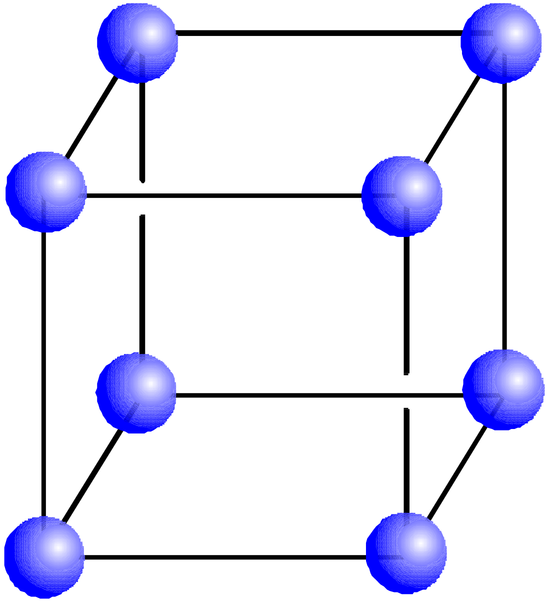
Hartmut S. Leipner, Reinhard Krause-Rehberg

Structure of imperfect solids (2)



A. Advanced topics
B. Methods

Syllabus

1–2. Defects and crystal growth
3–4. Defects and semiconductor technology
5–7. * Defect engineering; diffusion
8. Optical methods
9. * Electrical methods
10. * Positron annihilation
11. * Resonance techniques
12. X-ray methods
13. * Probe techniques

(* given by Reinhard Krause-Rehberg)

Summary

As the continuation of the introduction into crystal defects (in the SS 2001), advanced topics of solid state physics related to defects are treated in this semester. Topics are the crystal growth from the point of view of crystal imperfections, diffusion in solids, and the role of defects in the production and the function of solid state devices.

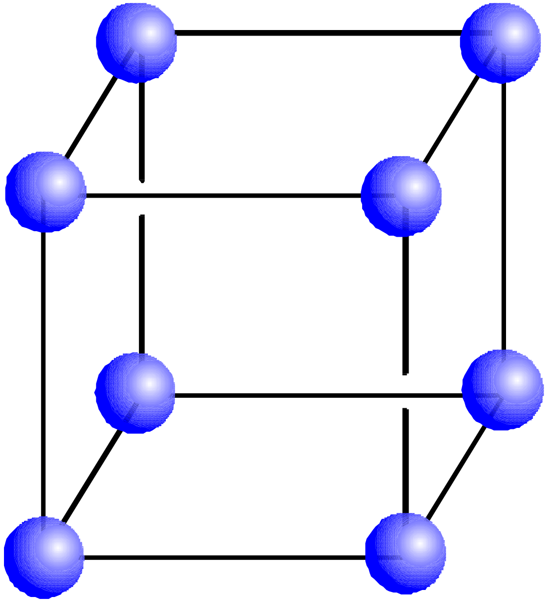
In the second part of this lecture, basic experimental techniques of the investigation of defects are introduced. The following methods are treated: optical and electrical methods (luminescence, Hall effect, DLTS), X-ray techniques, probe and resonance techniques (positron annihilation, pertubed angular correlation, electron paramagnetic resonance). The pieces of information to be extracted from the particular methods for the characterization of the defect structure are discussed.

Literature

- K.-T. Wilke: *Kristallzüchtung*.
  Berlin: Deutscher Verlag der Wissenschaften 1988.
- *Silicon devices*. Ed. K. A. Jackson.
  Weinheim: Wiley-VCH 1998.
- *Bergmann Schäfer Lehrbuch der Experimentalphysik*. Band 6 Festkörper. Hrg. W. Raith. Berlin: De Gruyter 1992.
- B. G. Jacobi, D. B. Holt: *Cathodoluminescence microscopy of inorganic solids*. New York: Plenum 1990.
- S. Pfüller: *Halbleitermeßtechnik*. Berlin: Verlag Technik 1976.
- G. Schatz, A. Weidinger: *Nukleare Festkörperphysik*.
  Stuttgart: Teubner 1992.
- *Identification of defects in semiconductors*. Ed. M. Stavola.
  San Diego: Academic Press 1998

Hartmut S. Leipner

1. Crystal growth and defects



- 1.1 Methods of crystal growth
- 1.2 Nucleation theory
- 1.3 Kinetics of crystal growth
- 1.4 Impurity distribution

1.1 Methods of crystal growth

Historical digression

- Mass crystallization in ancient technologies: bronze, iron
- Development of ceramic industry; salt crystallization
- Term crystal originates from Greek *κριος* (coldness) or *κριμος* (ice)
- Development of philosophy related to crystallographic ideas: conjugation of four elements and the definition of regular solids (Aristotle, Plato)

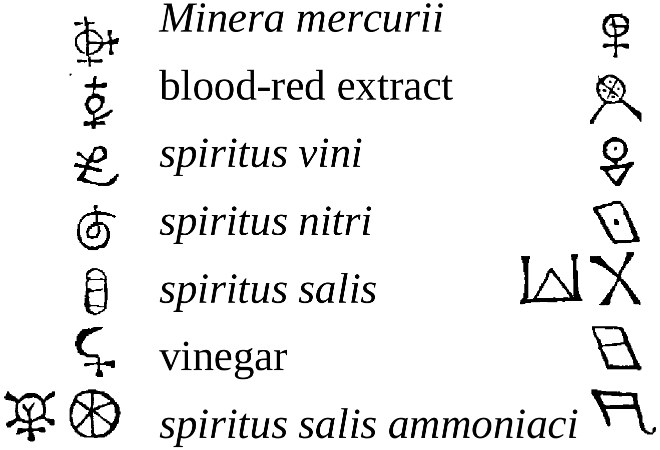
Snow flakes from the work *Kristallseelen* of Haeckel (1917)

Snow flakes [Scheel:93]

Philosopher's stone

[redacted]

Alchemical recipe for preparation of a universal medicine (*quinta essenca*), discovered in 1403 and published in 1769



Minera mercurii

blood-red extract

spiritus vini

spiritus nitri

spiritus salis

vinegar

spiritus salis ammoniaci

spiritus tartari

caput mortuum

oil of *materia philosophorum*

melt furnace

moderate fire

melting

liquid as a water

▷ Philosopher’s stone recipe [Scheel:93]

Verneuil technology

- First commercial process for growing large crystals
- Synthesis of sapphire and ruby for jewelry and watch stones; laser rods
- General application to substances with a high melting point

Flame fusion growth apparatus of Verneuil

Verneuil [Scheel:93]

Principle of the Verneuil method

owder

Gas burner

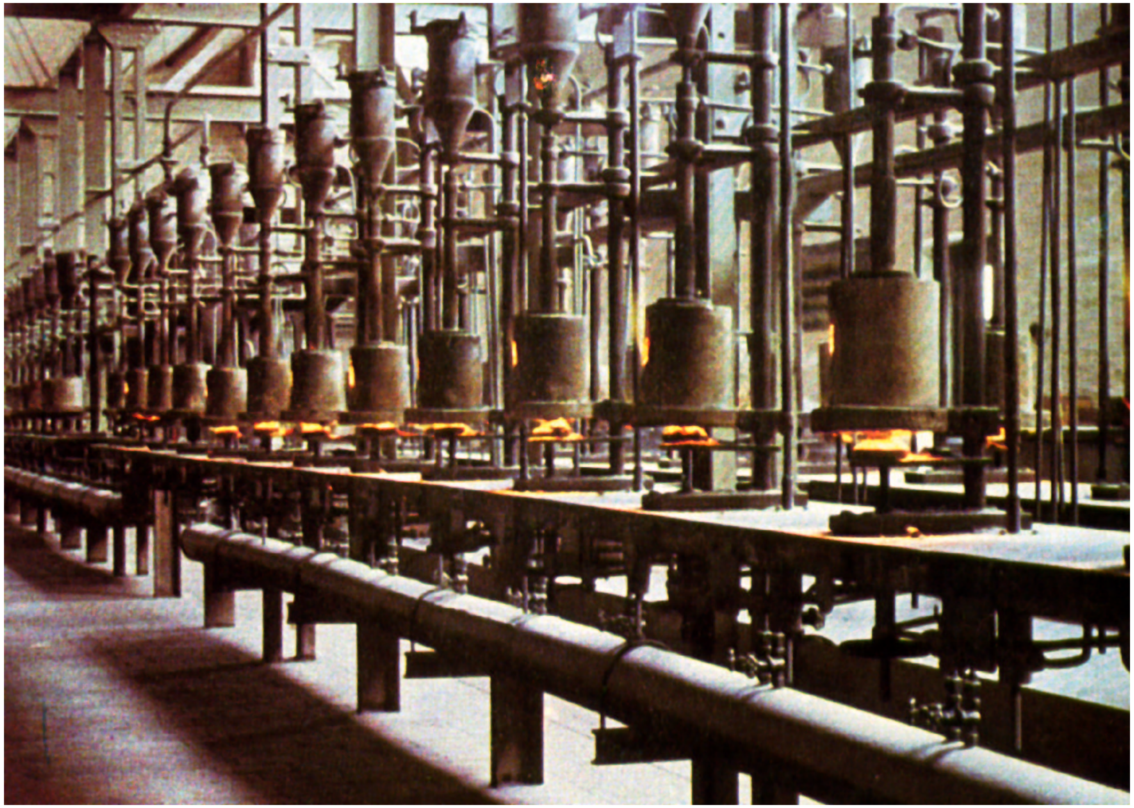
Growing
e crystal

ement
of the crystal

Crystal growth from the melt
according to Verneuil

Flame fusion [Weißmantel:89]

Ruby production line



Ruby production line according to the Verneuil technique in the Chemiekombinat Bitterfeld (around 1970)

Electrolytic gas burner with a growing crystal

Verneuil Bitterfeld
Verneuil burner [Große:79]

Growth from the solution

- Application for substances which do not melt or suffer phase transitions
- Supersaturation by cooling or evaporation of the solvent
- Salts; organic crystals

High-pressure synthesis of quartz and diamond

- Special procedure of hydrothermal synthesis of quartz (transition between growth from the solution and from the vapor phase)
- H_2O above the critical point can solve high amounts of otherwise insolvable substances
- High-pressure synthesis of diamond from carbon solved in a Ni melt (10^{10} Pa, 2500 °C)

b. C.

1940

1953

Crystal growth from the melt

Crystallization at a cooled finger according to Kyropoulos (*a*)
and the selection of the seed (*b*)

Kyropoulos [Scheel.93]

Bridgman method

Scheme of the Bridgman technique.
1 crucible, 2 growing crystal, 3 seed, 4 furnace.

Bridgman [Kleber:90]

Stress cracking

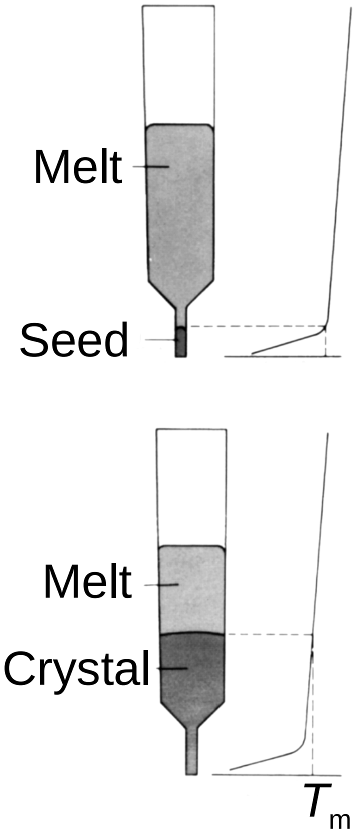
Stress cracking in a single crystal of InP grown in a silica crucible with B_2O_3 encapsulant [Monberg:94]

Horizontal Bridgman growth

Modified horizontal Bridgman furnace configuration for the growth of GaAs

Horizontal Bridgman [Monberg:94]

Vertical gradient freeze technique



Vertical gradient freeze temperature profile (T_m melting temperature) and configuration for the liquid encapsulated VGF growth of GaP

VGF profile
VGF [Monberg:94]

Pulling technique according to Czochralski

Pull rod

Seed

Envelope

r. f. coil

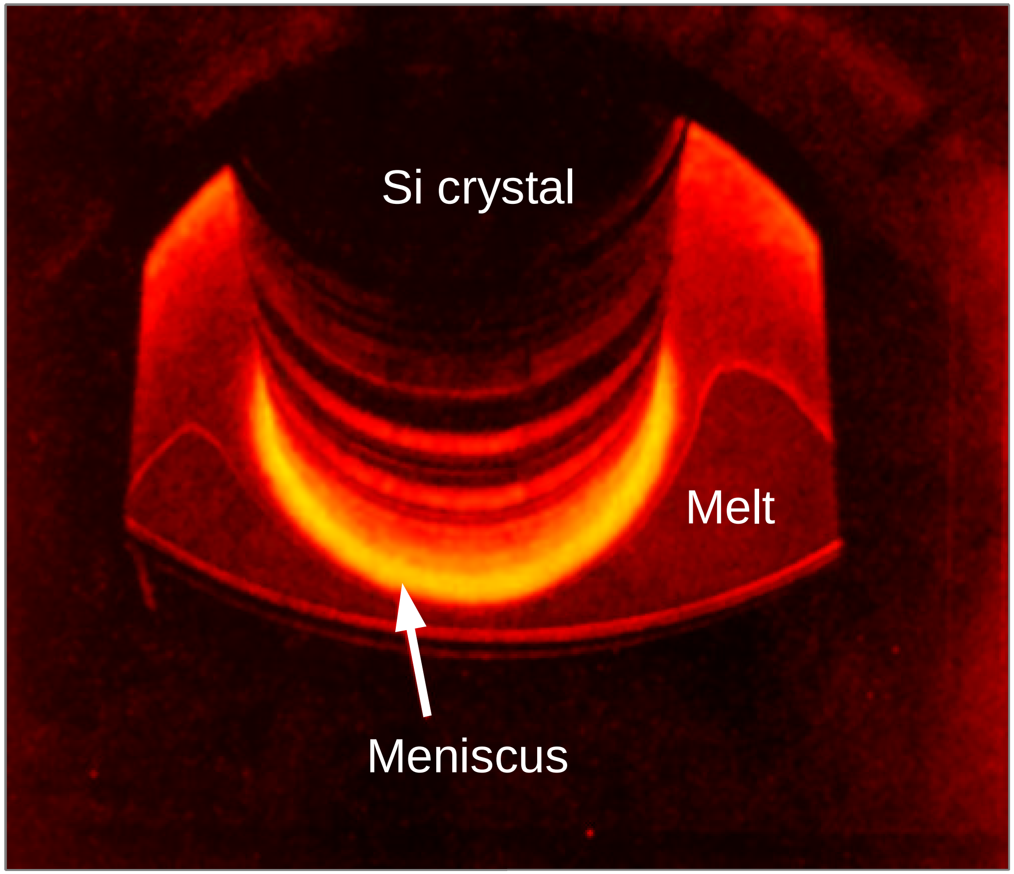
Melt

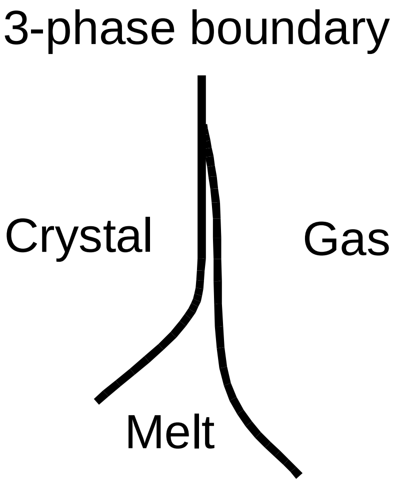
Crucible/ susceptor

Czochralski method of crystal growth from the melt

Czochralski [Hurle:94]

Czochralski growth





Silicon crystal being pulled. The arrow shows the meniscus bright ring.

▷ Meniscus colored [Hurle:94]

Liquid encapsulation

Crystal

Boric oxide

Quartz or
PBN crucible

Graphite

Melt

Scheme of the liquid encapsulation principle used for the growth of compound semiconductors (PBN – pyrolytic boron nitride)

Encapsulation [Hurle:94]

Floating zone melting

Scheme of crucible-free zone melting.

1 rod holder, 2 melting polycrystal, 3 molten zone, 4 induction coil, 5 growing single crystal.

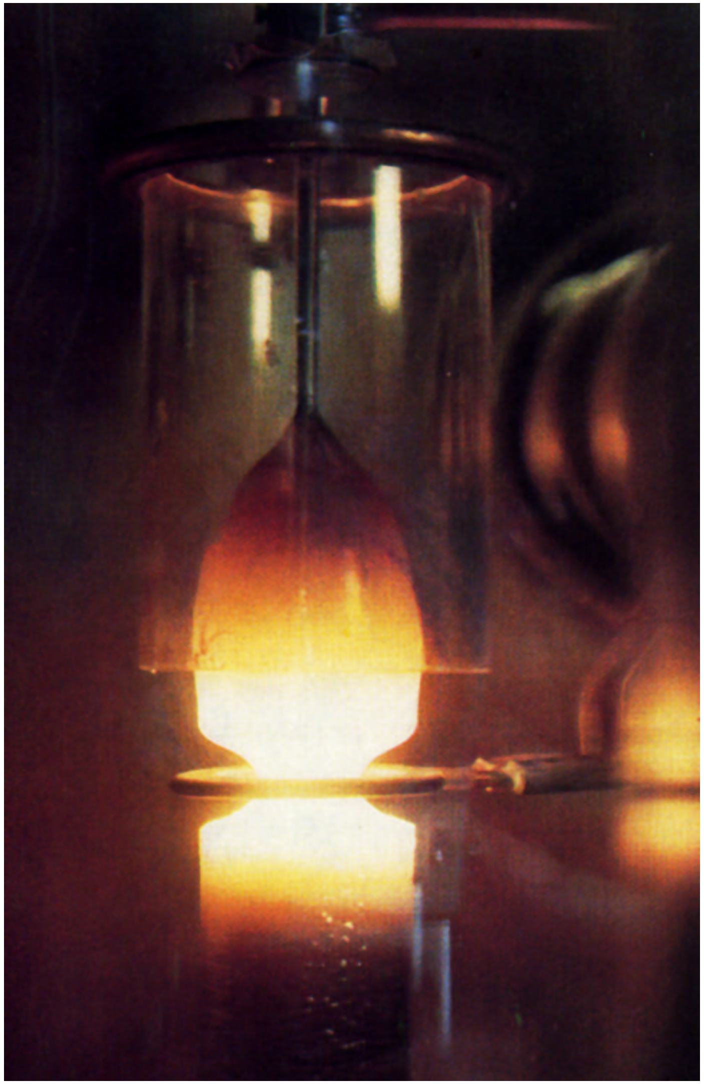
Maximum zone length

$$h_{\mathrm{max}} = 2.8\sqrt{\frac{\sigma}{g\,\rho}}$$

σ surface tension
g gravitational acceleration
ρ density of the liquid

FZ [Wilke:88]

Float zone growth of Si



Float zone growth of silicon

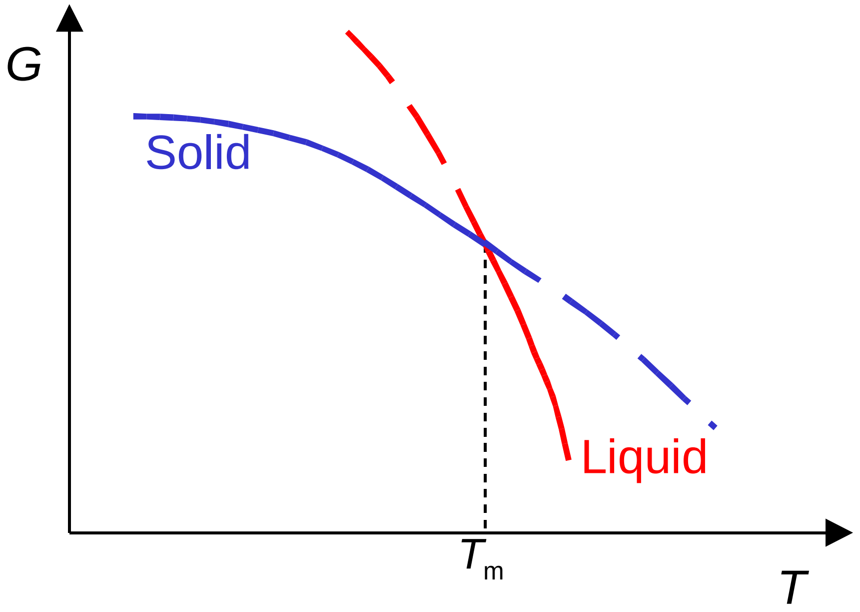
FZ Si growth [Große:79]

Convection and phase boundaries

Convection scheme and phase boundaries (*a*) for low and (*b*) for higher pull rates. 1 feed rod, 2 molten zone, 3 inductor, 4 limiting diffusion layer, 5 crystal rod with isotherms.

1.2 Nucleation theory

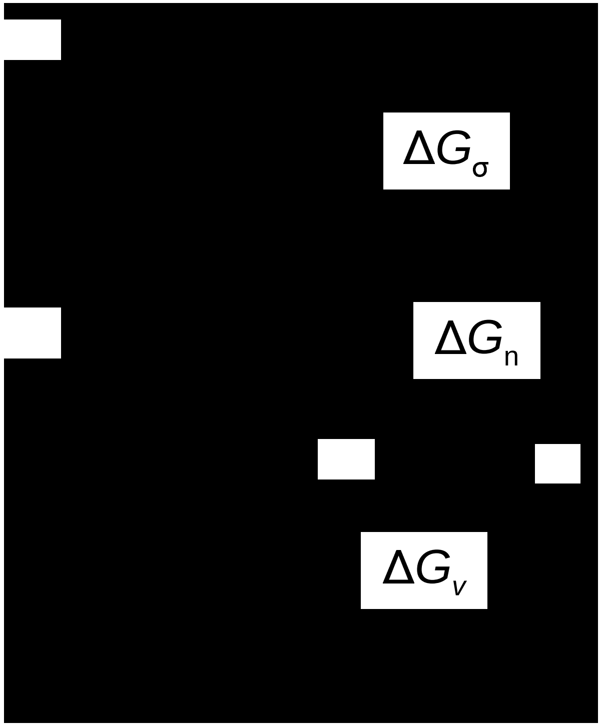
- Crystallization as a 1st order phase transition, at T_m: $\Delta G = 0$
- From the thermodynamic definition of $G = H - TS$ follows for the melting heat $\Delta H = T_m \Delta S$
- Formation of a well defined phase boundary



Course of the free enthalpy G as a function of the temperature T for constant pressure

Homogeneous nucleation

- Crystallization does not set in immediately when the stability region of the crystal is reached in the phase diagram
- Certain supersaturation or supercooling necessary for spontaneous nucleation
- Change in the free enthalpy during nucleation



$$\Delta G_n = \Delta G_V + \Delta G_\sigma = \frac{4}{3}\pi r_n^3 \Delta g/v + 4\pi r_n^2 \sigma$$

(Δg difference of the molar free enthalpies of both phases, v molar volume of the crystal, σ specific free surface energy)

Change in the free enthalpy ΔG_n as a function of the radius of the nucleus r_n ($\Delta G_V^* < 0$ volume part, ΔG_σ^* surface part, ΔG_n nucleation work, r_n^* critical radius).

Nucleation [Kleber:90]

Critical radius

$$r^* = \frac{2\,\sigma\,T_m}{\Delta H\,\Delta T}$$

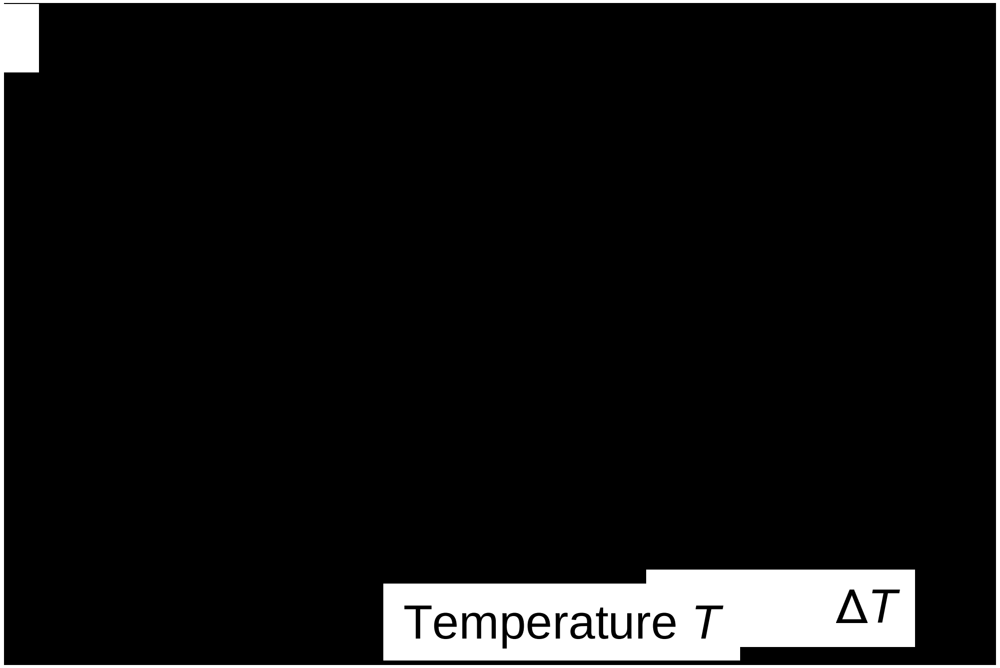
$$(\Delta T = T_m - T)$$

Material	T_m/°C	$\Delta H/10^6\ \mathrm{J\,m^{-3}}$	$\sigma/10^{-3}\ \mathrm{J\,m^{-2}}$	ΔT/K
Ga	30	488	56	76
Pb	327	237	33	80
Cu	1085	1628	177	236
Fe	1538	1737	204	420
H_2O	0			40

[Askeland:98]

Typical undercooling for homogeneous nucleation

Nucleation rate



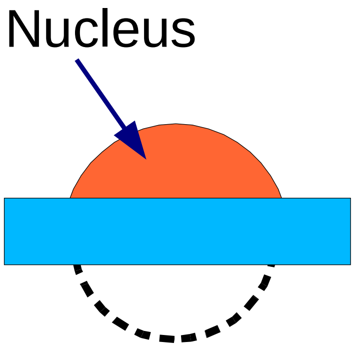
Nucleation rate J and growth velocity v_g as functions of the supercooling ΔT.

T^* is the critical nucleation temperature.

$$J = A \exp\left(-\frac{\Delta G_n^*}{k_B T}\right) = \tilde{A} \exp\left(-\frac{\Delta G_n^* + \Delta G_d^*}{k_B T}\right)$$

Growth rate [Kleber:90]

Heterogeneous nucleation



- Crystallization at foreign particles (dust), container walls or substrates
- Use of a seed (*Impfkristall*, *Keimkristall*)
- Two steps: a) formation of an adsorption layer, b) formation of a critical nucleus in this layer and its growth
- Rate of heterogeneous nucleation:

$$J_{\mathrm{het}} = \tilde{A}\, k_{\mathrm{B}} T \exp\left(-\frac{\Delta G^{*}_{\mathrm{het}} + \Delta G_{\mathrm{d}} - \Delta G_{\mathrm{a}}}{k_{\mathrm{B}} T}\right)$$

- $\Delta G^{*}_{\mathrm{het}} < \Delta G^{*}_{\mathrm{n}}$, ΔG_{d} activation energy of diffusion in the adsorption layer, ΔG_{a} adsorption energy
- Lower value of the critical supersaturation

1.3 Kinetics of crystal growth

Nucleation sites on a crystal surface

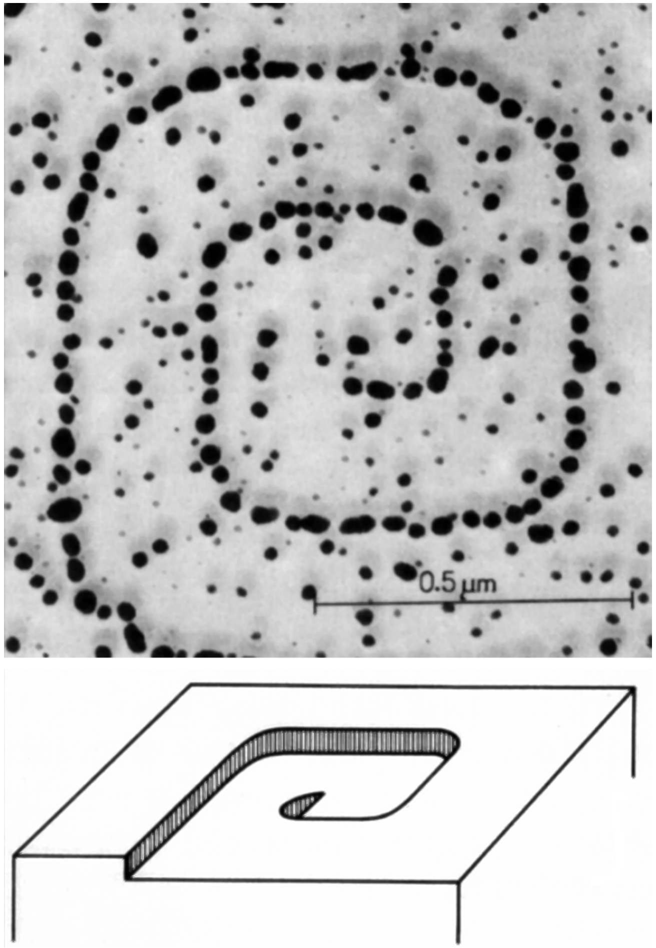
→ highest energy gain for nucleation in the ***halfcrystal position*** *1*

Relative nucleation energies in different positions for the NaCl structure

ϕ_1	ϕ_2	ϕ_3	ϕ_4	ϕ_5	ϕ_6
0.8738[*]	0.1806	0.0662	0.4941	0.2470	0.0903

[*] Half the Madelung constant of the NaCl structure

Growth spirals



Decoration of a spiral monoatomic step on a KBr surface by evaporation of Ag. The growth spiral is caused by the presence of a screw dislocation.

[Bethge *et al.* 1987]

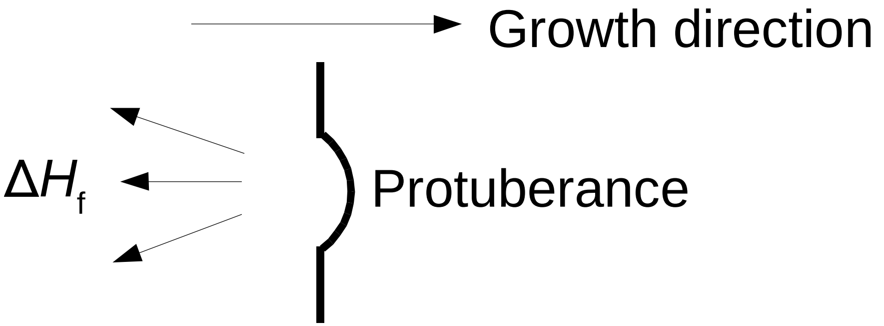
Shape of crystals

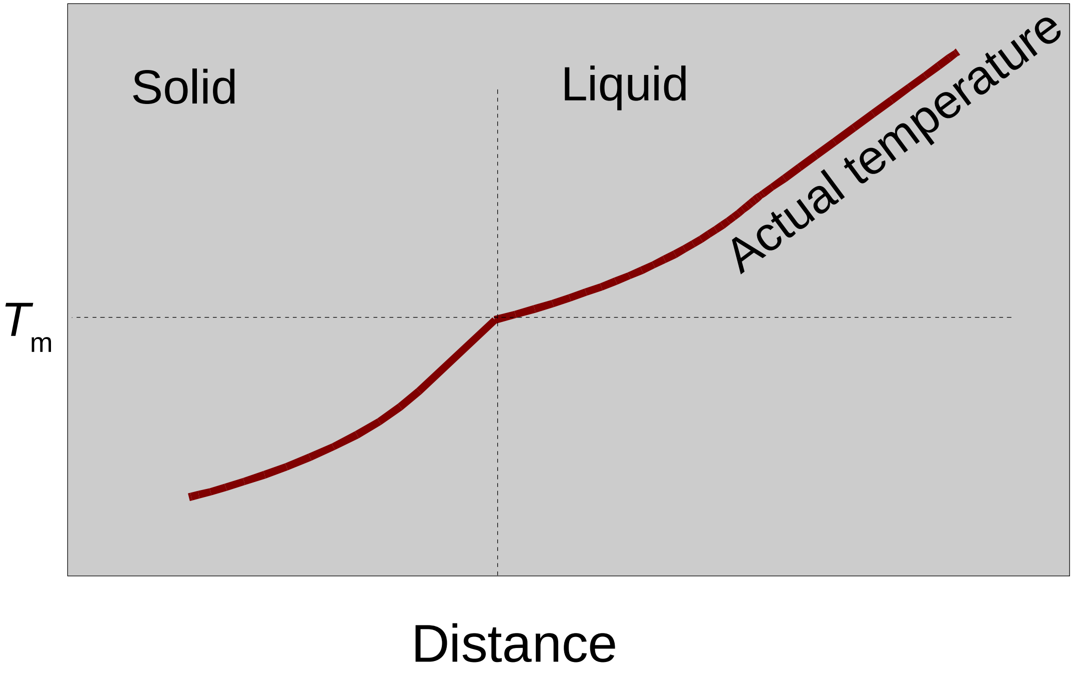
- Final shape of crystal determined by planes with lowest growth velocities
- Depends on external parameters of crystallization, *e.g.* impurity content (***exomorphosis***)

Kinematics of the growth of a sodium alum crystal. The relative growth velocities are for {111}: 1.0, {110}: 4.8, {001}: 5.3, {221}: 9.5, {112}: 11.0. The faces with higher growth rates are more and more eliminated; the remaining planes are of the {111} type.

Crystal shape [Kleber:90]

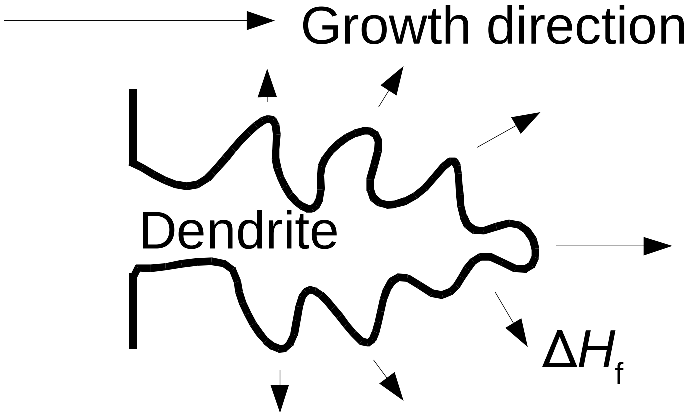
Planar growth

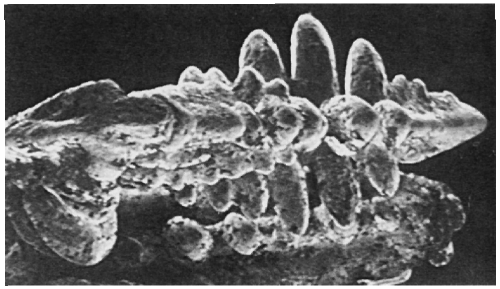




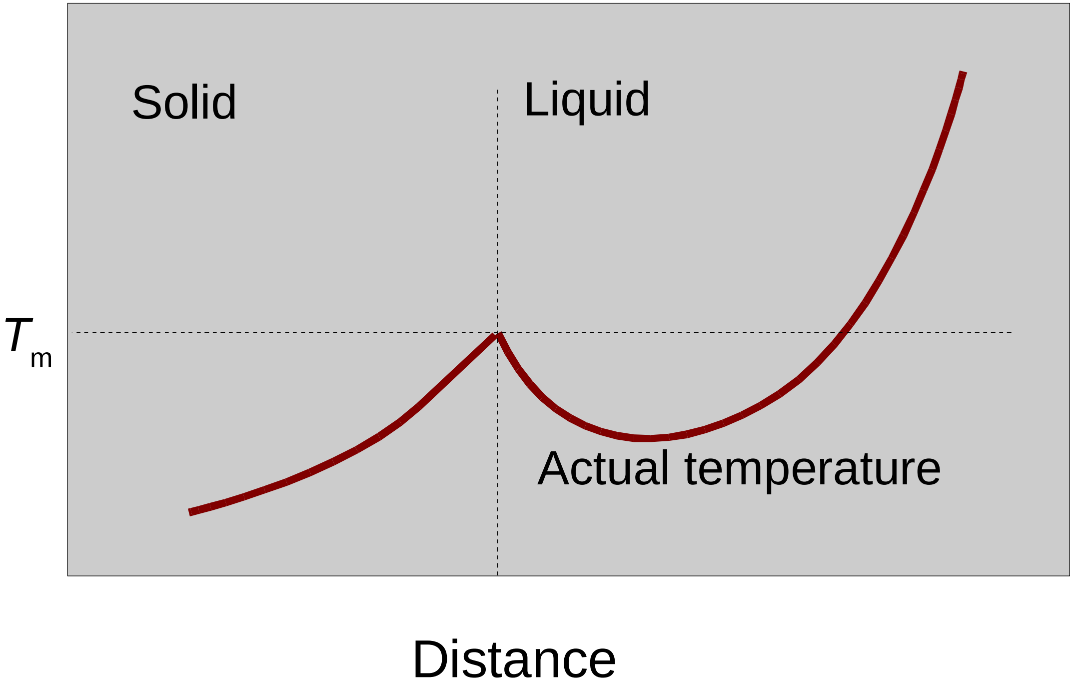
When the temperature of the liquid is above the freezing temperature, a protuberance on the solid–liquid interface will not grow, leading to maintance of a planar interface. Latent heat is removed from the interface through the solid.

Dendritic growth





Dendrites in steel
[Askeland:98]

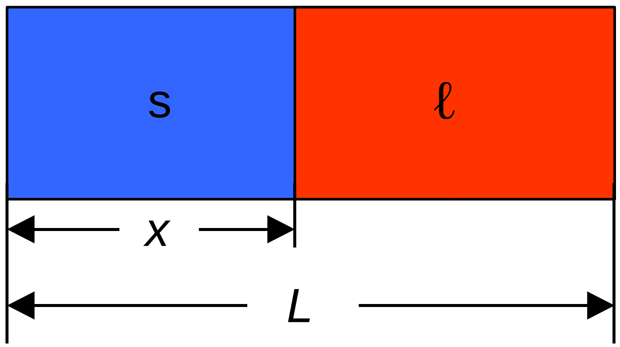


If the liquid is strongly undercooled, a protuberance on the solid–liquid interface can grow rapidly as a dendrite. The latent heat of fusion is removed by raising the temperature of the liquid back to the freezing temperature.

1.4 Impurity distribution

- Distribution of dissolved impurities at the phase boundary given by the distribution coefficient $\kappa = c_s/c_\ell$

  (c_s, c_ℓ concentration in the solid, liquid phase)
- Normally, $\kappa < 1$, enrichment of foreign atoms in the melt



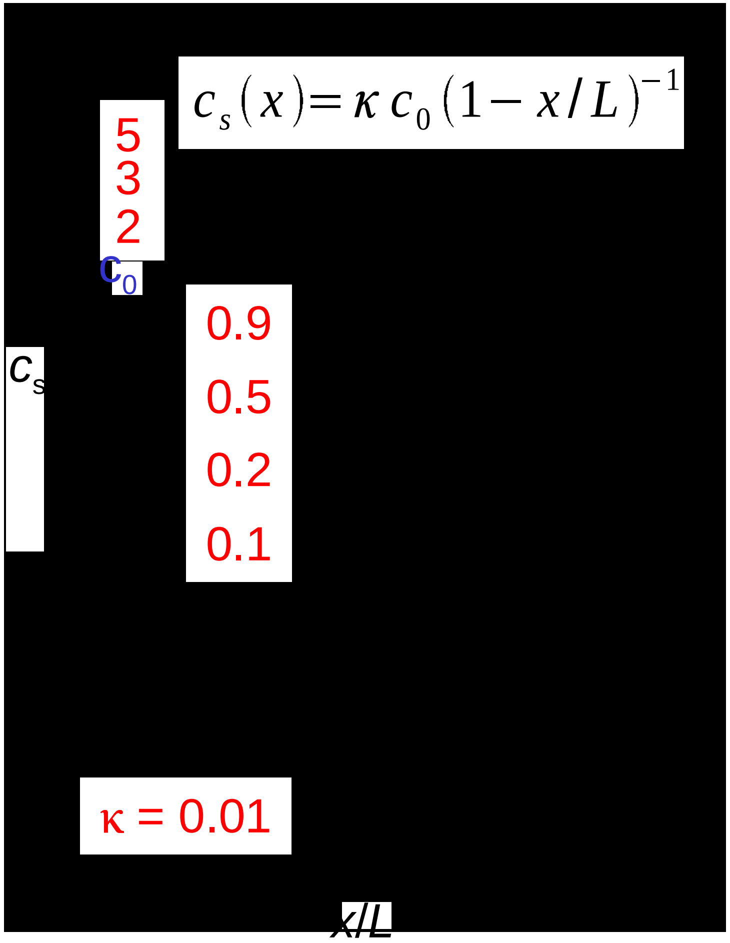
$$c_s(x) = \kappa\, c_\ell = \kappa \frac{L\, c_0 - \int_0^x c_s(\xi)\, \mathrm{d}\xi}{L - x}$$

$$\frac{\mathrm{d}\, c_s(x)}{\mathrm{d}\, x} = (1 - x) \frac{c_s(x)}{L - x}$$

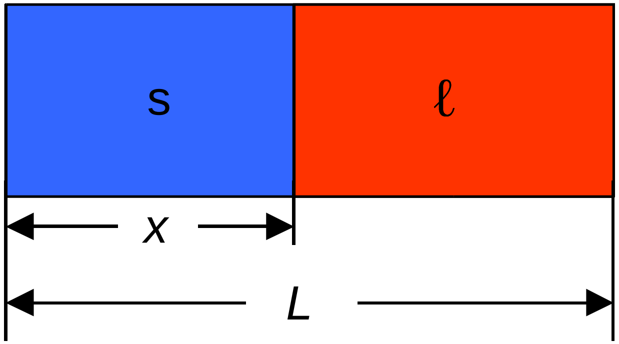
Solution of the differential eq.

$$c_s(x) = \kappa\, c_0 (1 - x/L)^{-1}$$

Impurity concentration



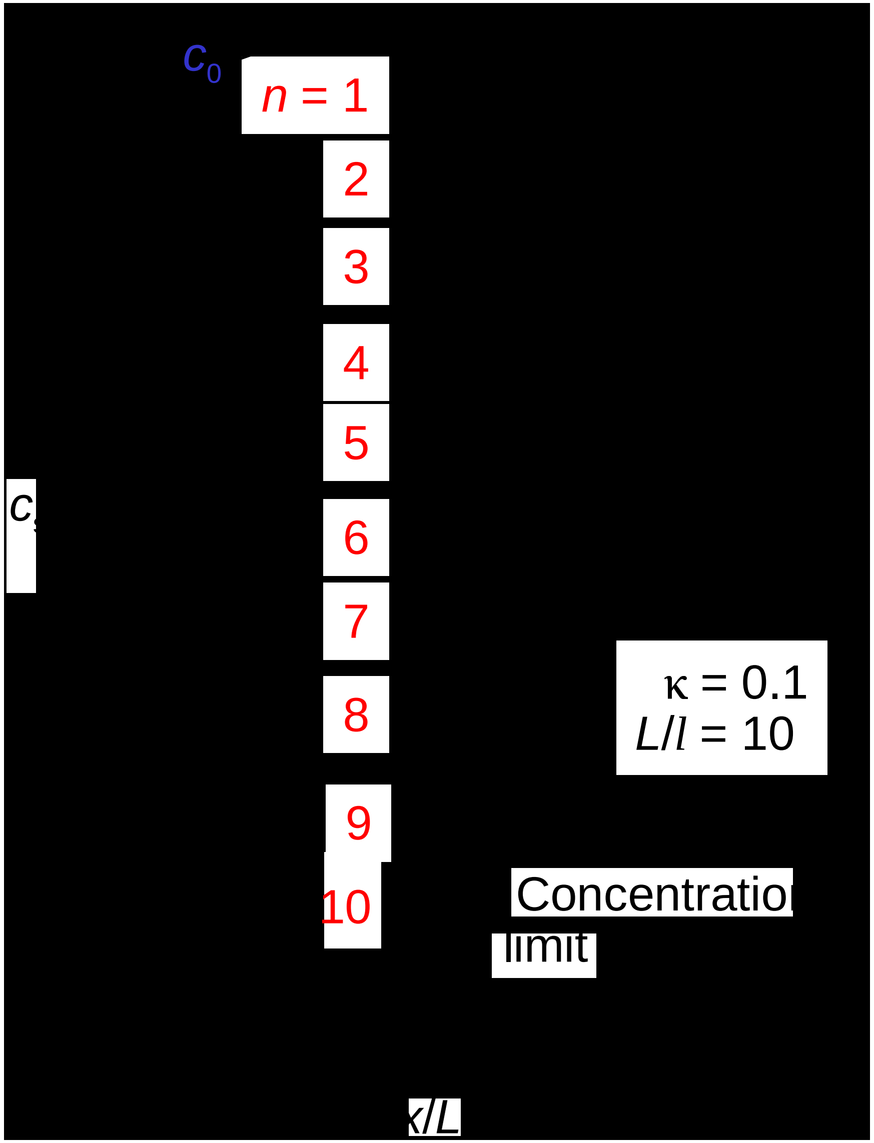
$$c_s(x) = \kappa\, c_0 (1 - x/L)^{-1}$$

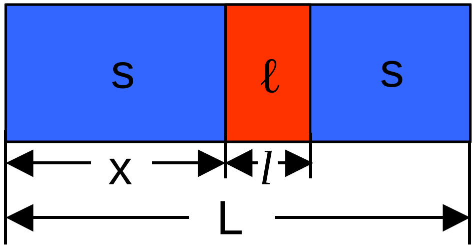


Course of the impurity concentration c_s as a function of the amount of material in the melt x/L for different distribution coefficients κ

Impurity distribution function [Weißmantel:89]

Cleaning by float-zone melting



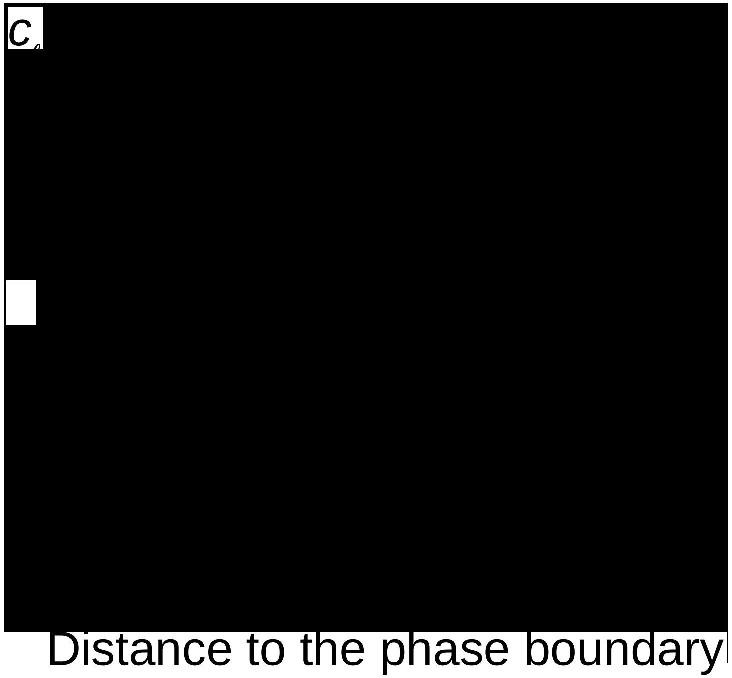


$$c_s(x) = c_0[1-(1-\kappa)\exp(\kappa\frac{x}{l})]$$

Concentration c_s as a function of the amount of material in the melt x/L for the first until the 10th run n for a distribution coefficient κ = 0.1 and L/l = 10

FZ cleaning [Weißmantel:89]

Constitutional supercooling



Enrichment of components with $\kappa < 1$ at the growth front resulting in the shown change in the melting temperature. *I* and *II* are possible slopes of the temperature in the liquid phase.

- ***Constitutional supercooling***

  case *II* gives an unstable plane growth front
- Condition for the ratio of the temperature gradient and the growth velocity v_g can be given; v_g should not be smaller than a certain value for a plane phase boundary

Constitutional supercooling [Kleber:90]

Striations

- Local fluctuations of the growth velocity – variation in the distribution coefficient
- Typical inhomogenities in the distribution, which reflect the course of the phase boundary during growth

Striations in a Si wafer visualized by double-crystal X-ray topography.

The marker corresponds to 1 mm.

[Höche, Brümmer 1980]