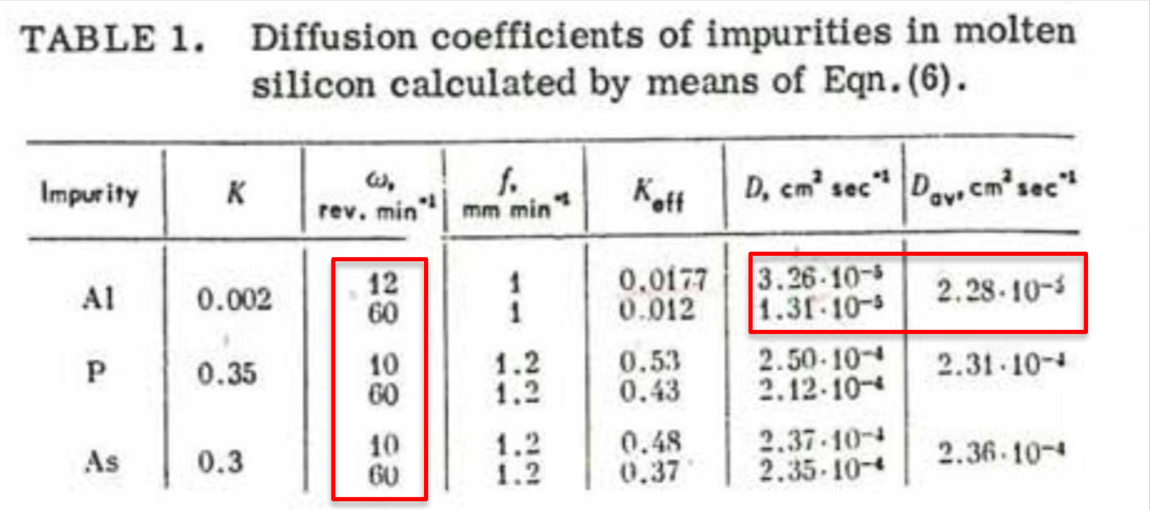


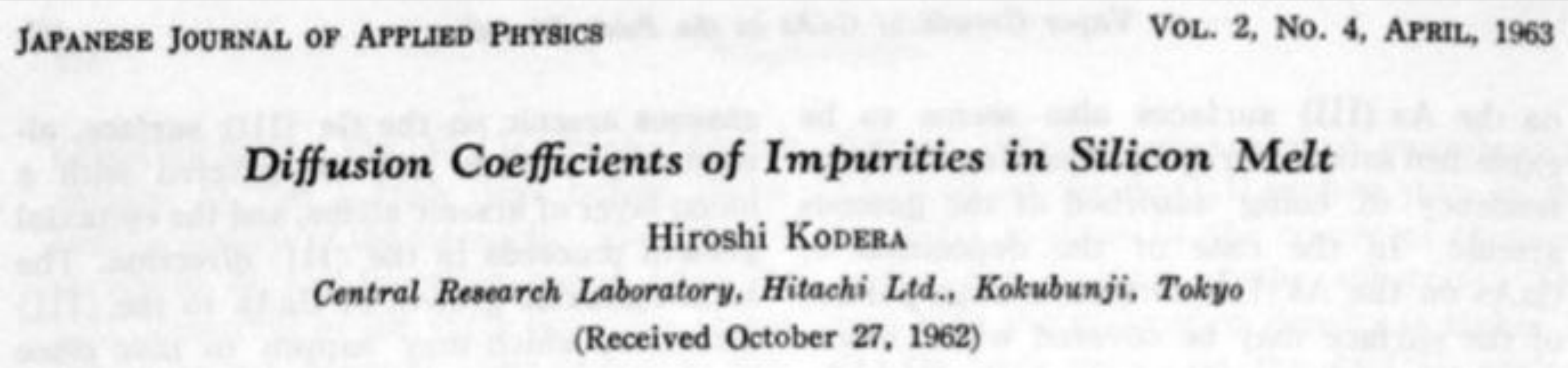
TABLE 1. Diffusion coefficients of impurities in molten silicon calculated by means of Eqn. (6).

Impurity	K	ω, rev. min⁻¹	f, mm min⁻¹	K_{eff}	D, cm² sec⁻¹	D_{av}, cm² sec⁻¹
Al	0.002	12	1	0.0177	$3.26 \cdot 10^{-5}$	$2.28 \cdot 10^{-5}$
		60	1	0.012	$1.31 \cdot 10^{-5}$	
P	0.35	10	1.2	0.53	$2.50 \cdot 10^{-4}$	$2.31 \cdot 10^{-4}$
		60	1.2	0.43	$2.12 \cdot 10^{-4}$	
As	0.3	10	1.2	0.48	$2.37 \cdot 10^{-4}$	$2.36 \cdot 10^{-4}$
		60	1.2	0.37	$2.35 \cdot 10^{-4}$	

D = function of ω or rpm.

*B.M. Turovskii, Russian Journal of Physical Chem. 36, No.8 **(1962)** 983-985*

CZ Silicon 2: Kodera (1963)



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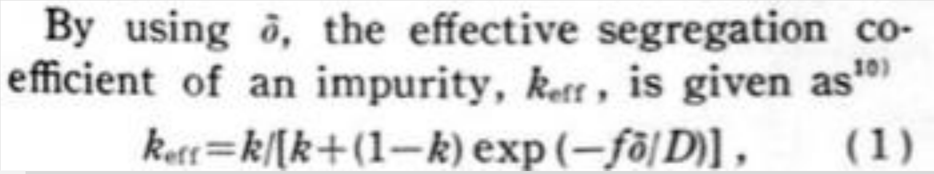
Diffusion Coefficients of Impurities in Silicon Melt

Hiroshi KODERA

Central Research Laboratory, Hitachi Ltd., Kokubunji, Tokyo

(Received October 27, 1962)



By using $\bar{\delta}$, the effective segregation coefficient of an impurity, k_{eff}, is given as[10)]

$$k_{eff}=k/[k+(1-k)\exp(-f\bar{\delta}/D)], \qquad (1)$$

BPS

$$k_{eff}=\frac{C_S(x)}{C_0}=\frac{k}{k+(k-1)\exp\left[-f\left(\frac{\delta}{D}\right)\right]} \qquad (1)$$

$$\bar{\delta}/D=1.60D^{-2/3}\nu^{1/6}\omega^{-1/2}$$

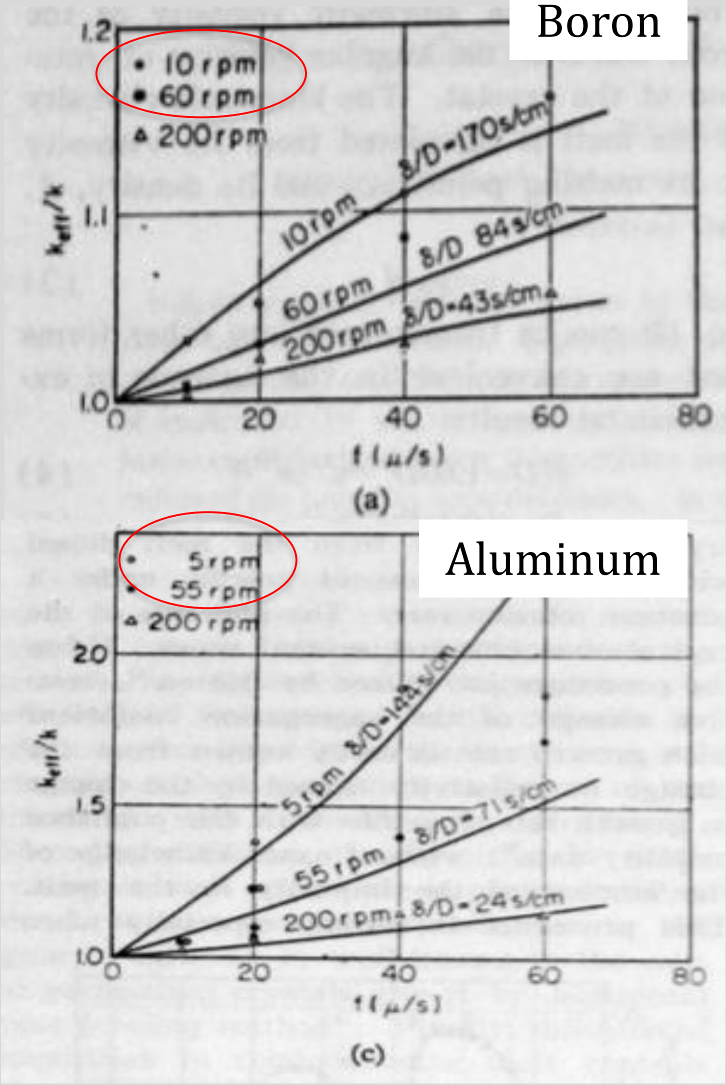
Levich's solution $$\frac{\delta}{D}=1.61\cdot D^{2/3}\nu^{1/6}\omega^{-3/4} \qquad (2)$$

D

- Rotating ∞ disk
- Laminar flow
- Sc=ν/D= ∞

$g,\ \Delta T,\ L^3$ *not included*

CZ Silicon 2: Kodera (1963)



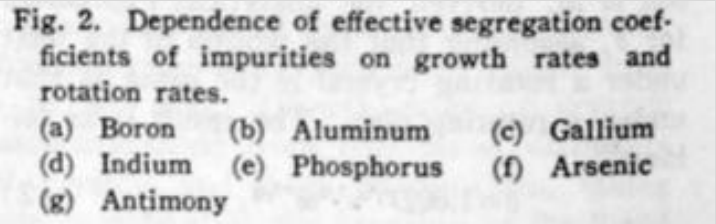
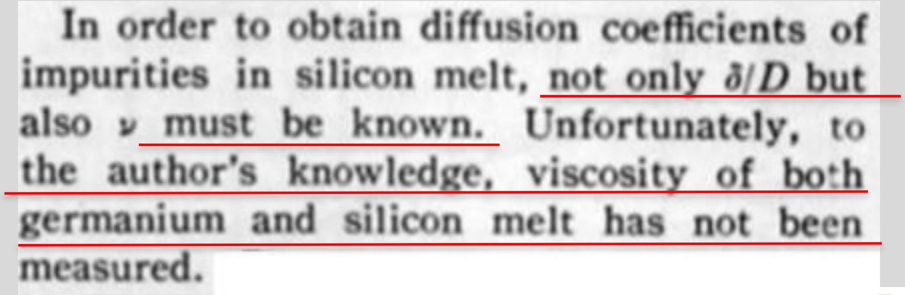
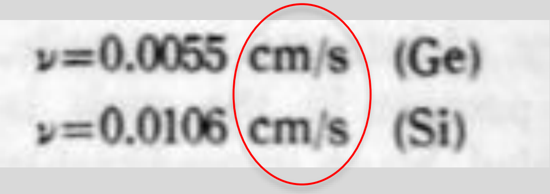


Fig. 2. Dependence of effective segregation coefficients of impurities on growth rates and rotation rates.
(a) Boron (b) Aluminum (c) Gallium
(d) Indium (e) Phosphorus (f) Arsenic
(g) Antimony

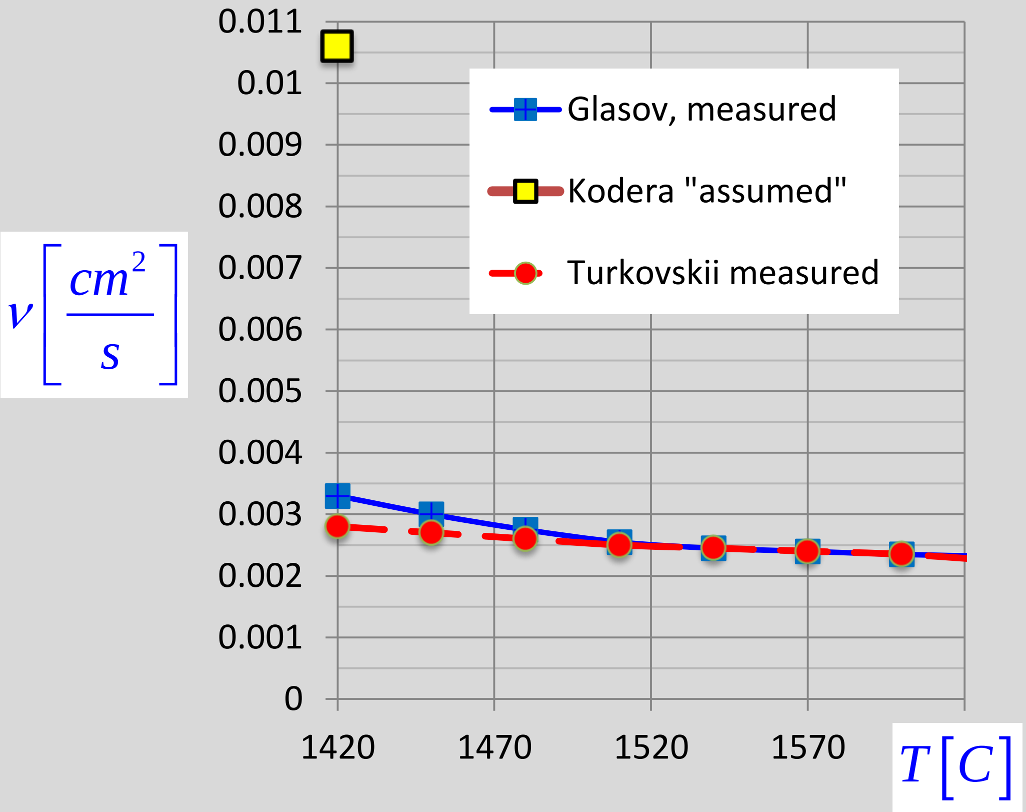


In order to obtain diffusion coefficients of impurities in silicon melt, not only δ/D but also ν must be known. Unfortunately, to the author's knowledge, viscosity of both germanium and silicon melt has not been measured.



$\nu=0.0055$ cm/s (Ge)
$\nu=0.0106$ cm/s (Si)

$$Sc \equiv \frac{\nu\left[\frac{cm^2}{s}\right]}{D\left[\frac{cm^2}{s}\right]}$$



CZ Silicon 2: Kodera (1963)

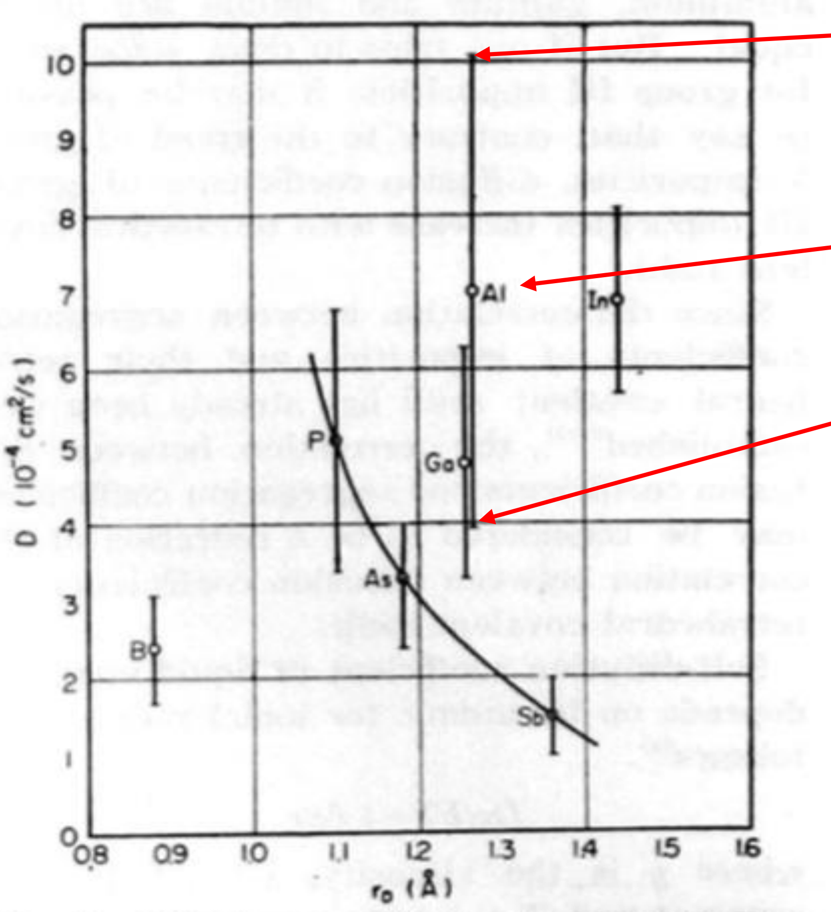


Fig. 5. Diffusion coefficients of impurities in silicon melt plotted against tetrahedral co-valent radii.

$\omega = 5\ rpm, \quad \frac{Gr}{Re^2} < 1$ NC dominated

$\omega = 55\ rpm, \quad \frac{Gr}{Re^2} \sim 1$ FC and NC

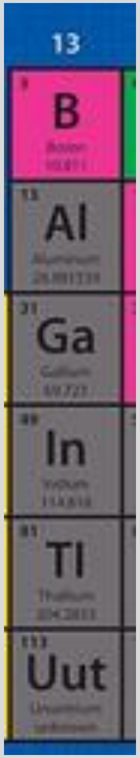
$\omega = 200\ rpm, \quad \frac{Gr}{Re^2} << 1$ FC convection

Issues :

- $D_{crystal}$= ?
- D_{melt}=?
- Viscosity

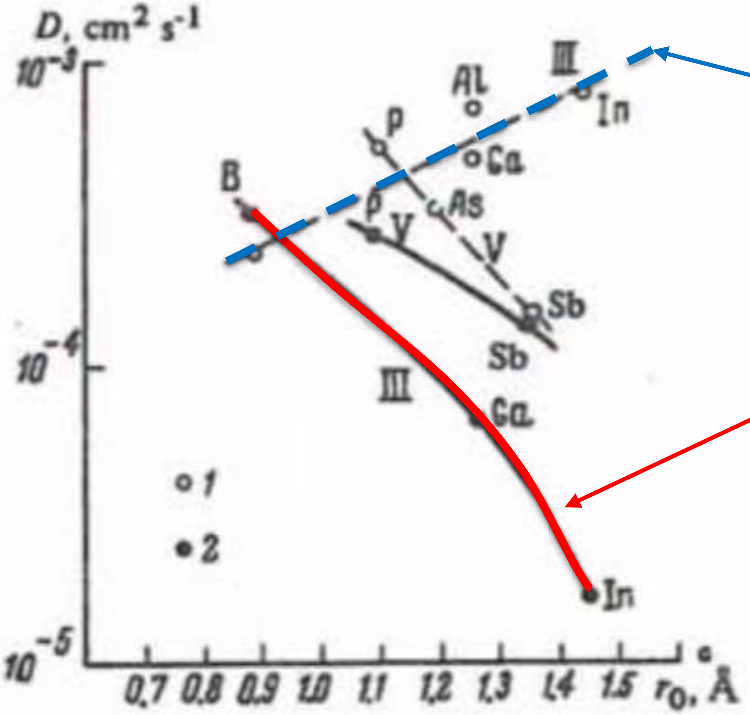
Erroneous trend

$D_B < D_{Ga} < D_{In}$



- “Inflated” ***D***-values were obtained at low rotation rates (5 and 10, 12 RPM)
- BPS model: laminar flow driven by an infinite rotating disc.
- Buoyancy driven flow is ignored,
- Schmidt number, Sc = v/D is assumed to be infinite, although it is 10<Sc<30.

Silicon 3 Capillary-Reservoir



Shaskov and Gurevich
Capillary – reservoir (1968)

Kodera
CZ growth (1963)

Figure 1. Relationship between the diffusion coefficients and the tetrahedral radii for impurities of groups (III) and (V):
1) our experimental data; 2) published data[2].

Yu.M. Shaskov and V.M. Gurevich, Russian J. Physical Chemistry 24 (1968) 1082-1083.

Proposed Experiments 1:

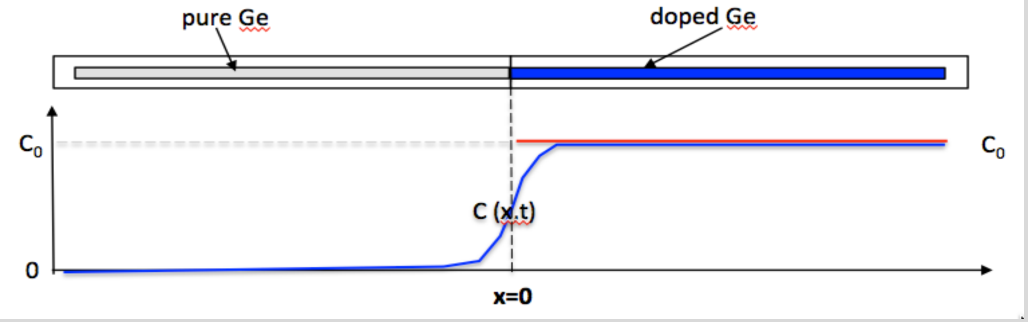
Bundle of capillary tubes in Sample Cartridge Assembly (SCA)

Earth:

- SCA → horizontal furnace
- SCA → Small furnace/magnet

ISS μg

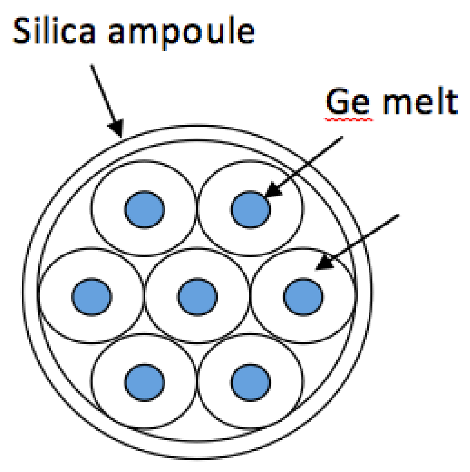
- **SCA → LGF**



- two capillary tube sections, joined by the fastener nut.
- Quartz (graphite, BN ?)
- On earth, transverse magnetic fields
- ANSYS, to optimize the geometry, justify magnets…

Proposed Experiments 2:

Bridgman growth, bundle of 3 mm to 5 mm ampoules



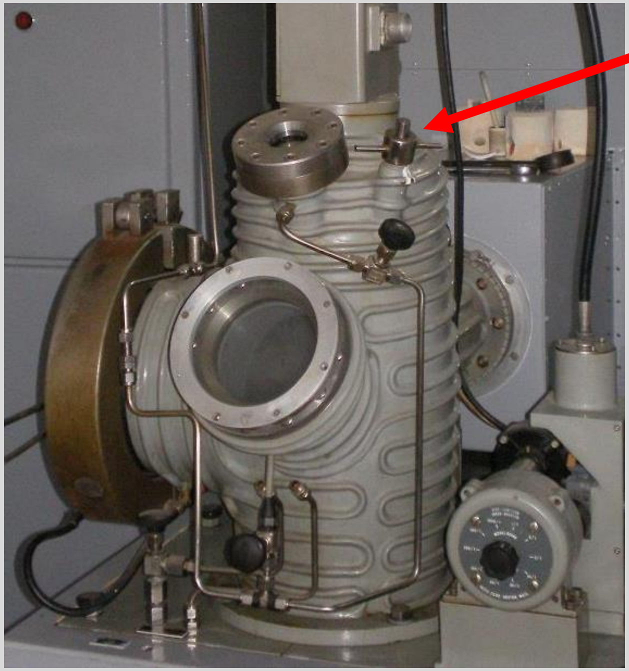
- On Earth: 17 zone Mellen furnace.
- **ISS, at 1 µg LGF**

- Grow bundles of doped Ge crystals in silica ampoules
- **Seven in SCA**
- High growth rate.
- 7 axial profiles, Cs(x) will be produced in each experiment.
  - ✓ Low radial segregation; 1D concentration profile, C(x);
  - ✓ Fat solid-liquid interface
  - ✓ Gr reduced ~ 100x lower Gr compared to the experiment by Witt at al.

$$\frac{Gr_{d=10mm}}{Gr_{d=3mm}} \sim \frac{d^3_{10mm}}{d^3_{3mm}} \times \frac{\Delta T_{10mm}}{\Delta T_{3mm}} \sim 100 \ \ to \ \ 1000$$

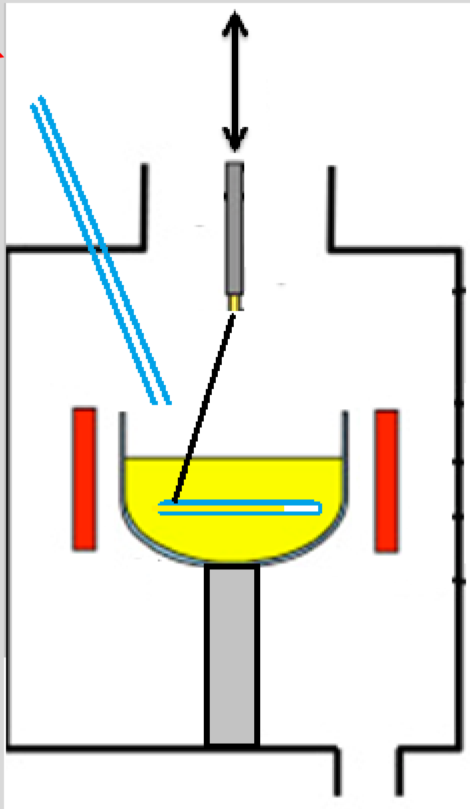
Proposed Experiments 3:
Capillary-Reservoir method

Doping port



ADL MP (20 atm) CZ puller

Ge
and Si



- Reservoir is CZ melt is doped.
- Buoyancy driven flow ensures that the reservoir is “perfectly mixed”
- Vacuum to empty the capillary. Ar in, to force melt into capillary
- At t=0, dope the melt
- At t_{end}, freeze (withdraw the capillary).
- ANSYS, to optimize the geometry (d, L=?) pulling rate. t_{end} = ?

Proposed Experiments 4:

CZ growth supported by modeling; Ge and Si

- ANSYS
- k_{eff} based on Nusselt number correlations

$$\delta \to Nu_M = \frac{h_M\, L}{D}$$

$$\mathrm{Re} = \frac{\omega R^2}{\nu}$$

$$Gr_d = \frac{g\,\beta\,\Delta T\, d^3}{\nu^2}$$

$$\frac{Gr}{\mathrm{Re}^2} << 1$$

Summary

The fidelity of the FE models is only as good as the diffusion coefficients.

Goal:

- to determine D of dopants in Ge and Si melts
- D at the S/L interface – in the solute layer
- Capillaries, Bridgman, with/without magnets
- Si melts: Capillary-Reservoir method, CZ growth.
- Determine sources of errors; temperature dependence
- Experiments in LGF furnace → to obtain reference D-values.

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