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Perfect Crystals and Epitaxial Layers: Proposed Education of Crystal Technologists

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Perfect Crystals and Epilayers:
Proposed Education of Crystal Technologists

Dislocations

Inclusion-free Crystals

Forced Convection

Striation Problem

Epitaxy Growth Modes, Liquid Phase Epitaxy

High Temperature Superconductivity

$SrTiO_3$ Story > Sufficient Characterization

Crystal Technology for Energy

Complexity of Optimized Crystal Fabrication

Education of Crystal Technologists

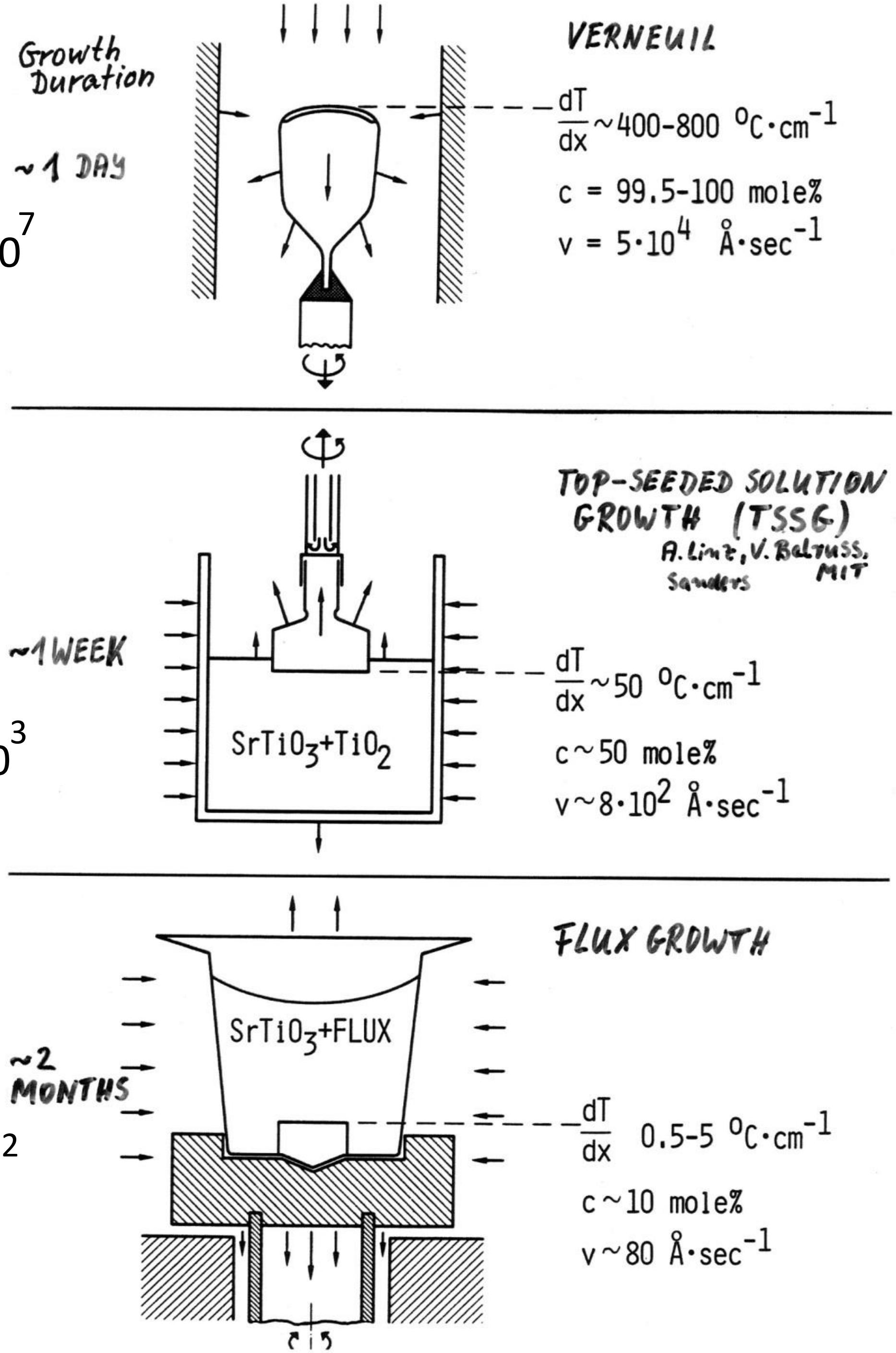
Conclusions

Dislocations & Temperature Gradient

J.G. Bednorz & H.J .Scheel
J. Crystal Growth **41**(1977)5-12

$SrTiO_3$

V. Belruss, J. Kalnajs, A. Linz
Mater.Res.Bull . **6**(1971)899-906



$10^6 - 10^7$

$10^2 - 10^3$

$0 - 10^2$

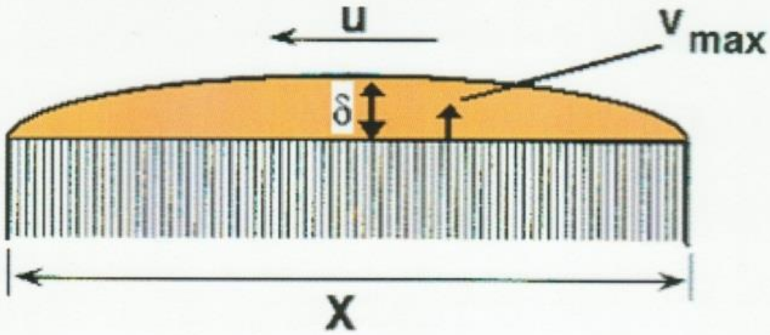
EPD / cm ^{2}

Dislocations

W.C. Dash 1959; E. Billig 1956
H. Alexander & P. Haasen 1968
A.S. Jordan et al. 1980/1985
J. Völkl & G .Müller 1989
X-Ray Topography & Pol.Microsope
A.R. Lang 1970 J.W. Matthews
A. Authier 1970
H. Klapper 1975

H.J. Scheel, J.G. Bednorz, P. Dill
Ferroelectrics **13**(1976)507-509
H.J. Scheel:
Z.f.Kristallographie1**43**(1976)417-428

Conditions for stable growth



$$\delta_t = \left[2/3 \cdot Sc^{1/3} \cdot \left(\frac{\rho_s u}{\eta X} \right)^{1/2} \right]^{-1} \quad (1)$$

$$v_{max} = \left(\frac{0.214 \; D \, u \, \sigma^2 \, n_e^2}{Sc^{1/3} \rho^2 X} \right)^{1/2} \quad (2)$$

Sc = Schmidt Number = $\frac{\eta}{\rho_s D}$ $\sigma = \frac{n_s - n_e}{n_e}$

δ = thickness of the solute diffusion boundary layer

n_e = equilibrium solute concentration

n_s = concentration in the bulk of the solution

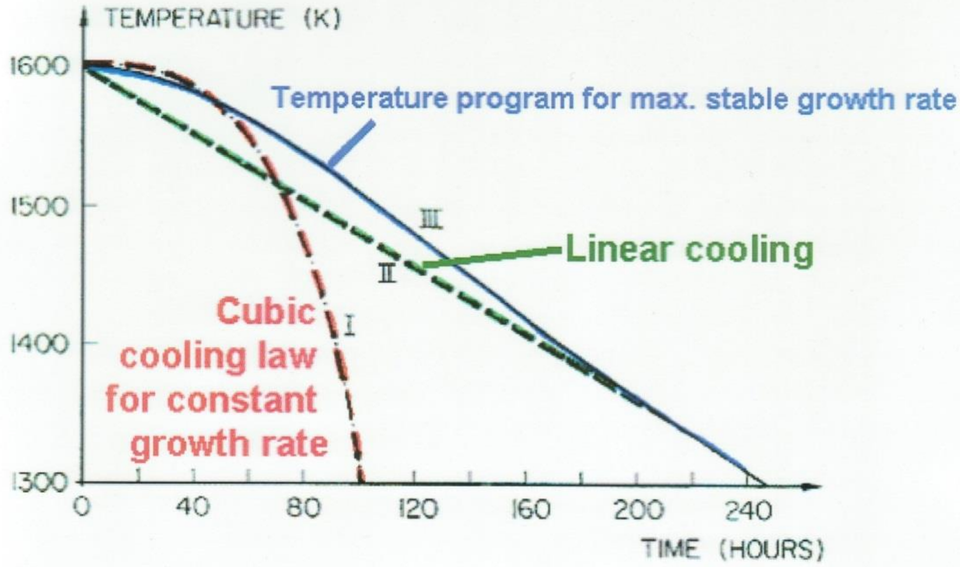
ρ_s = density of the solution

u = solution flow rate ($u \approx 0.1$ cm/s for stirring by natural convection)

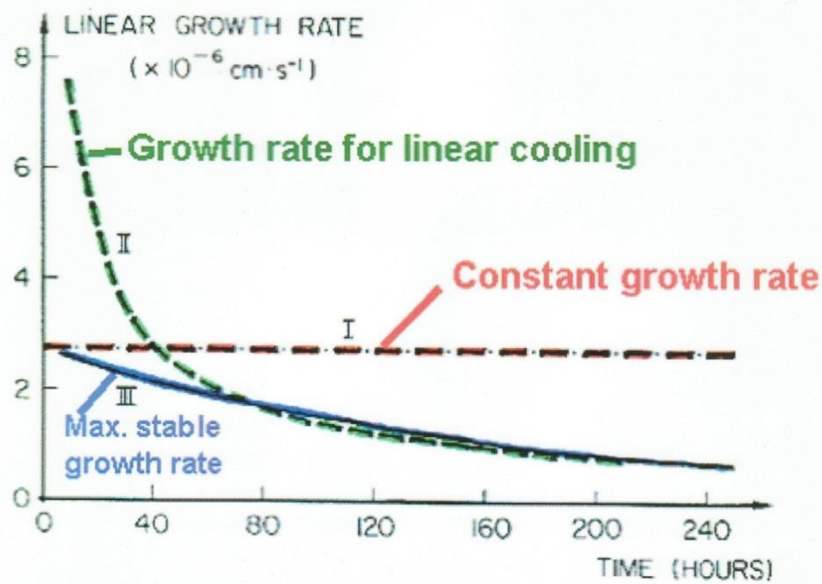
Growth of Inclusion-free Crystals

Maximum Stable Growth Rate

A.Carlson, PhD Thesis 1958
H.J. Scheel, D.Elwell: JCG 12(1972)153
D. Elwell, H.J. Scheel: Ch.6 in «*Crystal Growth from High-Temperature Solutions*« 1975
Hergt & Goernert: Confirmation in phys. stat. solidii A21(1974)



(a)



J. Crystal Growth 12 (1972) 153. (H. J. Scheel, D. Elwell)
& Ch. 6 of Elwell & Scheel book

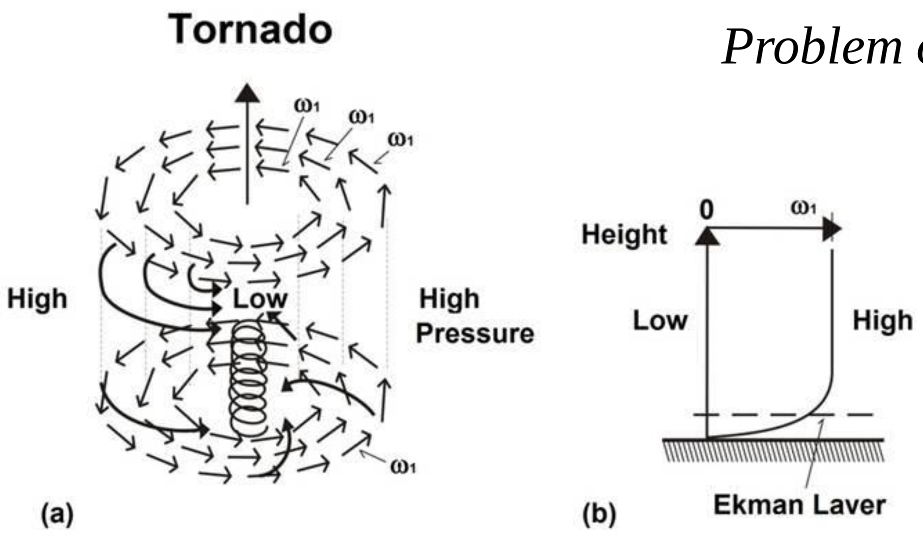
Observed Maximum Stable Growth Rates

(For 1cm crystals)

Crystal	Solvent	Concentration	v_{max} (Å s^{-1})
$SrTiO_3$	TiO_2	~50%	800
$Y_3Fe_5O_{12}$ (YIG)	PbO-PbF_2-B_2O_3	~30%	500
$GdAlO_3$	PbO-PbF_2-B_2O_3	~15%	250
$YBa_2Cu_3O_{7-x}$	BaO-CuO	~2%	30
ADP "Fast Growth"	H_2O	~40%	1300*

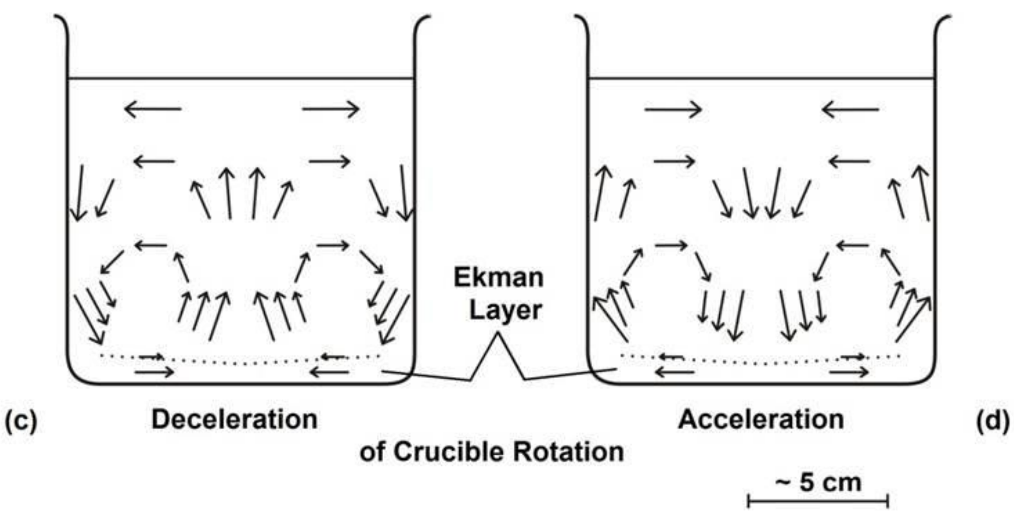
* 600 g ADP in 1l solution at 60°C (~40%) and flow rate >10 cm s^{-1}, cooling rate 2 - 3° / day, growth rate ~11 - 15 mm / day

Problem of H. Rohrer 1969: Large $GdAlO_3$ crystals



Schematic View of a Tornado with Flow Profile (a) and Velocity Distribution in the Surface Friction (Ekman) Layer (b).

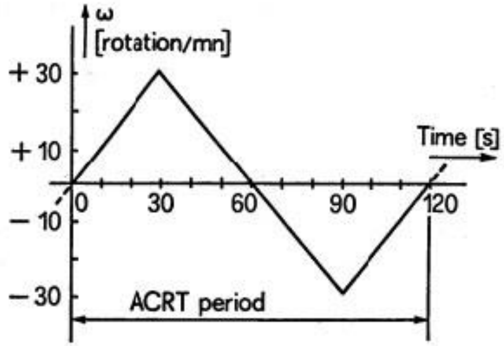
Spiral-Shear Flow and Ekman-Layer Flow, Movie at ICCG Marseille 1972

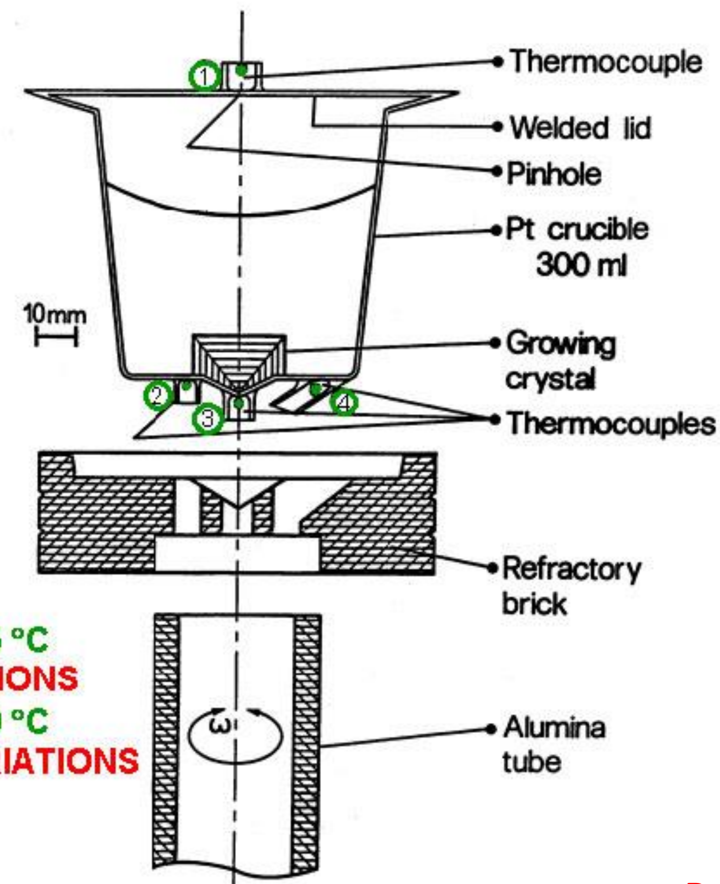


The Ekman Layer Flow occurs also in a circular Container with flat Bottom (c) when its Rotation is decelerated, and the opposite Flow upon Acceleration (d).

Accelerated Crucible Rotation Technique (ACRT)
H.J.Scheel, J. Crystal Grrowth 13/14(1972)560-565

Accelerated Crucible Rotation Technique ACRT





$T_1 - T_3 \approx 25$ °C
→ STRIATIONS
$T_1 - T_3 \approx 10$ °C
→ NO STRIATIONS

- Theory & Film with Erich Schulz-DuBois 1971, IBM
- Computer Simulation & Film M. Mihelcic 1979 KFA Jülich

ACRT in Growth from High-Temperature Solutions

- $GdAlO_3$ & Solid Solutions, $GdAlO_3$:Cr, $LaAlO_3$, KTN, Magnetic Garnets, $SrTiO_3$: H.J. Scheel, IBM Zurich
- Magnetic Garnets: W. Tolksdorf, Philips Hamburg
- Magnetic Garnets: P. Görnert, Jena/DDR
- Emerald: G. Bukin, Novosibirsk
- $Pb(Fe_{0.5}Nb_{0.5})O_3$, $Pb(Mn_{0.5}Nb_{0.5})O_3$ with Hans Schmid et al. and P. Tissot.

ACRT in Bridgman Growth (> flat growth surface)

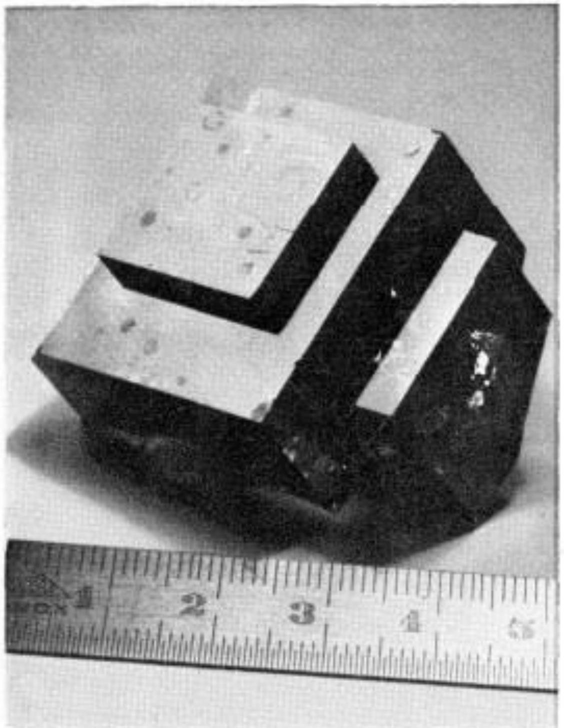
- Halogenides: A. Horowitz, Israel
- CdTe/HgTe Solid Solutions: P. Capper, Millbrook Southampton UK
- III-V Solid Solutions: P. Dutta, Rensselaer Polytechnic Troy N.Y.

ACRT in Growth from Vapor

- CdS: H.J. Scheel (unpublished)

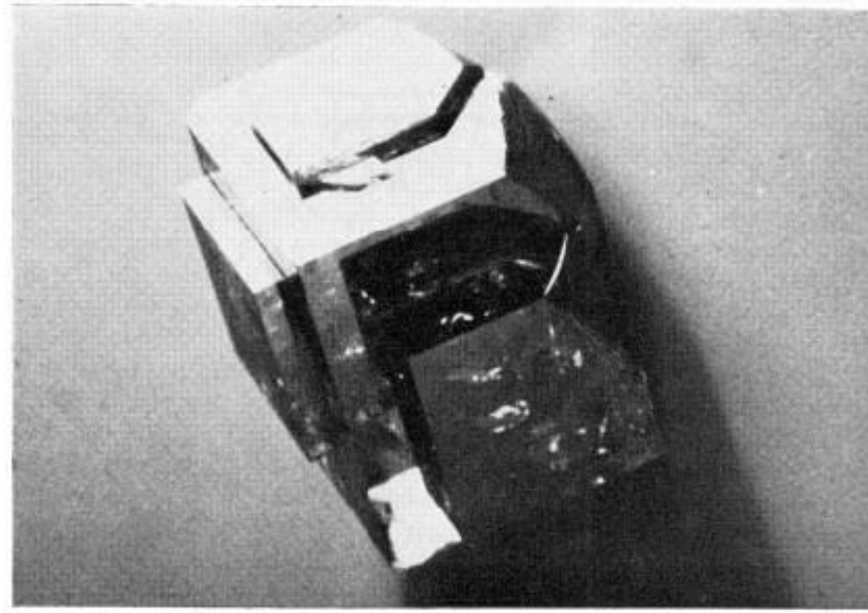
List not complete

Temperature Measurement
at Rotating Crucible at high Temperature



(a)

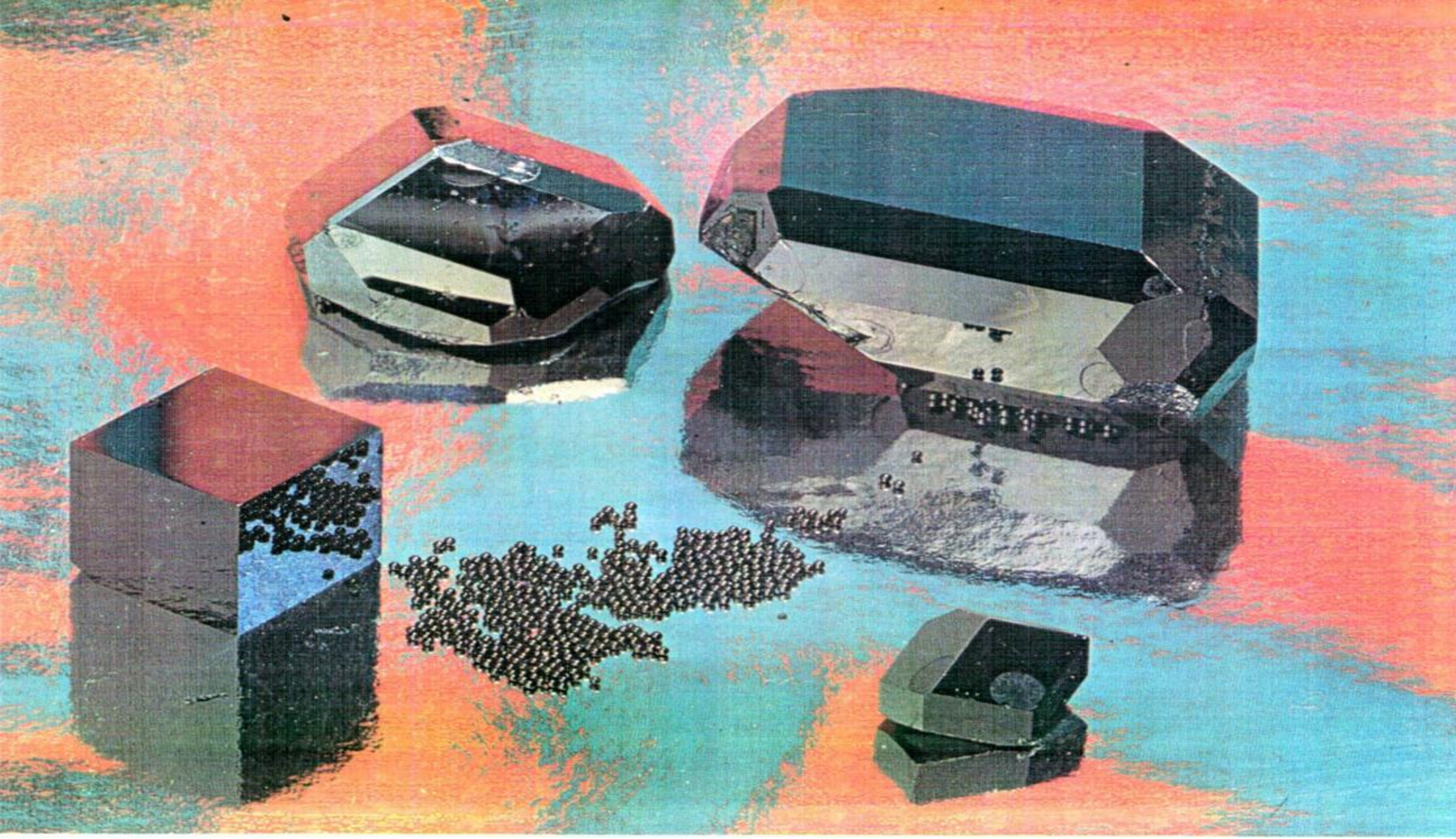
ACRT
$GdAlO_3$
Perovskite
$Gd_{1-x}La_xAlO_3$
$Gd_{1-x}Y_xAlO_3$
$Y_3Fe_{5-x}Ga_xO_{12}$



(b)

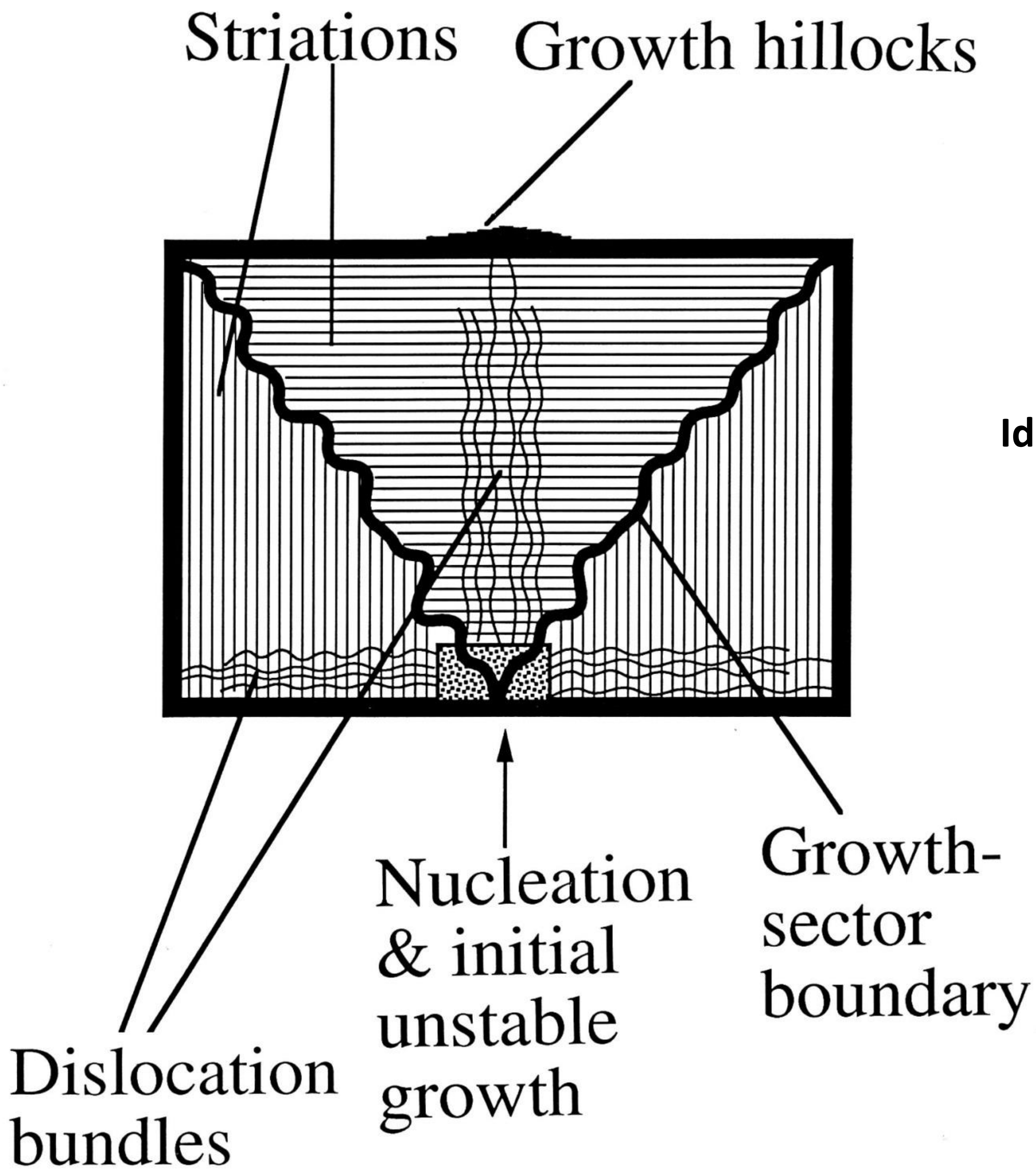
$GdAlO_3$ and Solid Solutions for H. Rohrer /IBM for Magnetic Phase Transitions, Magnetic Phase Diagram.

YIG and Solid Solutions for Magnetic Bubble Project at IBM Yorktown Heights



YIG Crystals ACRT-grown by Wolfgang Tolksdorf for Philipps Microwave Devices

Homogeneity importance for magnetic, magneto-optic, ferroeletric, nonlinear-optic and photorefractive applications: Crystal Growth and Electro-optic Properties of Oxide Solid Solutions: H.J. Scheel and P. Günter, Chapter 12 in *Crystal Growth of Electronic Materials*, editor E. Kaldis, Elsevier 1985.



Idealized Cross Section

PhD Thesis at ETH Lausanne IBM Zurich Research Laboratory

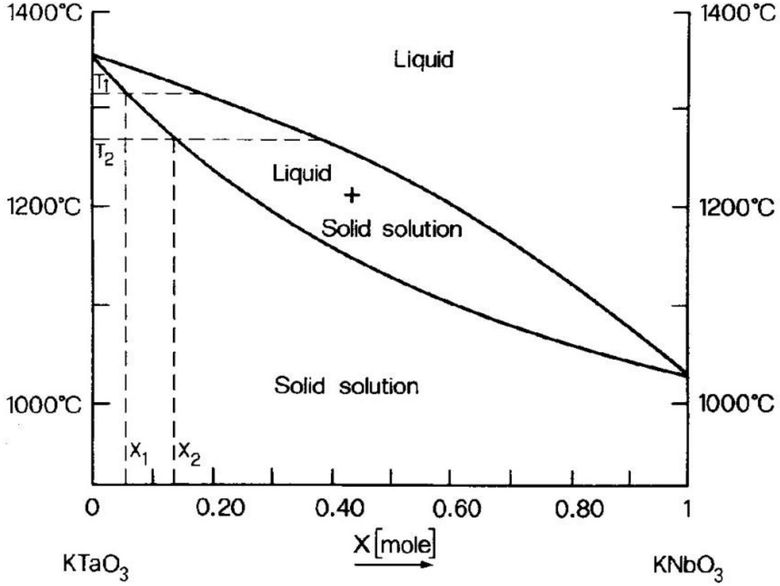


Fig. 2. Schematic solid-solution phase diagram (after ref. [5]). Growth starts at temperature T_1 with an initial concentration x_1, and ends at temperature T_2 with a final concentration x_2.

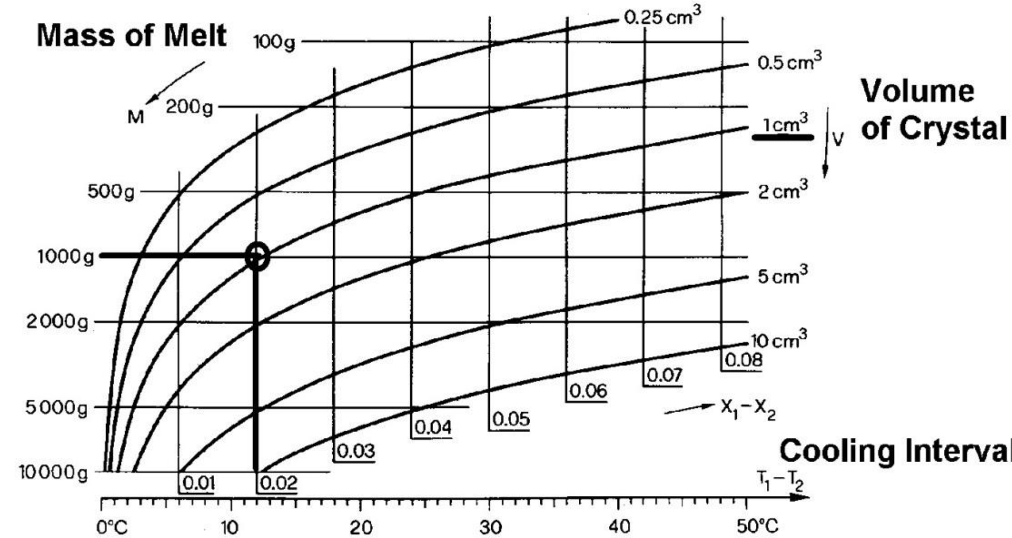


Fig. 3. Plot of crystal size V and inhomogeneity $x_1 - x_2$ as a function of experimental parameters (mass of melt M and cooling interval $T_1 - T_2$). A numerical example is detailed in the text.

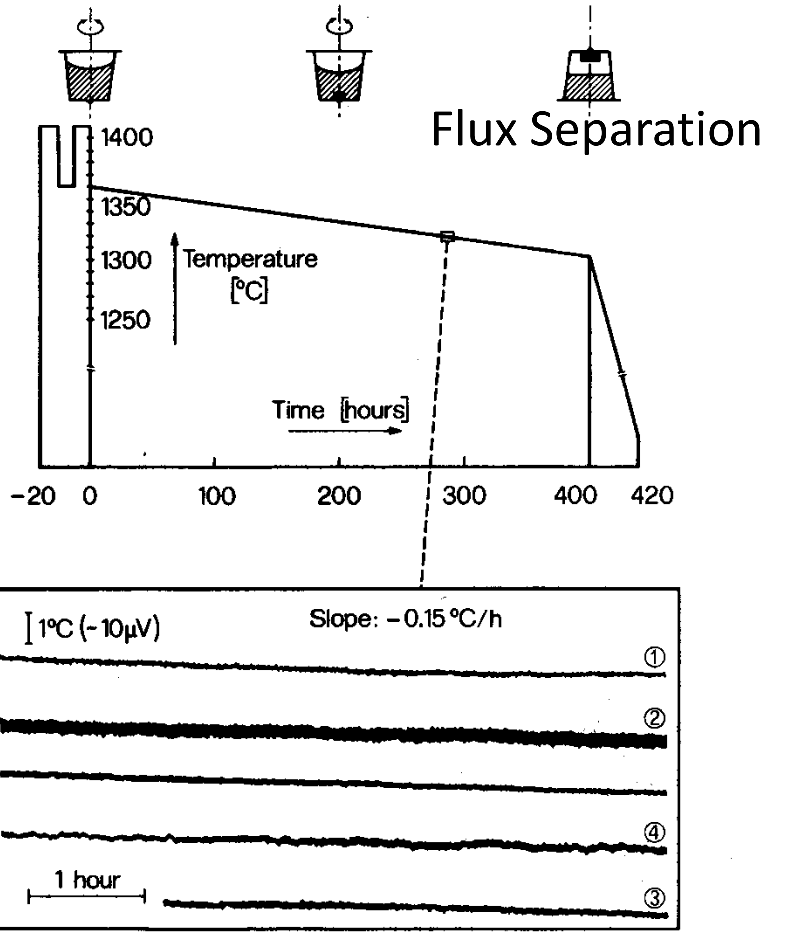


Fig. 7. Different steps of a growth experiment. A short interv during cooling is shown on a real temperature plot. The nur bers correspond to the thermocouples of fig. 6. The unlabell thermocouple was located at the back of the furnace.

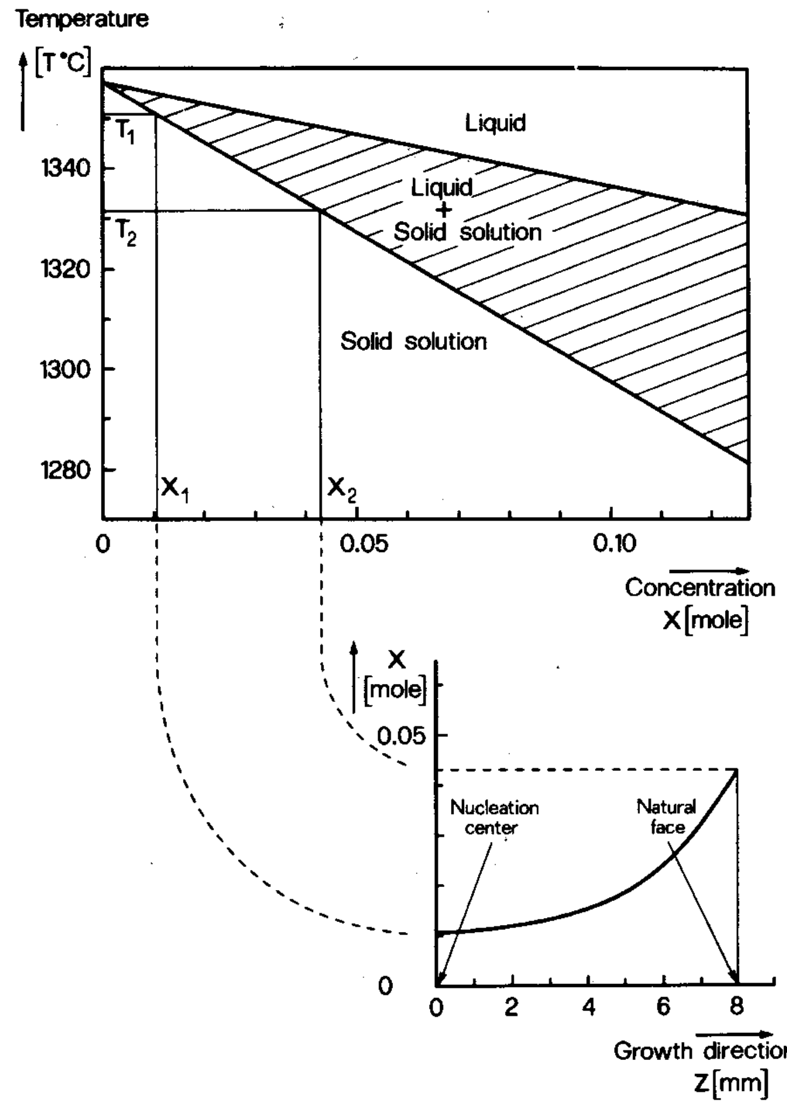


Fig. 4. Schematic phase diagram of $KTa_{1-x}Nb_xO_3$ and spatial variation of the concentration x along the growth direction z. The inherent bulk concentration gradient induced by the slow-cooling method is clearly shown. (The numerical values $T_1 - T_2 = 20°C$, $x_1 - x_2 = 0.03$ and $V \sim 8 \times 16 \times 16$ mm^3 correspond roughly to the numerical example detailed in the description of fig. 3.)

D. Rytz & H.J. Scheel
J. Crystal Growth 59(1982)468-484

Conditions for Growth of Striation-Free Crystals

1. Flat (smooth) Growth Surface
2. Isothermal Growth Surface ← $\Delta T/T < 10^{-5}$
3. Homogeneous Melt or Solution $\Delta n/n < 10^{-6}$
4. Constant Growth Rate $\Delta V/V < 10^{-5}$

When above conditions are established:

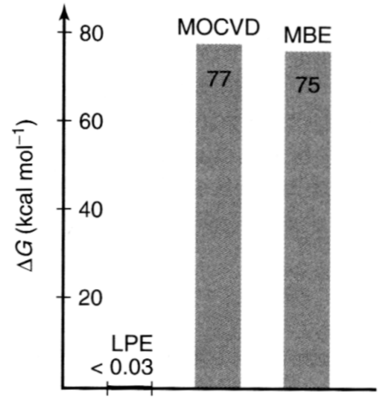
Hydrodynamic Fluctuations are not harmful.

Forced Convection and ACRT can Assist to Homogenize the Melt or Solution.

Precision temperature control with thermopile of PtRh 6/30 thermoelements:

H.J.Scheel & C.H.West: J. Phys.E (Scientific Instruments) **6**(1973)1178.

Supersaturation in Growth from Vapor and in LPE



G. Stringfellow 1991

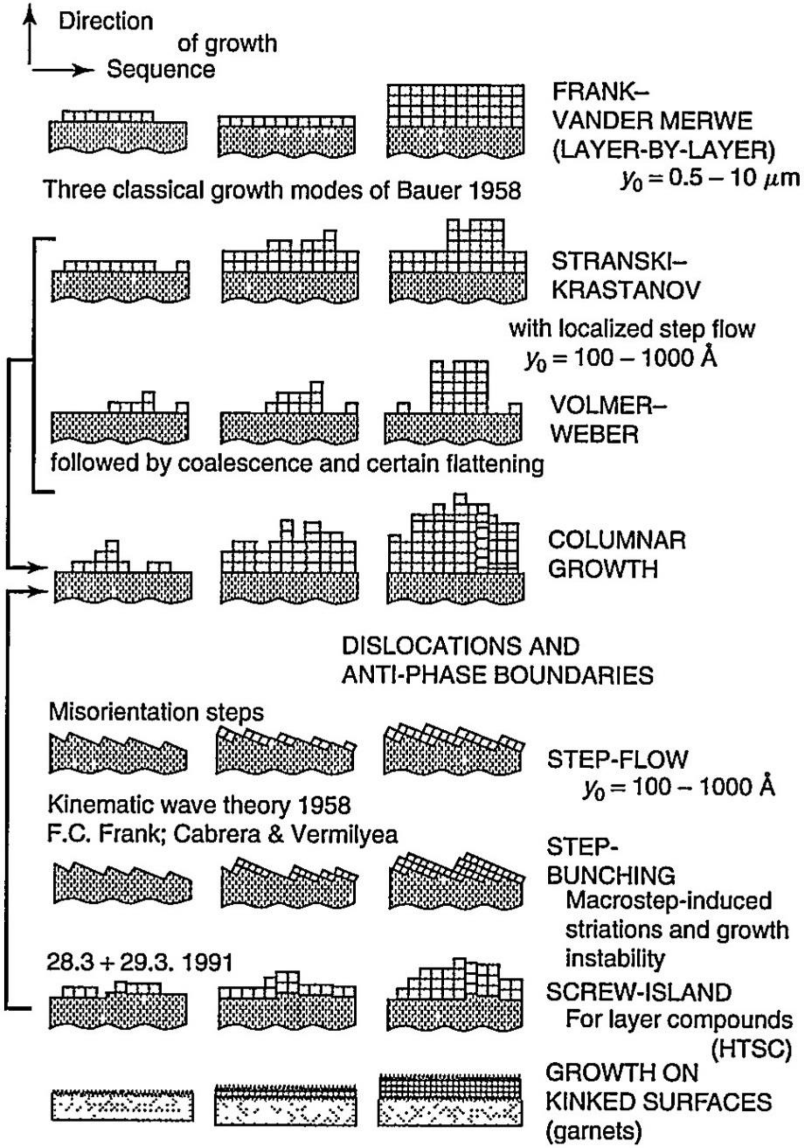
Gibbs free energy differences between reactants and products (layers, crystals). The estimated thermodynamic driving forces for LPE ($\Delta T < 6$ K), MOCVD (TMGa + arsine) and MBE (Ga + As_4) of GaAs at 1000 K. (After Stringfellow, 1991) Reprinted from *J. Cryst. Growth*, **115**,

Supersaturation ratios for VPE and LPE derived from interstep distances y_0 of GaAs and of the high-temperature superconductor $YBa_2Cu_3O_{7-x}$ (YBCO)

	For GaAs		For YBCO	
	MBE, MOVPE	LPE	VPE, MOVPE	LPE
y_0	20–100 nm	6 μm	14–30 nm	6 μm (0.6–17 μm)
r_S^*	1.1–5.5 nm	300 nm	0.8–1.6 nm	300 nm
	$\sigma_{MBE,MOVPE} \sim 60 \times \sigma_{LPE}$		$\sigma_{VPE,MOVPE} \sim 200 \times \sigma_{LPE}$	

T. Nishinaga and H.J. Scheel in Advances in Superconductivity VIII Vol.1, editors H. Hayakawa and Y. Enomoto, Springer Tokyo 1996, 33.

See also P. Clapper & M. Mauk: *Liquid Phase Epitaxy*, Chapter 1: H. J. Scheel



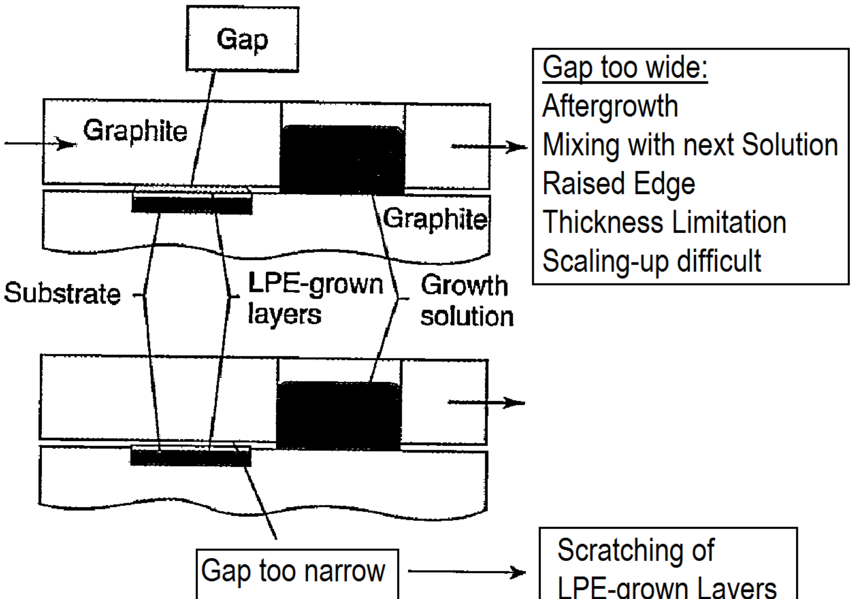
Eight epitaxial growth modes
in *Crystal Growth Technology*,
editors H.J. Scheel & T. Fukuda
Wiley 2003, Chapter 28

< 3 Classical Growth Modes

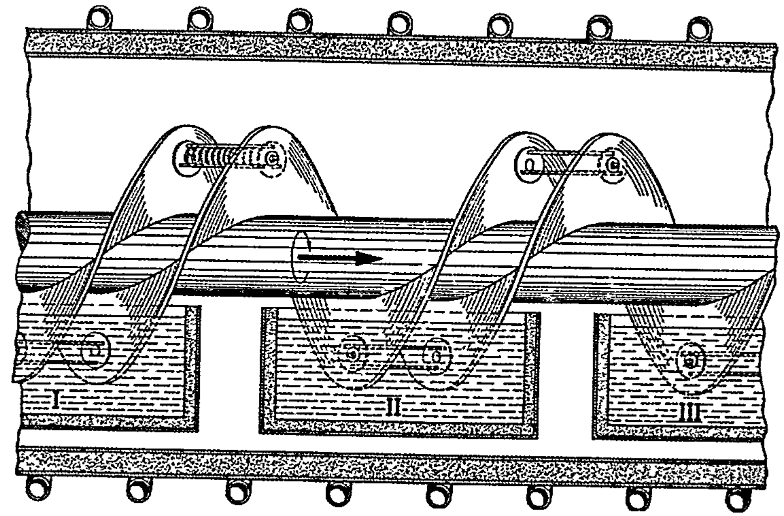
See also P. Clapper & M. Mauk: *Liquid Phase Epitaxy*
Chapter 1: H. J. Scheel

Liquid Phase Epitaxy

Problems in Slider Technology



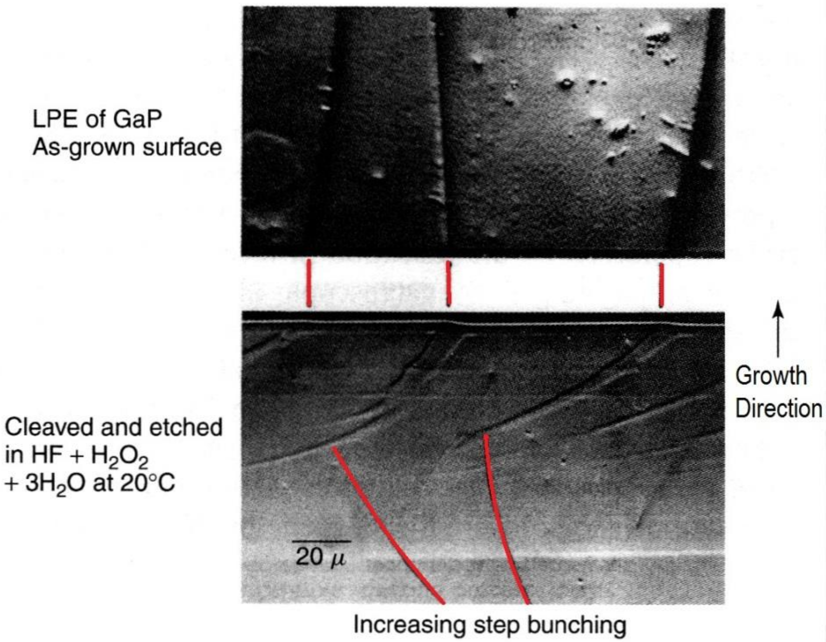
Sliding-free Technology for Mass Production



US Patent 3,858,553 (Jan.7, 1975, H.J.Scheel /IBM,
J. Crystal Growth 42(1977)301 - 308 (ICCG-5 Boston).

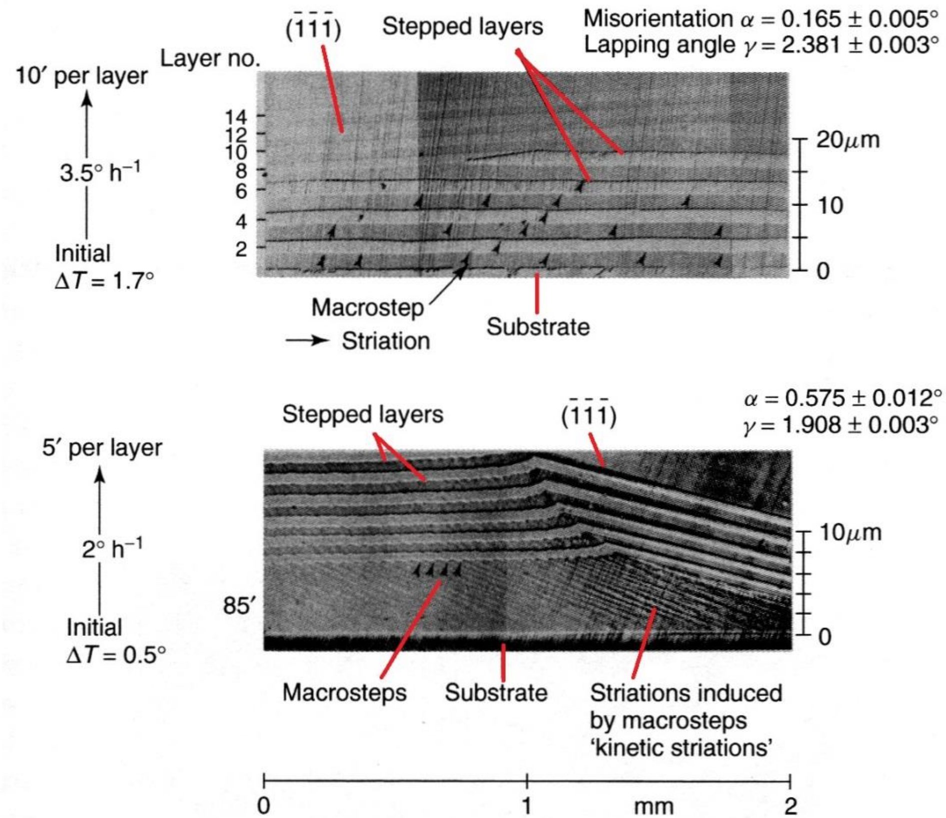
MultiLPE with Double-Screw Device

Macrostep-Induced Striations



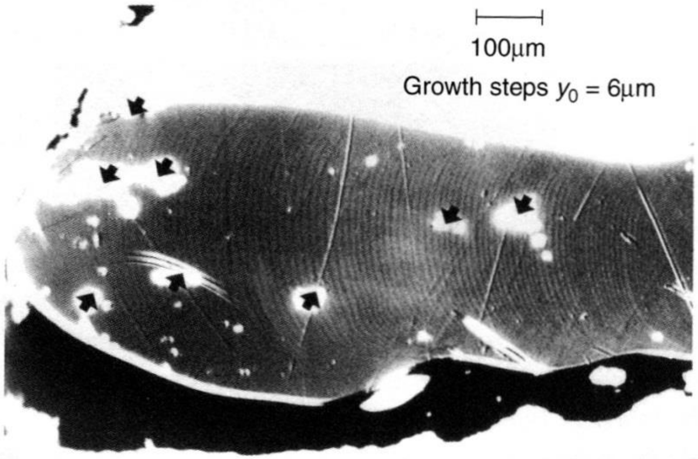
J. Nishizawa and Y. Okuno, Cetniewo, Poland 1978

Transition to Faceting in Multilayer LPE

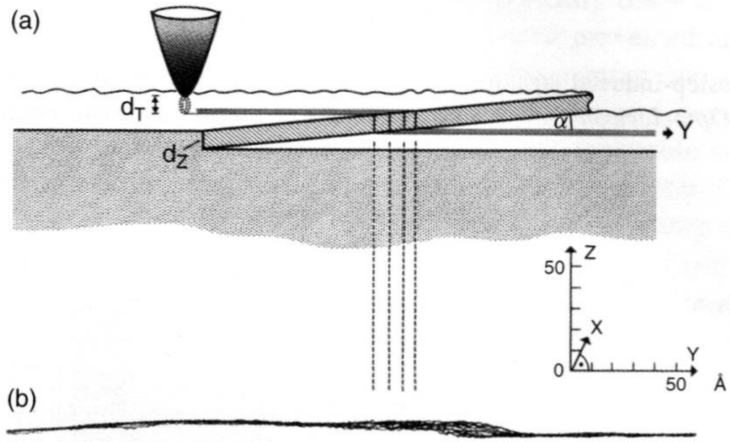


Appl. Phys.Letters 37 (1980) 70-73, H.J.Scheel

A. Chernov, H.J. Scheel:Extremely flat surfaces by liquid phase epitaxy. J. Crystal Growth 149(1995)187-195.



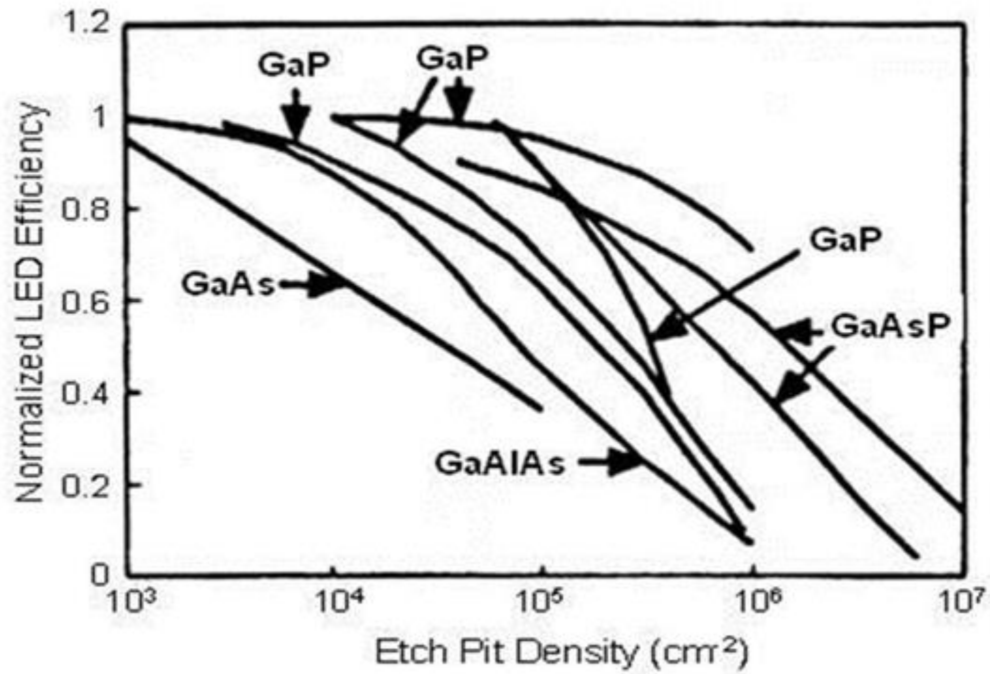
Differential interference contrast microscopy (Nomarski) of GaAs (111) facet. Step distances of 6 µm are visible.



Step heights of 6.5 A are measured by STM. (a) Principle, (b) Multi scan by STM.

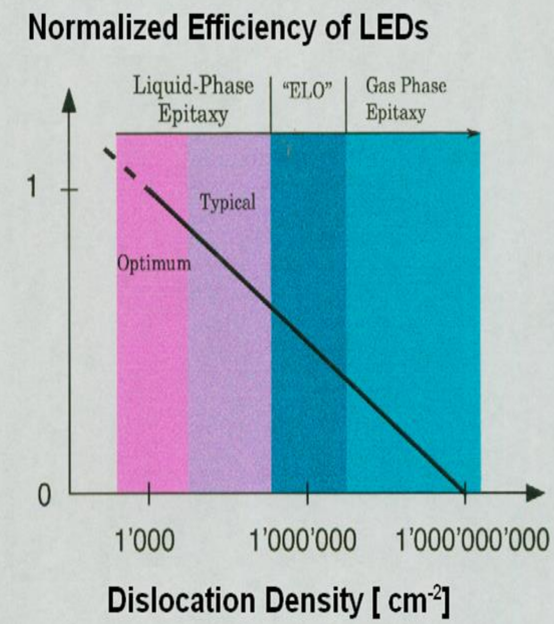
H.J. Scheel, G. Binnig and H. Rohrer: Atomically Flat LPE-grown Facets Seen by Scanning Tunneling Microscopy, J. Crystal Growth 60(1982)199 - 202.

Improved Light-emitting Diodes?



Dependence of LED efficiency on dislocation density.

S.D. Lester, F.A. Ponce, M.G. Craford, D.A. Steigerwald: Appl. Phys. Lett. 66(1995)1249- 1251.



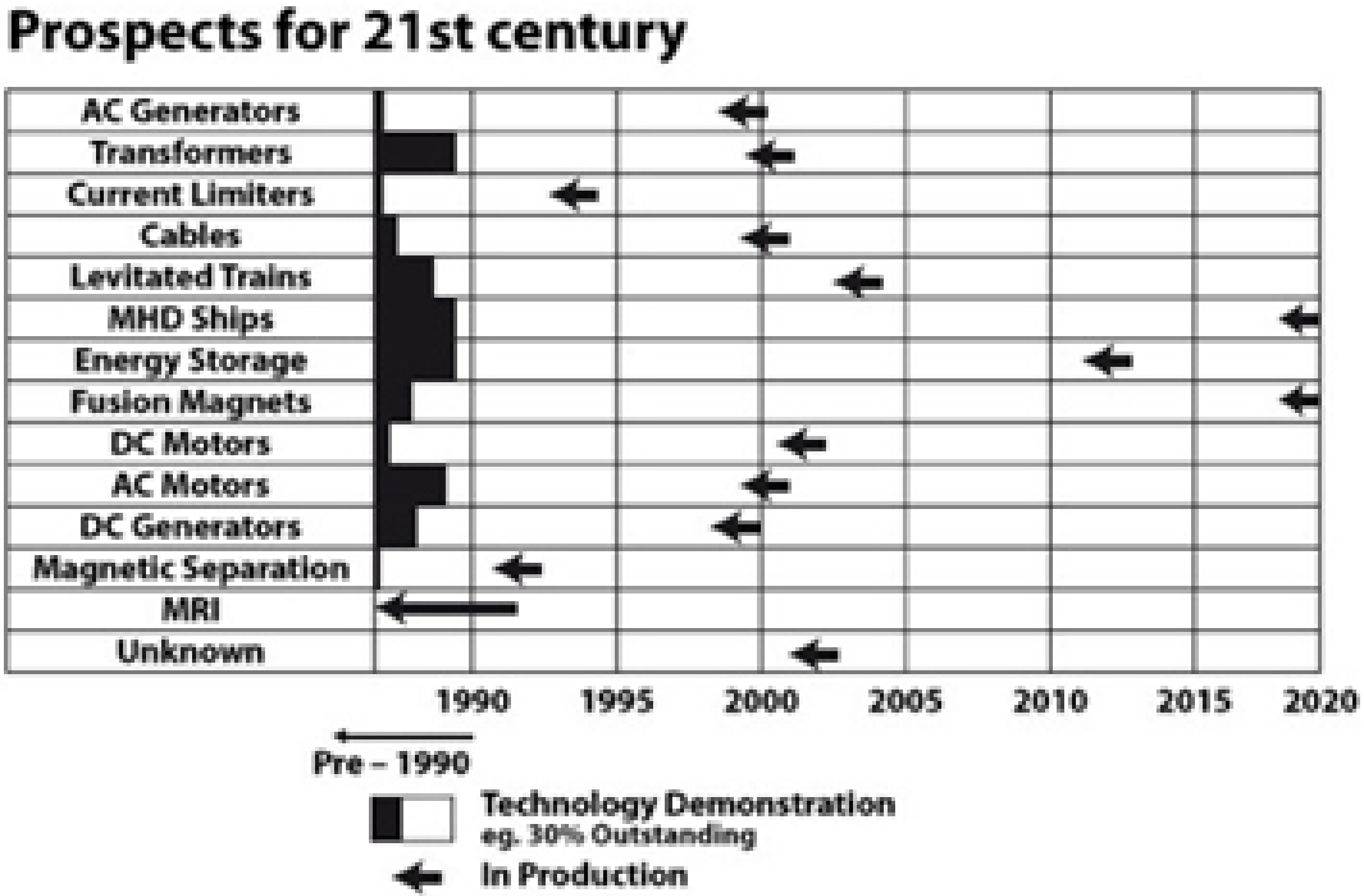
The normalized efficiency of typical light-emitting diodes as function of the structural imperfection expressed by the dislocation density. The structural perfection depends on the fabrication method.

Liquid Phase Epitaxy of Electronic, Optical and Optoelectronic Materials, Editors Peter Capper and Michael Mauk, Wiley 2007, ISBN 978-0-470-85290-3

Predicted Applications of High-Temperature Superconductors for Energy Storage & Electricity Transport and for Fusion Magnets

A.D. Appleton 1989

NATO Advanced Study Institute Greece 1992



<u>The Failure of High-Temperature Superconductivity</u> (HTSC)

- **Complex Composition and Structure, many possible defects**
- **Limited Thermodynamic Stability (P_{O_2} – dependent)**
- **Phase transition with large Change of Lattice Parameters**
  from non-superconducting tetragonal $YBa_2Cu_3O_6$ *
  to superconducting orthorhombic $YBa_2Cu_3O_{\sim 6.85}$ with T_c 92K

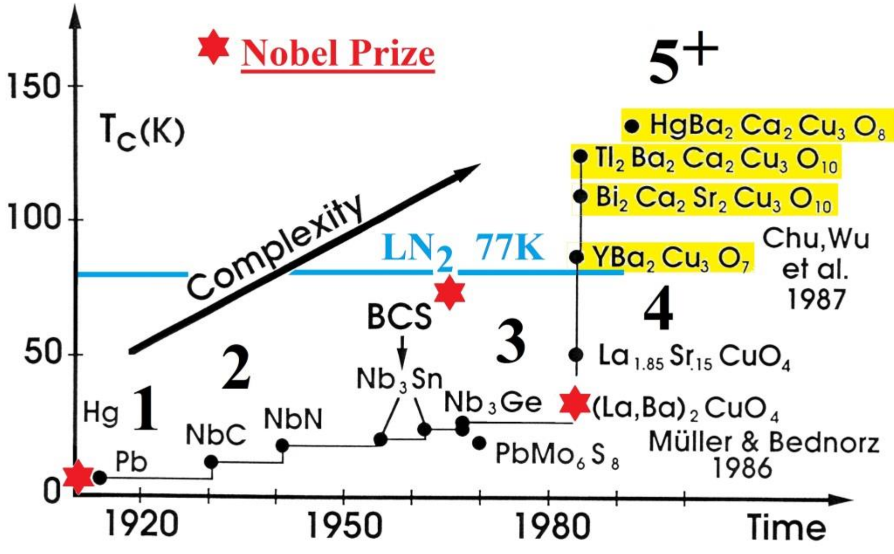
<u>The Development of High-Temperature Superconductivity and its important Applications is limited by Crystal-Material-Chemical-Mechanical Problems, not by Physics! The Crystal Grower proposed minimum 50% funding for Material Problems.</u>

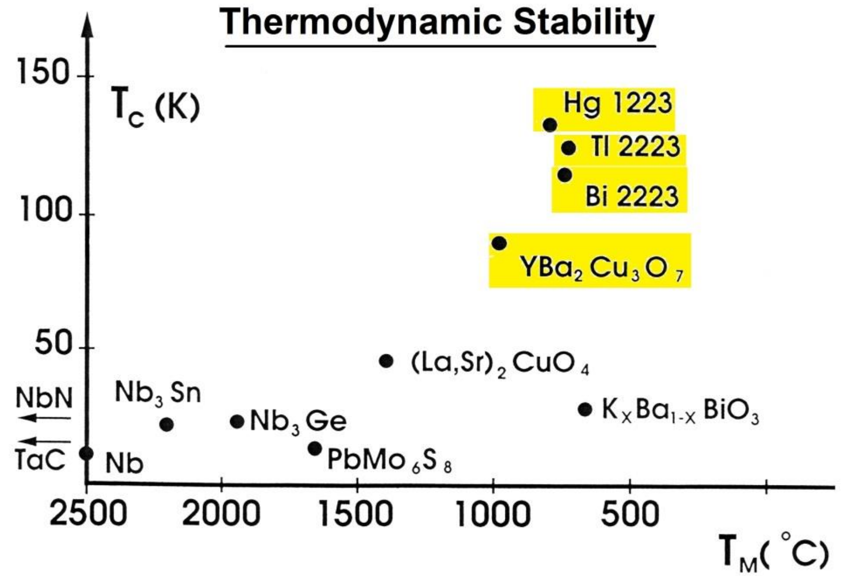
First International Conference on High Temperature Superconductors and Materials and Mechanisms of Superconductivity: February 28-March 4, 1988 Interlaken/Switzerland:
After one hour personal discussion:
K.A. Müller did not agree, was interested to support physics only, said that crystal growers can be proud to deliver crystals and materials.

After one hour personal discussion:
Third International Conference on High Temperature Superconductors and Materials and Mechanisms of Superconductivity: 1991 Kanazawa, Japan.
K.A. Müller did not agree, was interested to support physics only.

The special Committee on Superconductivity of Swiss National Science Foundation consisted of physicists only, no chemist or material scientist or crystal grower. Future committees should have less than 50% of demanding scientists' category.

***From high-temperature synthesis**





Increasing critical superconducting temperature T_c corresponds to increasing chemical and structural complexity and to decreasing thermodynamic stability, thus to increasing difficulty of crystal growth and material preparation.

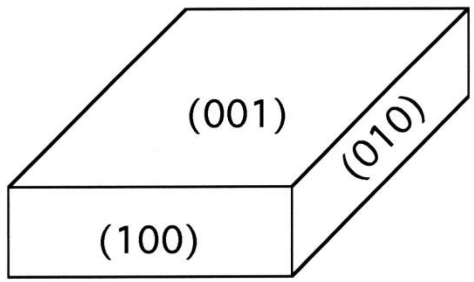
Hans J. Scheel in Materials Research Society MRS Bulletin ***19*** *No.9 (Sept. 1994) 26-32.*

A. Abrikosov and other theorists could not explain these relationships.

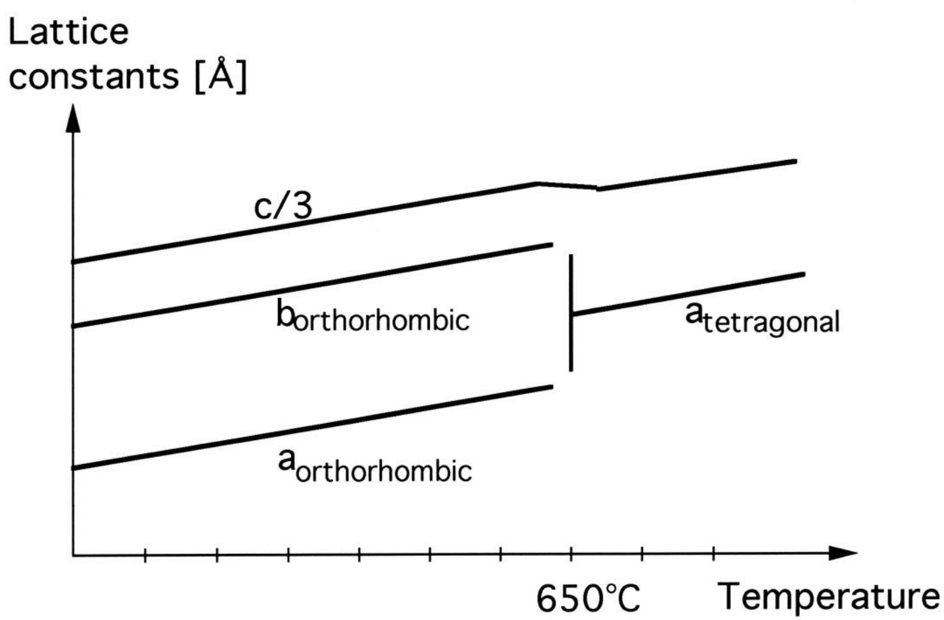
Oxidation and Epitaxy Problems with High-Tc Superconductors

$YBa_2Cu_3O_7 \xleftarrow{[0]} YBa_2Cu_3O_6$

orthorhombic ← tetragonal



D [0] // [010]
>> D [0] // [100]
>> D [0] // [001]



Growth of $YBa_2Cu_3O_6$ which has to be oxidized to $YBa_2Cu_3O_{6.85}$ to become superconducting at 92K.

Problems:

Phase transition,
Anisotropic diffusion coefficients,
Thermal expansion difference
Mechanical properties.

Goal: Prevent cracking, twinning, grain boundaries/dislocations, strain/bending.

Similar problems in epitaxy:

Substrate with low misfit, fititng thermal expansion and phase transition, mechanical properties..

A task for well-educated crystal technoogists in collaboration with physico-chemists, mechanical engineers, structure engineers.

Comparison of PVD/CVD Surfaces with LPE Surfaces of High-Temperature Superconductors

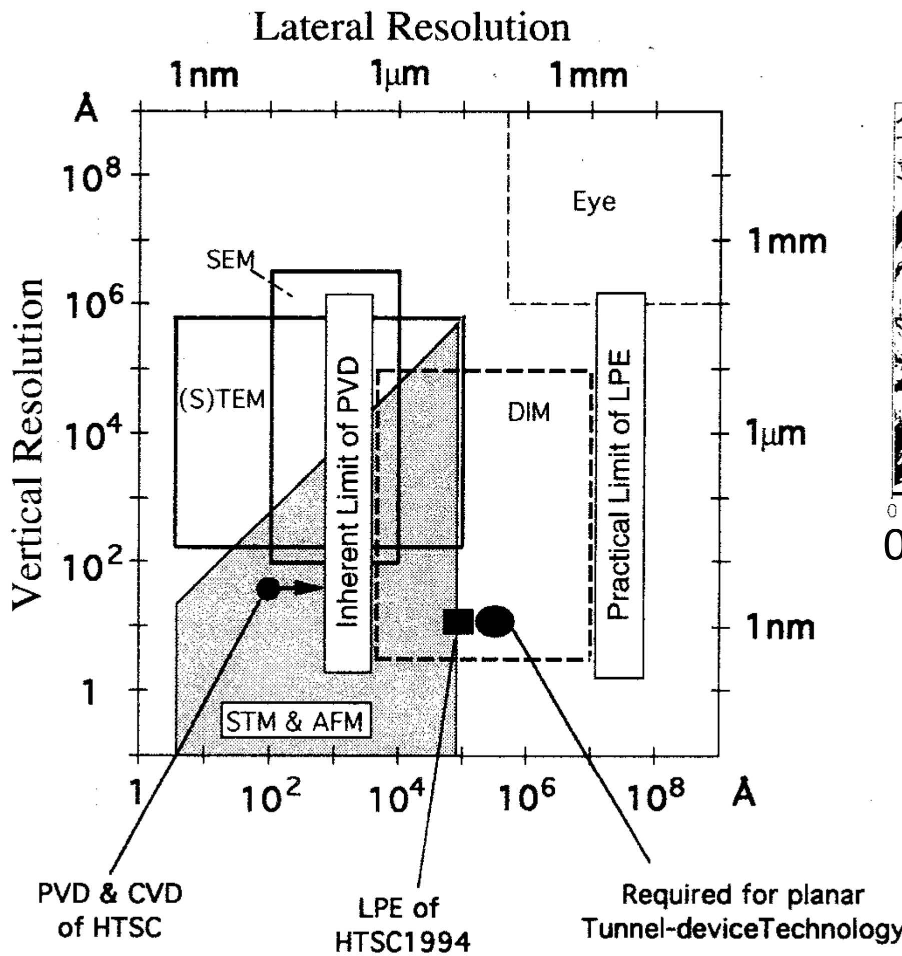


Figure 11. Surfaces (step heights and lateral step distances) of YBCO grown by PVD, CVD, and LPE and the detection limits of electron microscopes (SEM, TEM), scanning tunneling microscopy (STM) and atomic force microscopy (AFM), and of the optical differential interference contrast (Nomarski) microscope (DIM). Also shown are the inherent limit of PVD and the practical limit of LPE by vertical bars, and the step distances required for a planar HTSC tunnel-device technology.[34]

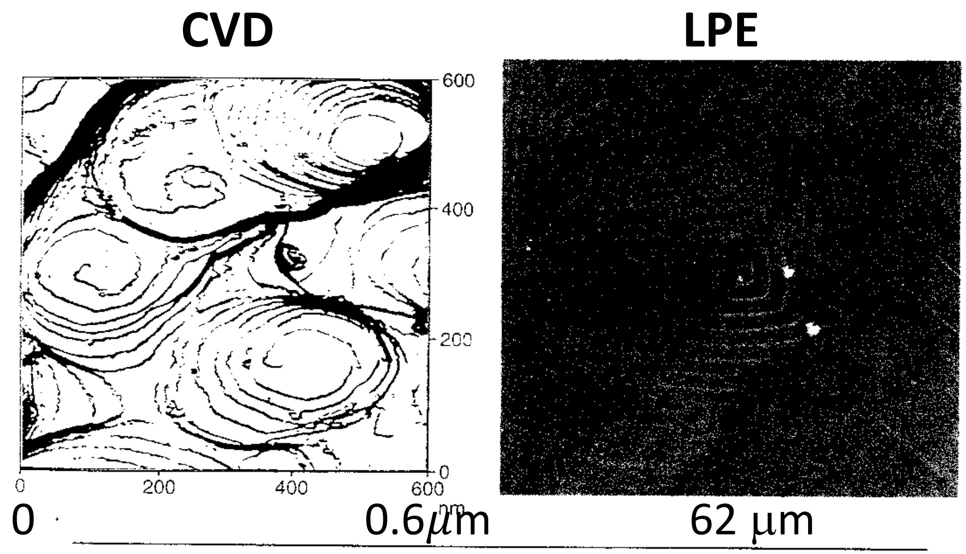


Figure 12. Typical spiral structures of (a) CVD-grown[36] and (b) LPE-grown YBCO layers. The LPE spiral has a diameter of 62 μm. Note the different scales which correspond to >3 × 10⁸ spiral islands/cm² in vapor-grown and to about 10³ spirals/cm² in LPE-grown layers.

- *Monosteps on extremely flat $YBa_2Cu_3O_{7-x}$ surfaces grown by liquid-phase epitaxy,* Appl.Phys.Lett. **65 (**1994)901-903. (H.J. Scheel, C. Klemenz, F.-K. Reinhart, H.P. Lang, and H.-J. Güntherodt)
- *Materials Engineering Problems in Crystal Growth and Epitaxy of Cuprate Superconductors,* MRS Bulletin **19**(1994)26-32 (H.J. Scheel)

<u>IBM Zurich Research Laboratory</u> (HJS 1968-1982)

<u>Device Department:</u> Si- and GaAs-MESFET, then Josephson Devices

<u>Physics Department:</u> Phase Transitions.Magnetic: H.Rohrer ($GdAlO_3$ & Solid Solutions),
Structural/Dynamics, Ferroelectric: K.A. Müller, later Superconductivity

<u>Crystal Growth:</u> H.J. Scheel

Strontium Titanate $SrTiO_3$

Crystal Sructure: Framework of TiO_6 –Octahedra with central Sr. Cubic Pm3m, a=3.9053 A,
Below Phase Transition (99K-110K) tetragonal I4/mcm

$n_D = 2.41$, n_F-$n_C = 0.108$, H = 6 – 6.5

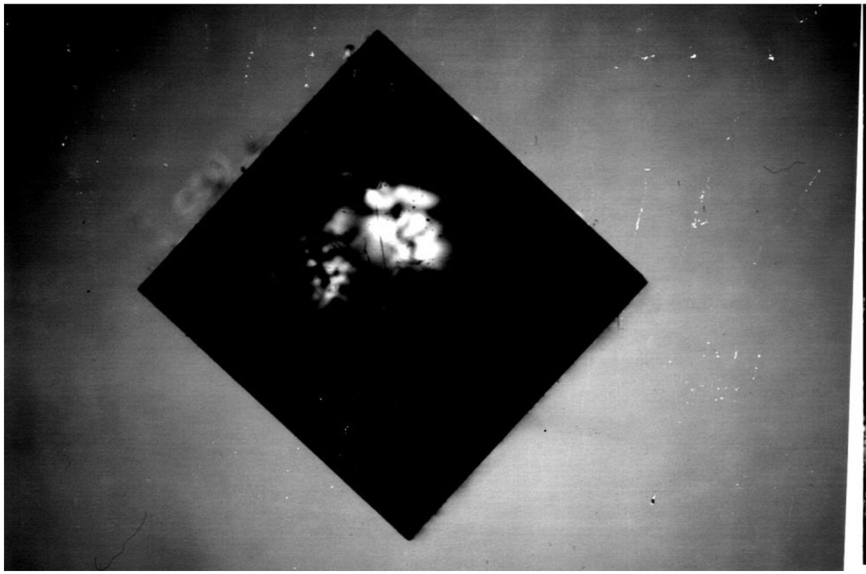
Dislocation Density of Verneuil-grown Crystals $10^6 – 10^7 /cm^2$, Polarized Light>!

<u>At End of Seminar</u> of HJS 1971/1972 (before the ICCG Conference in Marseille 1972) about Crystal Growth , $NaCrS_2$ and Accelerated Crucible Rotation Technique ACRT:

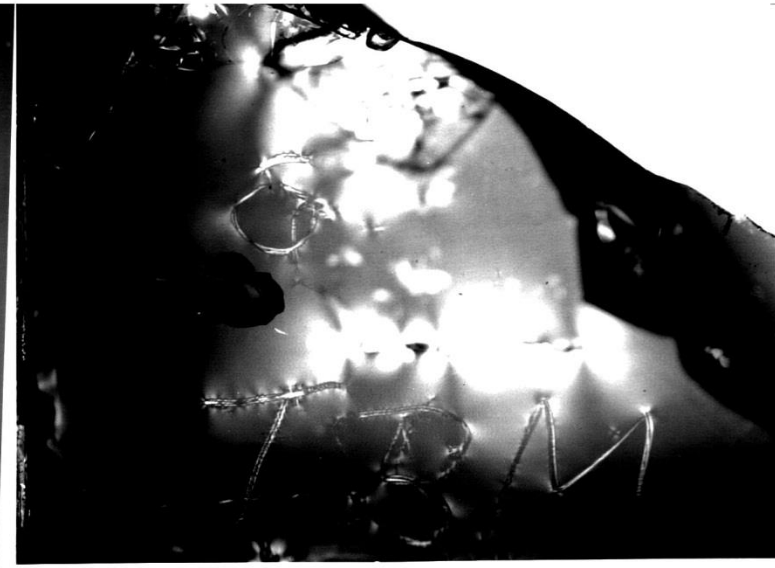
<u>Crystal Grower</u> (HJS)	**<u>Physicist (KAM)</u>**
1.Dynamics at T_c is influenced by Dislocations due to their Strain Field, he recommended X-Ray Topography Collaboration & Etching	***No! T_c and Dynamics are intrinsic!***
2.Impurities have a Strain Field the defect and should be chemically characterized by ICP	***No! Tc and Dynamics are intrinsic! Joke about Non- physicist!***

1975: Growth of First Cubic «Dislocation-free» SrTiO3 Crystal from Borate Flux.

Squeezing by finger in polarizing microscope introduced strain field.



4 x 4 mm crystal wit «X» removed
by annealing at 1250°C (crossed Nicols)



$SrTiO_3$ crystal surface with «IBM»
not annealed

Writing on flux-grown isotropic SrTiO3 crystals

Results:

First did not believe and had the crystal checked

- **B.I. Halperin and C.M. Varma: Defects and the central peak near structural phase transitions. Physical Review B14 No.9 (1976)4030-4043.**
  (Central peak, soft modes, mean-field theory, renormalization-group calculations)

- **H.J. Scheel, J.G. Bednorz and P. Dill: Crystal Growth of Strontium Titanate $SrTiO_3$, Ferroelectrics 13(1976)507-509.**
  In Polarized Light: Isotropic!

- **H.J. Scheel: Kristallzüchtung und Charakterisierung von Strontium Titanate $SrTiO_3$, Zeitschrift für Kristallographie 143(1976)417-428 (Laves-Festband)**
  (Rocking curves from F. Mezei, Grenoble: unresolved sharp)

- **J. Hutton, R.J. Nelmes and H.J. Scheel: Extinction Corrections for a Highly Perfect Crystal ($SrTiO_3$), Acta Crystallogr. A37(1981)916-920.**

- **Physicist: Flux-grown dislocation-free $SrTiO_3$ crystals showed “new” dynamics at phase transition!**

Conclusion:

“Sufficient” Characterization is required for reproducible high-quality Solid State Physics!

Questions to Solid State Physicists

Which Physical Properties and Phenomena are not influenced by

Dislocations & Grain boundaries	**>>**	**Strain**
Inclusions	**>>**	**Strain**
Twinning	**>>**	**Strain**
Impurities	**>>**	**Strain**
Striations	**>>**	**Strain**
Vacancies / Voids	**>>**	**Strain**

Goals: **Growth of Perfect Crystals; Reproducibility**

"Sufficient" Characterization of those Structural and Chemical Defects which have or may have an Influence on the Specific Physical Measurement or Application

Achievements:

Normal Solid State Physics: 66% (published estimate ~1978)

High Temperature Superconductivity: 0%

Actions: **Physicists, Crystal Growers, Journals & Reviewers, Funding Agencies (in committees max. 50% of demanding science field)**

Expected Results: **Accelerated Progress in Solid-State Sciences and in Technologies; Economics of Research**

"Sufficient" Characterization

High - Tc Update Vol. 5 No. 19, Oct.1, 1991 p.3

Overviews

Problems in the epitaxial growth of high-T_c superconductors are reviewed by H. J. Scheel et al. (Swiss Federal Institute of Technology, Lausanne), who discuss epitaxial deposition techniques and parameters, growth mechanisms and film orientation, substrates, and characterization. The authors stress that, since it is very difficult to achieve reproducibility of growth, "sufficient" characterization of the epitaxial films and surfaces (and crystals) is of utmost importance. The term "sufficient" means all those chemical and structural aspects of the layer which have or may have an influence on the measured physical phenomenon or on the specific application. The authors also note that film-growth processing with lower growth (substrate) temperatures (below 500°C, if possible) is desired for combining semiconductor and superconductor technologies (45 references).

NATO Advanced Study Institute
1992 and July 10-23, 1994
Greece

Prof. John Clem, AMES Labortory
Editor of High-Tc Update:

No HTSC paper with
sufficient characterization!

No reproducibility
in solid-state physics of
high-Tc superconductors!

Responsibility of Physicists
and of Crystal Growers!

Importance of Crystal Technology (and Material Technology) **for Energy**

For Saving Energy:

- **Illumination by economic (Ga,Al,In)N LEDs of higher efficiency (>150 lm/W,** compared to present LEDs with 60 to 100 lumen / W)
- **Improved High-Temperature High-Power Transistors (SiC, GaN)**
- **Improved DC/AC and AC/DC Converters for DC Current Transport**
- **High-Temperature Superconductivity (HTSC)**
  - **HTSC Transport of Electricity**
  - **HTSC Transformers**
  - **HTSC Generators**
  - **HTSC Current Limiters**
  - **HTSC for MHD Ships (magneto-hydrodynamic propulsion)**
  - **HTSC for Levitating Trains, etc.**

For Renewable Energy:

- **Photovoltaic Silicon Solar Cells (higher efficiency >18%, economic)**
- **Concentrated Photovoltaic Solar Cells (highest efficiency >35%, economic)**
- **Thermoelectric Photovoltaic Cells**

For Energy Storage:

- **New Battery System**
- **HTSC Energy Storage (Flywheel, SMES Superconducting Magnetic Energy Storage)**

For Future Nuclear Fusion Energy:

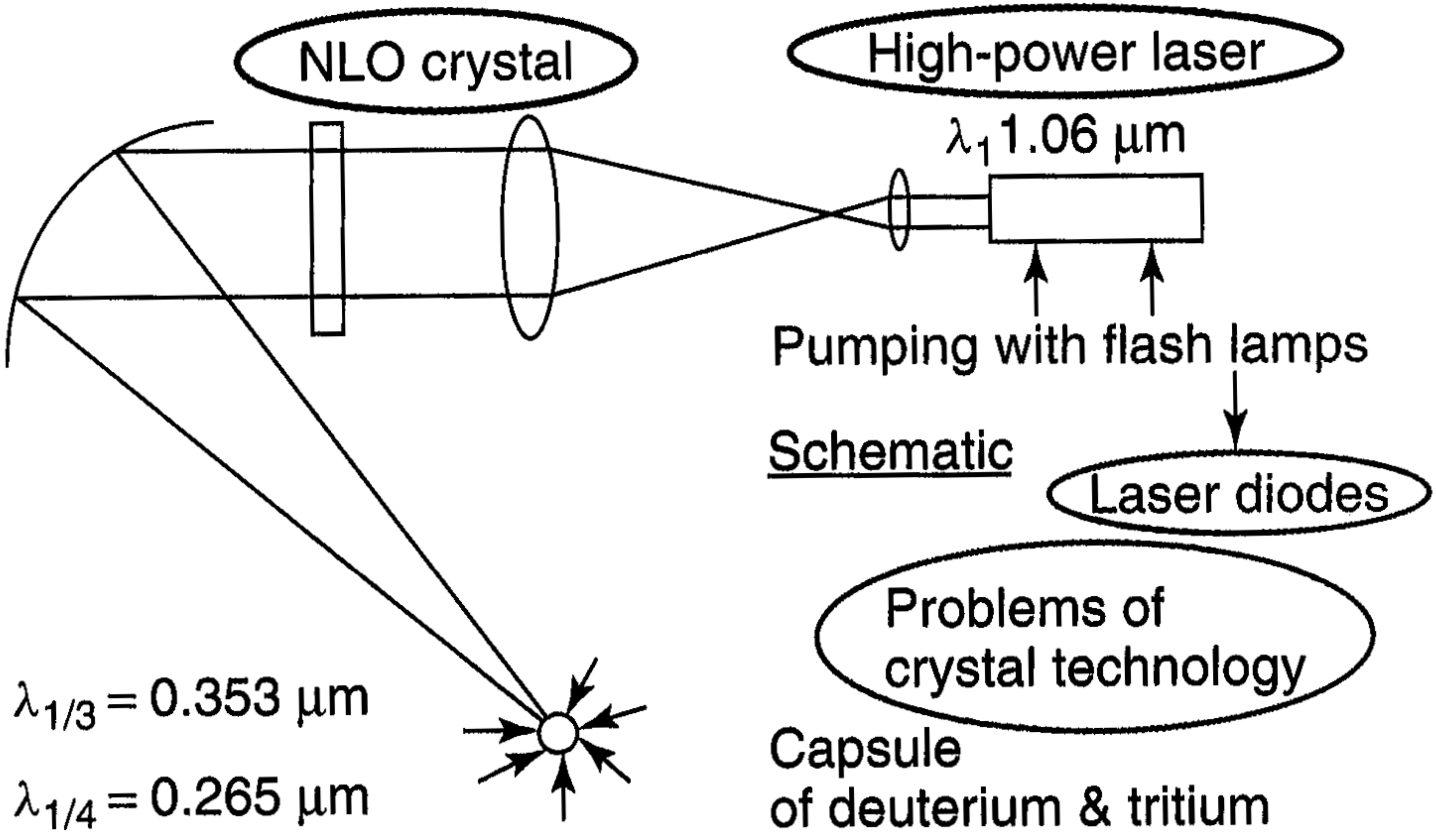
- **Large Radiation-hard High-Power LASER Crystals**
- **Large Radiation-hard NLO Crystals for achieving UV Radiation**
- **Economic LASER-Diode Arrays for Pumping the LASER Crystals**
- **First-wall Material for Tokamak (magnetic inclusion) Technology**

For Medicine & Novel Technologies, For Homeland Security

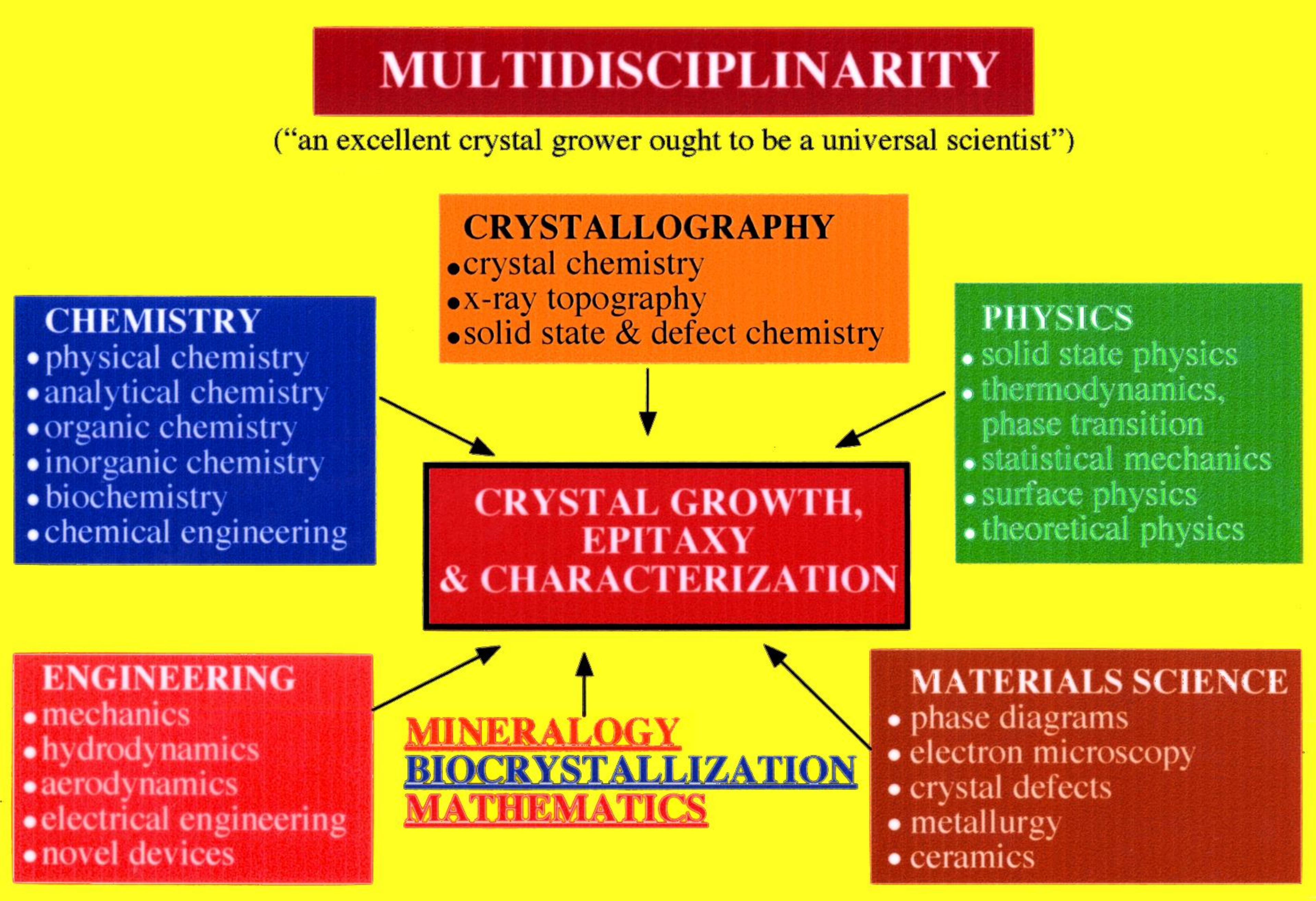
- **Scintillator Crystals**

Has Fusion Energy by Magnetic Inclusion (Tokamak) a Chance as long as the Problem of the "First Wall" is not solved?

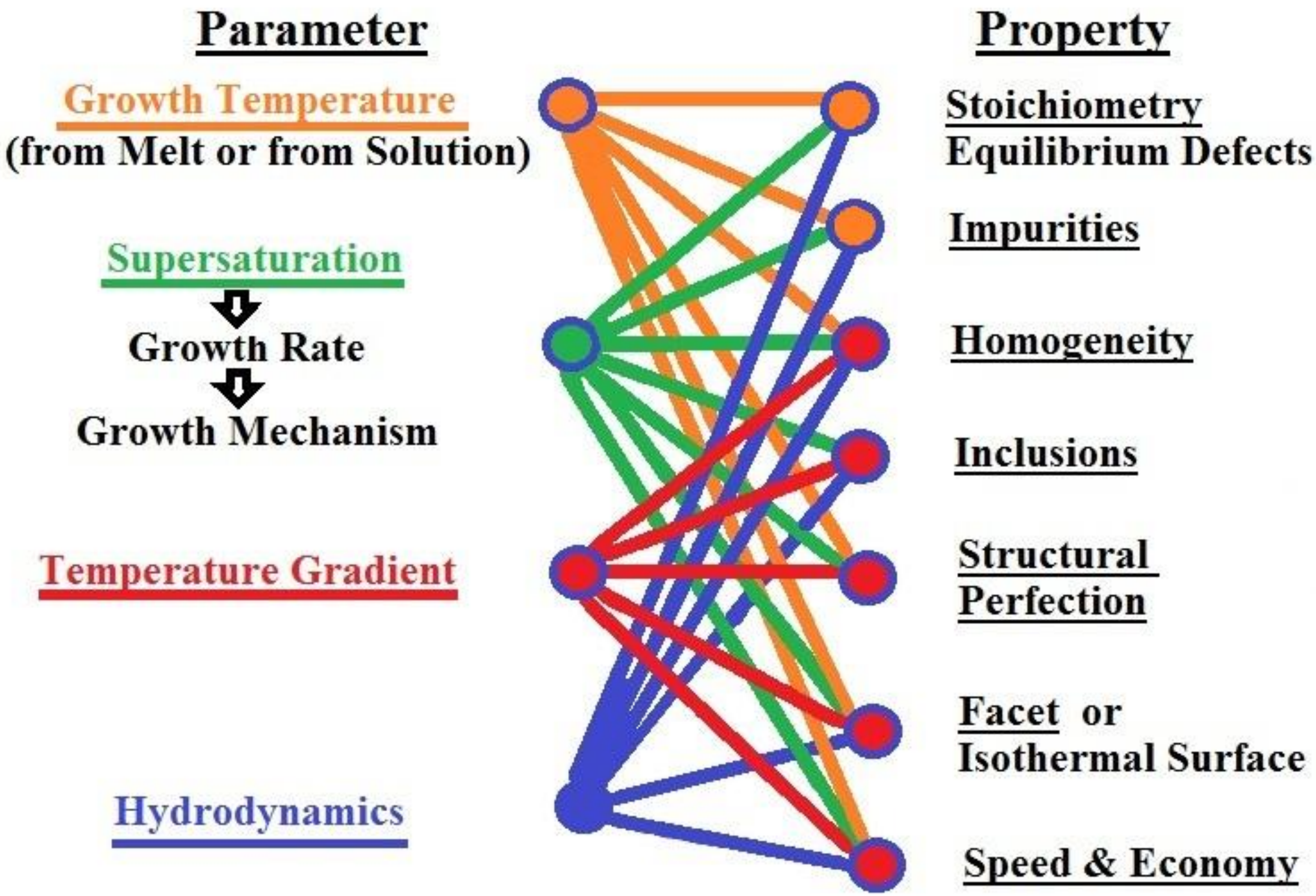
Laser Crystals and NLO Crystals for Laser Fusion Energy



NIF Lawrence Livermore Lab. 192 beams; Mégajoule Bordeaux 22 beams; Omega Laser Facility Univ. Rochester 60 beams; ILE Osaka Ubniv. GEKKO XII with 12 beams . **LMJ 2 tons KDP crystals, 300 tons Nd-glass laser**. (Bordeaux) **Future!**


MULTIDISCIPLINARITY
("an excellent crystal grower ought to be a universal scientist")
CRYSTALLOGRAPHY
• crystal chemistry
• x-ray topography
• solid state & defect chemistry
CHEMISTRY
• physical chemistry
• analytical chemistry
• organic chemistry
• inorganic chemistry
• biochemistry
• chemical engineering
PHYSICS
• solid state physics
• thermodynamics, phase transition
• statistical mechanics
• surface physics
• theoretical physics
CRYSTAL GROWTH, EPITAXY & CHARACTERIZATION
ENGINEERING
• mechanics
• hydrodynamics
• aerodynamics
• electrical engineering
• novel devices
MINERALOGY
BIOCRYSTALLIZATION
MATHEMATICS
MATERIALS SCIENCE
• phase diagrams
• electron microscopy
• crystal defects
• metallurgy
• ceramics

Effect of Growth Parameter on Crystal Property



Multi-Parameter Processes

Approach : Trial & Error
Systematic
Intuitive / Empirical
Design of Experiment
Fully Scientific

Complexity
Multidisciplinary
Scaling / Dimension Problem

Art
⇩
Science of Crystal Growth

Other Parameters
Chemicals Purity
Solvent
Transport Agent
Dopant
Crucible: Composition, Size, Shape, Purity
Atmosphere; Gravity

Single Optimum Technology
for Growing a Specific Crystal or Epilayer with Specifications for a Given Application

based on
- ► Thermodynamics / Phase Diagrams
- ► Principles of Crystal Growth and Epitaxy
- ► Energy Consumption
- ► Economics
- ► Timeliness
- ► Ecology

Requirements:
- ► **Education of Crystal Technologists**
  Engineers and Scientists with special Education in Crystal Technology including Crystal Machining, Epilayer & Multilayer Growth, and Characterization
- ► **Workshops and Schools on Crystal Technology**
  →ISCGT-1 1998 Beatenberg/ Switzerland; ISCGT-2 Zao/Japan; IWCGT-3 2005 & IWCGT-4 2008 Beatenberg; IWCGT-5 - 7 2011-2017 Berlin/Germany
- ► DGKK Arbeitskreise on specific Topics
- ► Discussion Meeting May 13-19, 2012 in Greece:
  WHITE PAPER in www.hans-scheel.ch

Results:
- ► Saving of more than 80% of Development Costs for Crystals and Epilayers, of Resources, and of Energy
- ► Enhanced Developments of Solid State Sciences and Technologies, in Saving Energy & Renewable Energy, Laser Fusion Energy
- ► Improved Recognition of the Field Crystal Growth

Example:

Large Sapphire Crystals by Czochralski, HEM, Kyropoulos?

Education of Crystal Technologists

Courses (before Master Program): Problem Multidisciplinary: only Basics*

The courses should enable crystal technologists to discuss with specialists (chemists for delivering chemicals, crucibles and gases), hydrodynamists, theorists, simulation experts, machine and furnace designers, device engineers, characterization experts, etc.

-**Chemistry:** General, Inorganic, Organic, Analytical Chemistry, Thermochemistry
-**Chemical Engineering** emphasis on Mass Crystallization, Recrystallization & Zone Melting
-**Materials Science & Engineering:** Metallurgy, Ceramics/Glasses, Polymers/Composites, Phase Diagrams/Thermodynamics, Transport Phenomena; Basic Crystal Growth; Dendrites; Casting
-**Crystallography:** Symmetry, Space Groups, Miller Indices/Lattice Constants, Crystal Orientation, Texture, Powder Identification, Crystal Chemistry, Crystal Structure – Growth Habit, Crystal Defects, Structural Characterization (Diffraction Methods using X-Rays, Electrons, etc.)
-**Mathematics & Informatics** including Basic Computer Simulation
-**Physics:** Solid State Physics, Statistical Mechanics, Surface Physics
-**Electrical Engineering:** General; Microelectronics, Electronic and Optoelectronic Devices, Detectors
-**Mechanical Engineering** Hydrodynamics (Expts & Simulation), Machine Design, Process Control
-**Ecology/Environment, Energy- and Climate problem**

*****similar to basic courses for other multidisciplinary studies like environmentalist, ecologist, however with emphasis on technology.

For details see WHITE PAPER, eidtors F.J. Bruni, H.J. Scheel, see in www.hans-scheel.ch

Results of International Discussion Group May 2012 in Greece

Education of Crystal Technology Engineers and Scientists*

Courses during Master Programme (3 years) including Practical Work & Internships in related Industries

-**Fundamentals of Crystal Growth:** Nucleation/Supersaturation, Growth Mechanisms, Growth Habit, Growth from Aqueous Solution with Experiment, Sublimation & Chemical Vapour Transport (with Experiments), Recrystallization for Purification (Experiment with Purity Control by Melting Point), Growth from Melts with Experiment, Zone Melting/Pfann

-**Fundamentals of Epitaxy:** Hetero- and Homo-Epitaxy, Growth Modes and their Control by Supersaturation & Substrate, Substrate Problems (Misfit, Misorientation, Thermal Expansion Differences, Dislocation Density, Surface Quality), Surfactants, Surface Reconstruction, Interfaces, Multilayers, Superlattices, Nano-structures

-**High-Temperature Technology:** Heating Methods (resistive, radiative, RF), Furnace Design, Heating Elements, Crucibles, Reactivities/Corrosion, Ellingham diagrams, Thermal and & Vibration Insulation, Temperature Measurements

-**Vacuum Technology:** Pumping Systems, Vaccuum Vessels & Lines, Permeability, Outgassing, Vacuum Measurement, Partial Pressure Adjustment, Measurement of Trace Gases (O_2 , H_2O, etc.), Vapour Pressures, Mass Spectrometry

-**High-Pressure Technology:** Compressors; Autoclave design, pressure systems and monitoring, safety valves etc.

-**Crystal Growth Methods:** From Solution (Slow Cooling/ACRT, Circulation/Stirrer, Evaporation, TSSG, Hydrothermal); from Melt (Tammann-Stöber/VGF/HEM, Bridgman-Stockbarger/ACRT, Czochralski (Little-Teal) and LEC, Skull, Float-Zone, Zone Melting); from Vapour (Piper-Polich, Chemical Transport/Schäfer). Growth experiments **Growth of Inclusion-free Crystals** (Ivantsov Diffusional Undercooling/Constitutional Supercooling of TJRCh, Maximum Stable Growth Rate of Scheel&Elwell); **Growth of Dislocation-free Crystals** (Dash, Billig, Indenbom, Milvidskij, Jordan, Müller & Völkl); **Growth of Striation-free Crystals** (Scheel, Rytz & Swendsen); Equipment & Resources; Simulation. Casting, dendritic growth, turbine blades; Solid-State Crystallization

-**Epitaxy Methods:** Liquid Phase Epitaxy LPE, Molecular Beam Epitaxy MBE, Organo-Metal-Vapour Phase Epitaxy OMVPE / MOCVD, Atomic-Layer Epitaxy ALE, Growth parameters to control the growth mode and perfection of epilayers

-**Single Optimum Growth Technology for a specific Crystal or Epilayer for a specific Application** based on all relevant parameters (thermodynamics, economy, ecology, infrastructure, timeliness, safety, etc.); examples of optimum growth (Si by Czochralski & Float Zone) and of non-optimized growth (Si for solar cells)

-**Important Materials / Production in Industry /Applications of Crystals and Epilayers, Multilayers:** Si, Ge, GaAs, InP, GaP, CdZnTe, ZnO, Quartz, Al_2O_3, SiC, GaN, AlN, YAG:Nd & other LASER crystals, $LiNbO_3$, KDP, KDDP & other NLO crystals, Halide Scintillation Crystals, Optical Crystals, magneto-optic garnets, ZrO_2, Diamond; Epilayers and Multi-layers of (Ga,In)(As,P), GaAlAs, CdHgTe (CMT), GaInAlN, magneto-optic garnets, High-Tc Superconductors

-**Characterization of Crystals and Epilayers/Multilayers** by analytical, spectroscopical (ICP, microprobe), diffraction (X-ray topography), optical (Polarizing Microscope, TEM) and electronic methods, infrared tomography; surface characterization by Nomarski, Tolansky, STM, AFM, SEM, LEED etc.

-**Crystal Machining:** Crystal Orientation, Sawing/Slicing, Lapping, Polishing, Wafering, Micromachining, etching, with practical work and defect/surface characterization; visits of industries

-**Design of Furnaces/Machines for Crystal Production, Epilayer Production, Crystal Machining**

-**Two weeks in Modelshop:** Metal working; Soldering; Welding; Glass- & Quartz-Glass Blowing

-**2 x Three-Summer-Months Internship in Industry:** Crystal Factory, Epilayer/Device Fabrication, Crystal Machining, Machines for Crystal and Epilayer Production

-**Infrastructure:** Clean room; reliable electricity and water supply; control of temperature, humidity and vibrations

-**Work Safety, Insurance Aspects**

-**Management:** Workplan; Spread-Sheet Analysis/ Cost-of-Ownership; Business Plan; Intellectual Property Aspects

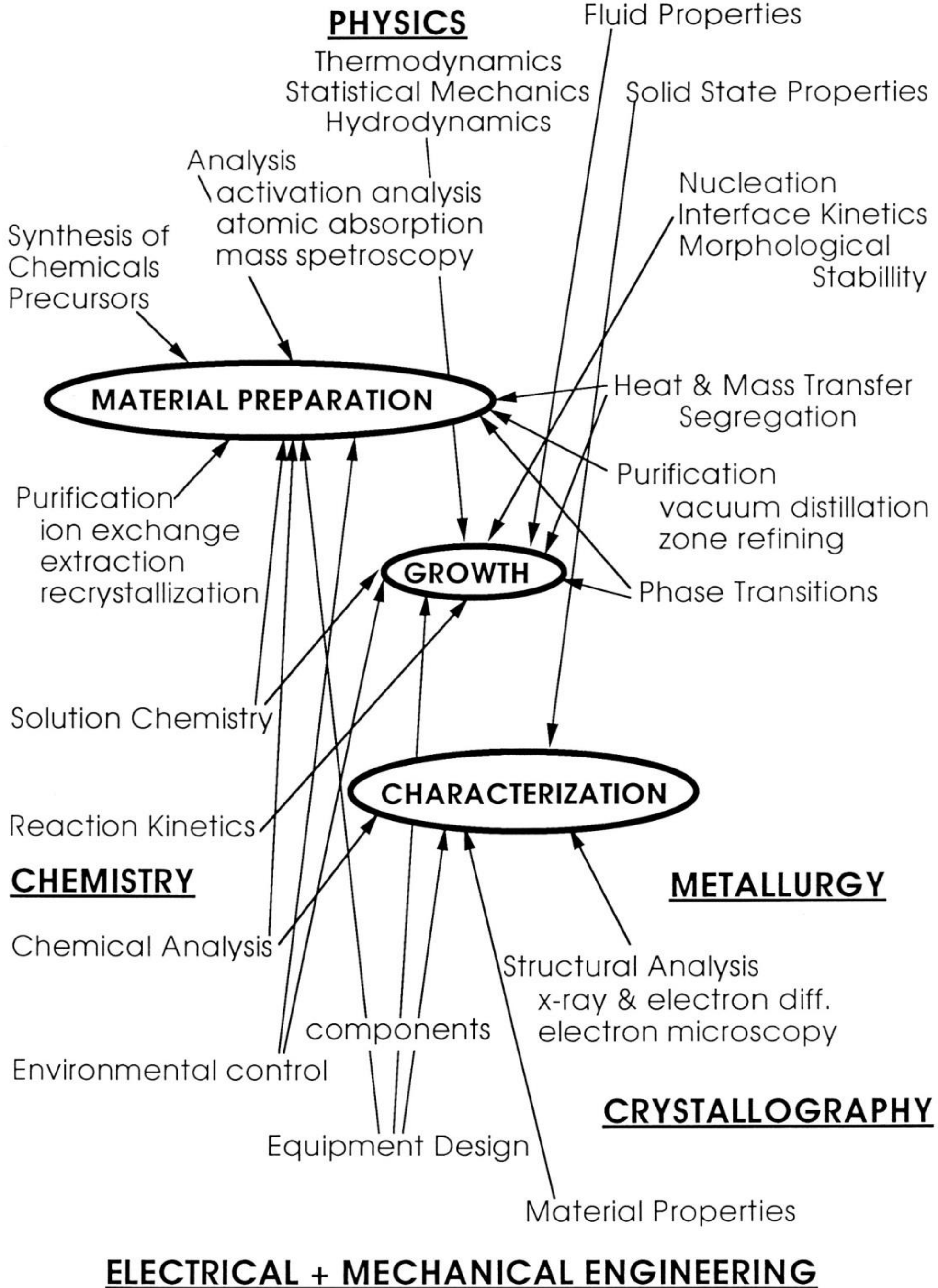
-**History of Crystal Growth, Crystal Technology & Materials Science**

*Compare with Bachelor and Master Courses in Metallurgy and Materials Engineering at Technical Universities.

Conclusion

**Well-educated Crystal Technologists
will Produce Perfect Crystals & Epilayers
to Accelerate Progress
in Reproducible Solid State Physics
and Increase Efficiency in Energy Technology**

Thank you!


PHYSICS
Thermodynamics
Statistical Mechanics
Hydrodynamics
Fluid Properties
Solid State Properties
Analysis
activation analysis
atomic absorption
mass spetroscopy
Synthesis of
Chemicals
Precursors
Nucleation
Interface Kinetics
Morphological
Stabillity
MATERIAL PREPARATION
Heat & Mass Transfer
Segregation
Purification
vacuum distillation
zone refining
Purification
ion exchange
extraction
recrystallization
GROWTH
Phase Transitions
Solution Chemistry
CHARACTERIZATION
Reaction Kinetics
CHEMISTRY
METALLURGY
Chemical Analysis
Structural Analysis
x-ray & electron diff.
electron microscopy
components
Environmental control
CRYSTALLOGRAPHY
Equipment Design
Material Properties
ELECTRICAL + MECHANICAL ENGINEERING

The Chances for well-educated Crystal Technologists

- to apply the single optimum technology for growth of highest-quality crystals for best research
- to develop optimum technology for crystal production thereby saving resources and time
- to collaborate with machine-, process- and material-engineers, hydrodynamic & thermodynamic experts, theorists and other specialists to develop optimum processes
- to collaborate with crystal consumers about optimum crystal material
- to collaborate with characterization experts

Driving forces and present situation

Development of crystal growth technology

1882-1930 Measurements of crystallization velocities: 1882 Gernez, 1903 Tammann, 1918 Czochralski, 1928 Kapitza

1902 Verneuil: Production of ruby for watchstones

1915-1939: Development of crystal growth methods for salts & metals for research and optics: Nacken, Stöber, Bridgman, Kyropoulos, Stockbarger

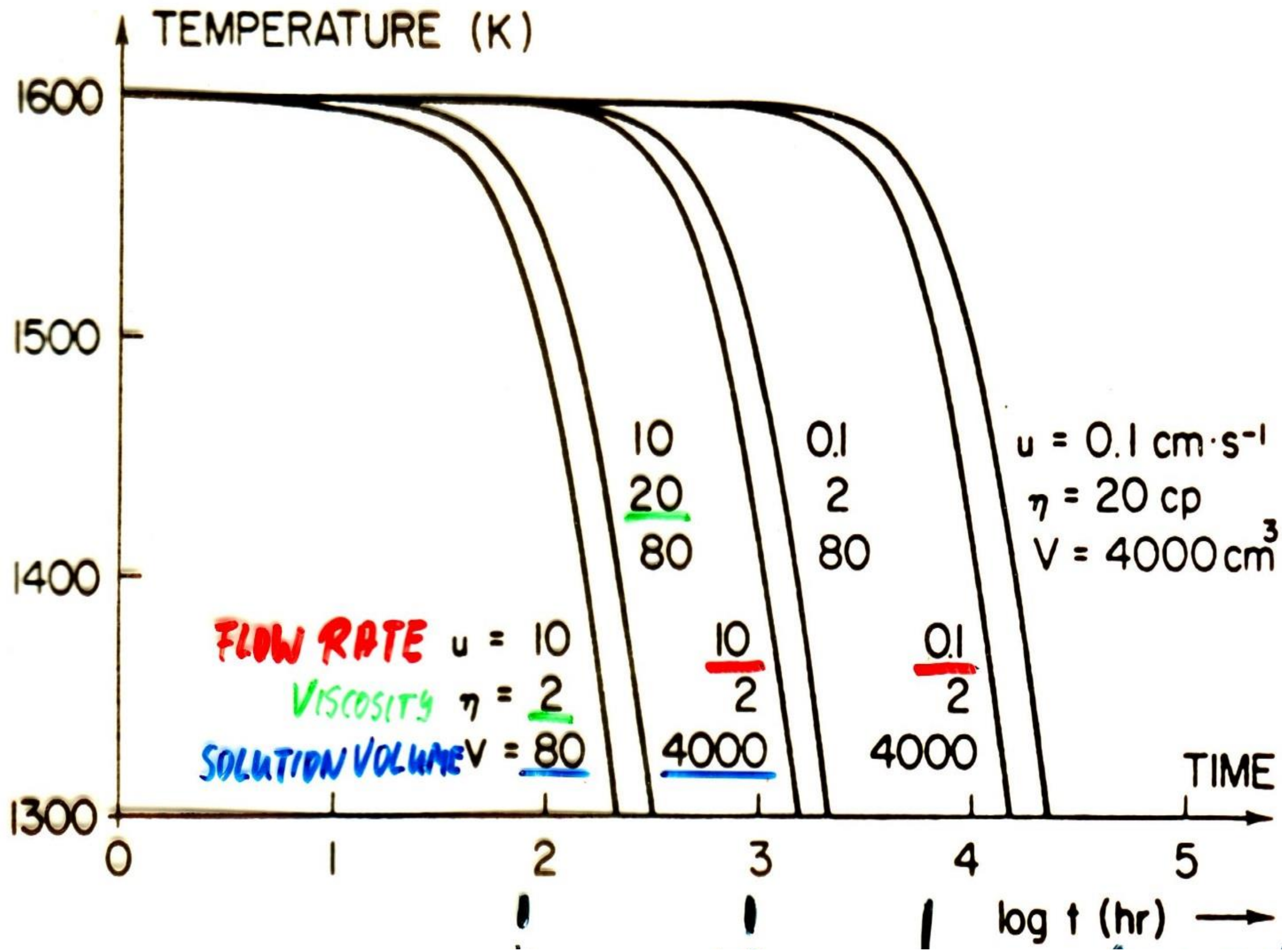
1939-1945: Crystal growth for military: infrared optics, quartz oscillators, detectors

1946-1995 Military support for crystal growth & epitaxy technology

1950- Semiconductors (Ge, Si, GaAs, InP, SiC, GaN) for microelectronics, optoelectronics etc.: Numerous industry and government crystal growth labs. formed.

1960- Laser crystals

1980-1999 Most industry and government growth labs. reduced or closed (end of cold war, shareholder value, recession):
Bell, Bellcore, RCA, IBM, Siemens, Philips, Battelle, Cyanamid, Alusuisse, Sandoz, NTT Japan, Fujitsu, NEC, KFA Jülich, RRE/RSRE Malvern, Institute of Single Crystals Kharkov etc.
Tremendous loss of crystal-growth knowhow: Initiation of new centers of competence requires 10 to 20 years.
Growth industries & new companies.



Temperature programs for various values of viscosity, solution flow rate u and solution volume V for growing crystals free of inclusions.

H.J.Scheel, D. Elwell, J. Crystal Growth **12**(1972)153

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GPE

General Protection Engineering GmbH

General Protection Engineering GmbH (GPE GmbH)
Dr.-Ing. Hans J. Scheel, Bromattenweg 2, 3805 Goldswil b. Interlaken, Schweiz
11.8.2017/HJS

Zweck der Gesellschaft:

Die Gesellschaft bezweckt die Entwicklung von Konzepten und Technologien und Ingenieurleistungen zur Prävention von Naturkatastrophen und zur Steigerung der Energieeffizienz und der Laserfusionsenergie sowie zur Sicherung der radioaktiven Abfälle. Erbringen von Beratungen und Dienstleistungen aller Art in diesem Bereich. Die Gesellschaft kann Patentanmeldungen vornehmen, Patentrechte verkaufen und Lizenzen vergeben. Sie kann im In- und Ausland Zweigniederlassungen errichten, sich an anderen Unternehmen im In- und Ausland beteiligen, gleichartige oder verwandte Unternehmen erwerben oder sich mit solchen zusammenschliessen sowie alle Geschäfte eingehen und Verträge abschliessen, die geeignet sind, den Zweck der Gesellschaft zu fördern, oder die direkt oder indirekt damit im Zusammenhang stehen.

Die Firma **General Protection Engineering GmbH** ist auf folgenden Gebieten aktiv:

- Tsunami Katastrophenschutz** inklusive Abfallentsorgung von MegaCities und Landgewinnung, hydroelektrische Energiespeicherung an Küsten, Fischfarmen.
- Hurrikan/Typhoon-Flut-Katastrophenschutz a) lokal, permanent**
  b) temporär, dynamisch auf See***
- Lokaler Tornadoschutz, z.B. an der Tornado-Alley in USA (Oklahoma, North-Texas, Missouri, Nebraska, South Dakota)***
- Erdbebenschutz bei der Geothermie (Publikation in NZZ Nr. 187 Seite 20, 15.8.2013)
- Erhöhung der Flugsicherheit, Verbesserung der Effizienz im Flugverkehr***
- Flut-Katastrophenschutz in der Schweiz
- Sicherung alter Gebäude und Kirchen gegen Zerfall bei Erdbeben
- Verhinderung der Ausbreitung von Waldbränden
- Schutzmassnahmen nach AKW-Unfall (in Fukushima nicht befolgt)
- Ausbildung von Kristalltechnologen für Verbesserungen in der Energietechnologie, für Laser-Fusions-Energie, und für Anwendungen der Hochtemperatursupraleitung, siehe WHITE PAPER in www.hans-scheel.ch

** Patente erteilt in 2 Ländern, andere Patent-Anmeldungen noch in Bearbeitung, Internationale Publikationen und Vorträge, NZZ vom Dienstag 3. November 2015 S.11, siehe Beilage

*** Nach Unterzeichnung der Vertraulichkeitsvereinbarung, mit finanzieller Unterstützung und nach Prüfung: Patentanmeldungen

Folgende Unfälle und Katastrophen sind ausgeschlossen:

- AKW-Unfälle; Grubenunglücke; Vulkanausbrüche; Erdrutsche
- Extrem-Wetter, Hagelschäden, Lawinen, Blitzschlag bei Gewitter
- Erdbeben (Ausnahmen Geothermie, Gebäude-Sicherung)
- Andere nicht aufgeführte Katastrophen

Beilagen: - Liste der Internationalen Vorträge und Publikationen
- Erteilte Patente, Patentanmeldungen

Tsunami Sumatra 26.12.2004

Tsunami Tohoku, Japan 11.3.2011

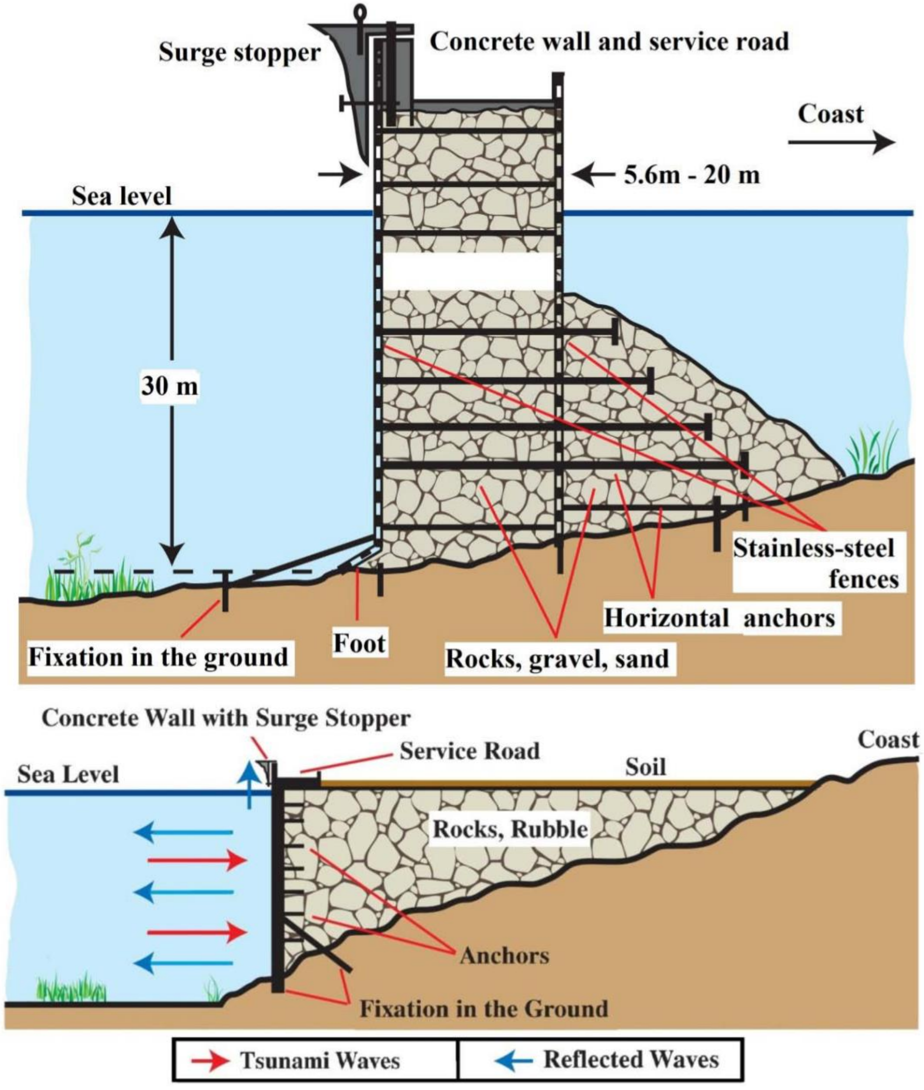
Hurricane Katrina 29.8.2004

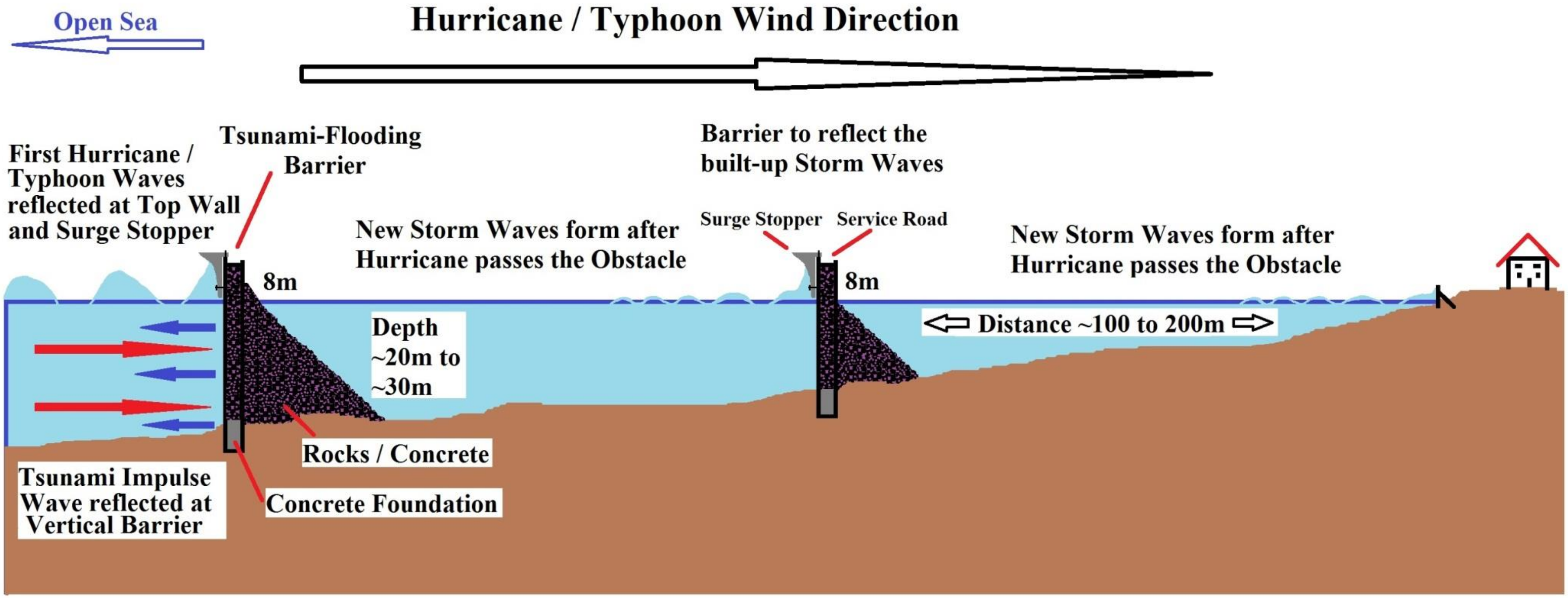
Typhoon Haiyan, Philippines 8.11.2013

Sumatra Tsunami 2004	210’ 000 Fatalities	Damage 10 billion $
Katrina Hurricane 2005	1’300 Fatalities	Damage 125 billion $
Tohoku Tsunami 2011	19’000 Fatalities	Damage 300 billion $
		+ global & Fukushima consequences
Haiyan Typhoon 2013	8’000 Fatalities	Damage 2.86 billion $
Total	238’300 Fatalities	Damage 438 billion $

Motivation

- Tsunami Flooding Barrier (TFB)
- The *TsuBar* project: Leichtweiß-Institute (LWI), TU Braunschweig, Germany – Funded by Scheel consulting
- Studying the hydro-dynamic processes
- Tsunami wave loads on TFB
- A numerical model of realistic waves on the structure

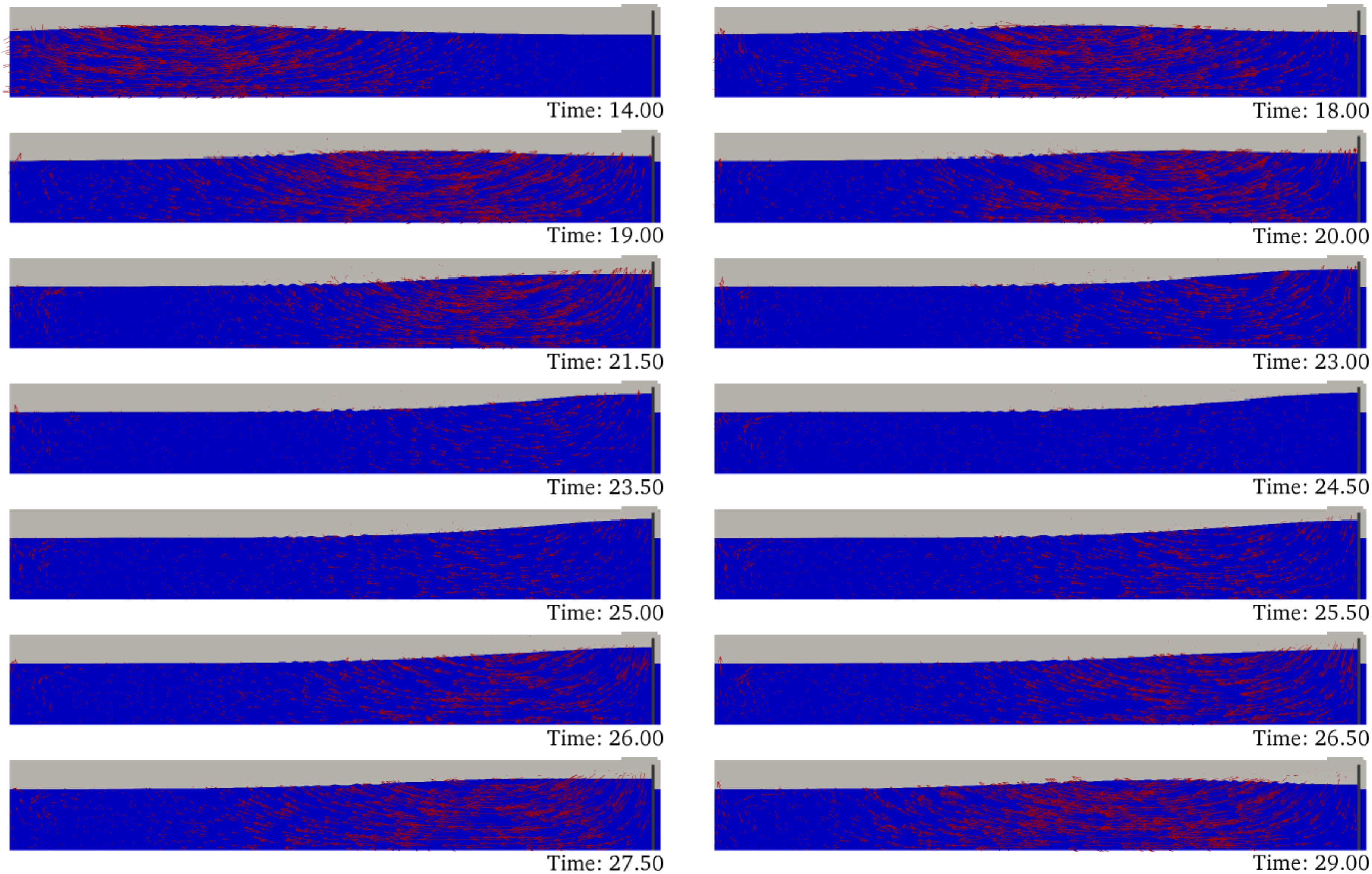




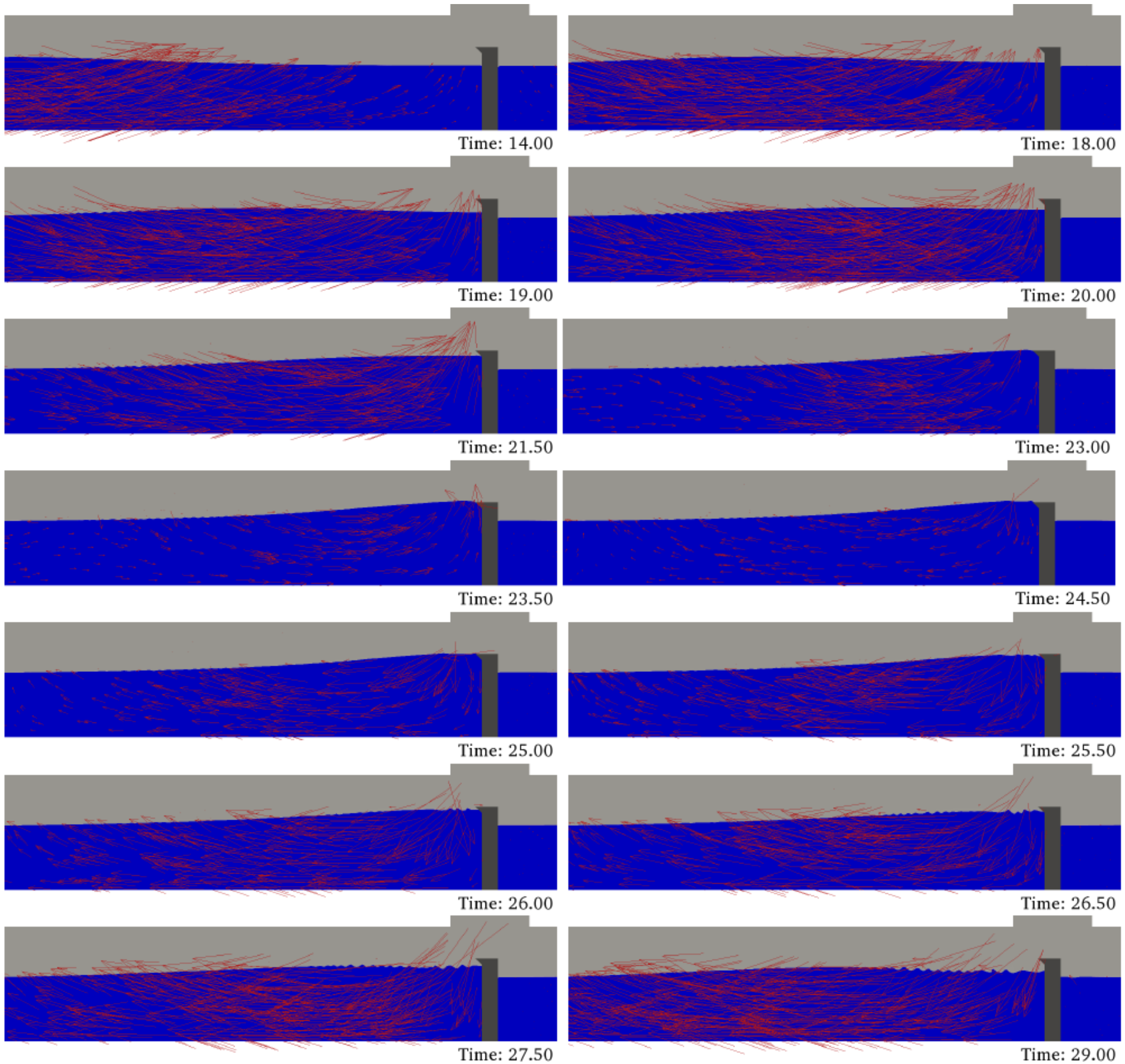
Protection against Tsunami and Against Tropical Storms

(Schematic Cross Section)

Solitary Wave Reflection



Efficiency of The Surge Stopper



Tsunami Run-up and Loads on TFB

- Max. run-up

$$\eta^* = \beta H$$

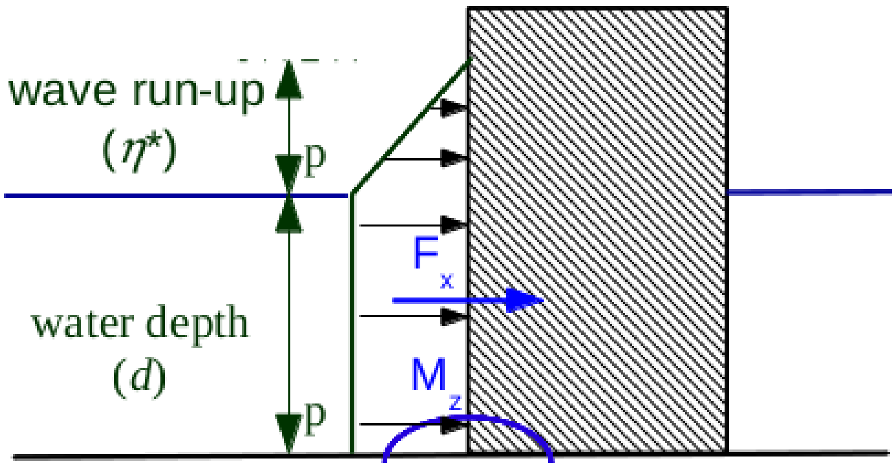
$$\beta = 2.19 - 0.000682L$$

- Pressure intensity

$$p = \frac{1}{2}\alpha\rho C^2$$

$$\alpha = 3.516\left(\frac{H}{d}\right)^3 - 7.213\left(\frac{H}{d}\right)^2 + 4.4455\left(\frac{H}{d}\right) - 0.0209$$

- The total horizontal force and the total moment at seabed



H → Wave height
d → Water depth
L → Wave length
C → Wave celerity (L/T)
T → Wave period

η^* → Run-up
p → Wave pressure
α & β → Empirical coefficients
ρ → Water density

NEW ZEALAND
INTELLECTUAL
PROPERTY OFFICE

LETTERS PATENT

Number **620978**

ELIZABETH THE SECOND, by the Grace of God Queen of New Zealand and Her Other Realms and Territories, Head of the Commonwealth, Defender of the Faith; To all to whom these presents shall come, Greeting:

WHEREAS pursuant to the Patents Act 1953 an application has been made for a patent of an invention for

SUBMARINE CONSTRUCTION FOR TSUNAMI AND FLOODING PROTECTION, FOR TIDAL ENERGY AND ENERGY STORAGE, AND FOR FISH FARMING

(more particularly described in the complete specification relating to the application) AND WHEREAS

Hans J. Scheel, c/o Scheel Consulting Sonnenhof 13, Pfäffikon 8808, Switzerland.

(hereinafter together with his or their successors and assigns or any of them called "the patentee") is entitled to be registered as the proprietor of the patent hereinafter granted:

NOW, THEREFORE, We by these letters patent give and grant to the patentee our special licence, full power, sole privilege, and authority, that the patentee by himself, his agents, or licensees and no others, may subject to the provisions of any statute or regulation for the time being in force make, use, exercise and vend the said invention within New Zealand and its dependencies during a term of twenty years from 7 February 2014 and that the patentee shall have and enjoy the whole profit and advantage from time to time accruing by reason of the said invention during the said term:

AND WE strictly command all our subjects whomsoever within New Zealand and its dependencies that they do not at any time during said term either directly or indirectly make use of or put into practice the said invention, nor in any way imitate the said invention without the consent, licence, or agreement of the patentee in writing under his hand, on pain of incurring such penalties as are prescribed by law and of being answerable to the patentee according to law for his damages thereby occasioned:

PROVIDED ALWAYS:

(1) That these letters patent shall determine and become void if the patentee does not from time to time pay the renewal fees prescribed by law in respect of the patent:
(2) That these letters patent are revocable on any of the grounds prescribed by the Patents Act 1953 as grounds for revoking letters patent:
(3) That nothing in these letters patent shall prevent the granting of licences in the manner in which and for the considerations on which they may by law be granted:
(4) That these letters patent shall be construed in the most beneficial sense for the advantage of the patentee.

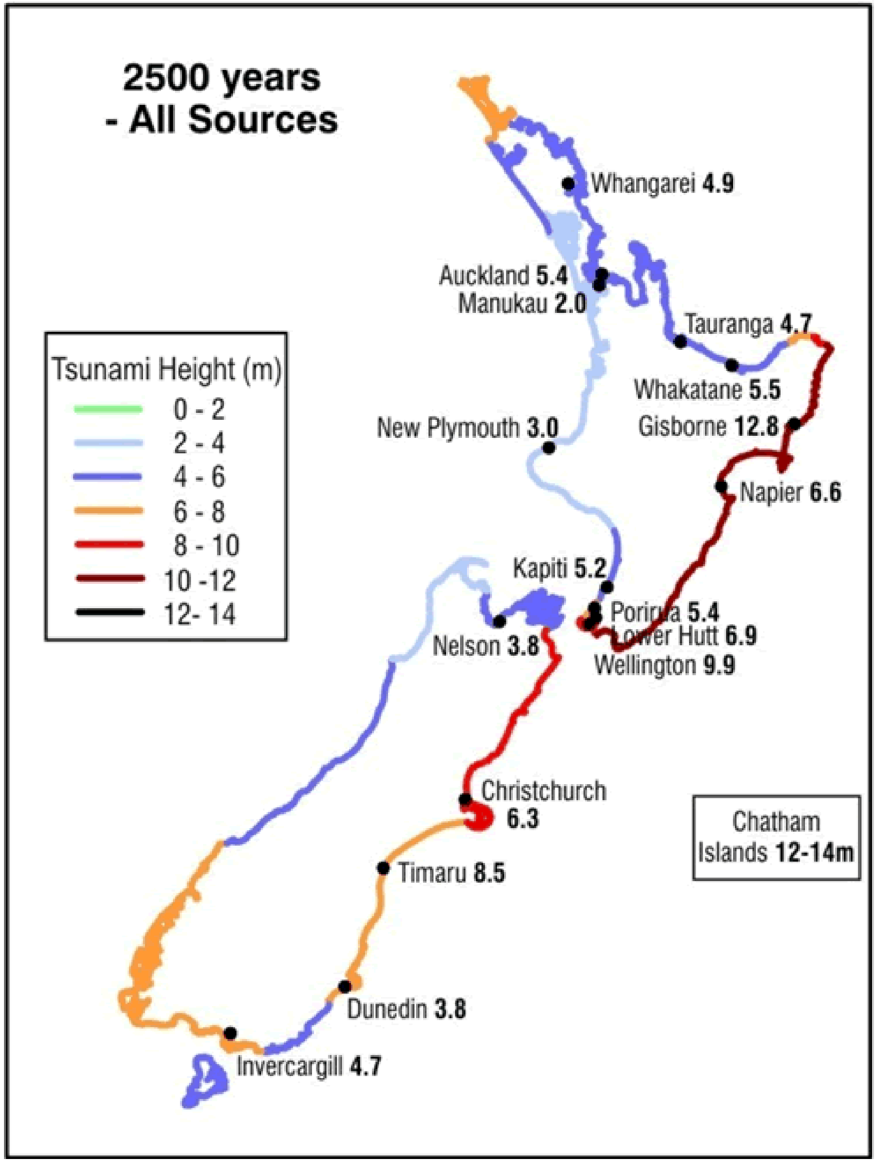
IN WITNESS whereof We have caused these letters patent to be signed and sealed on 1 December 2015 with effect from 7 February 2014.

COMMISSIONER OF PATENTS · NEW ZEALAND

Mandy McDonald

Mandy McDonald
Commissioner of Patents

2005 Tsunami Report



Tsunami heights calculated at urban centres and estimated by expert judgement elsewhere

Cross Section through Center (Eye) of a Hurricane

(schematic, not to scale)

After R.K. Smith: The Surface Boundary Layer of a Hurricane, Tellus XX(1968)3, 473-484