Invited Lecture at Annual Meeting of Swiss Society for Crystallography and Crystal Growth
at Paul-Scherrer-Institute / ETH, 12.9.2018

Crystal Growth and Crystal Technology

Hans J. Scheel

hans.scheel@bluewin.ch

Crystal Growth and Crystal Technology

- **Personal Introduction**
- **Energy and Sustainability:** Role of Crystal Growth and of Crystallography
- **Crystal Growth for Solid-State Research**
  - From Art to Science
  - Single Optimum Growth Technology for «Perfect» Crystals
  - «Sufficient Characterization» for Reproducible Physical Measurements
- **High-Temperature Superconductivity (HTSC)**
  - Discovery, Potential, Race for Higher Tc, Preparation Problems, Crystal Growth, Oxidation Problem, Epitaxy Problems, Future of HTSC Needs Crystal Technologists
- **Epitaxy:** Growth Modes > Perfection & Performance; PVD versus LPE
- **Education of Crystal Technologists : WHITE PAPER**
  - for Highest-Efficiency Energy Devices (Solar Cells, LEDs, Power Devices, etc.),
  - for HTSC, for Laser-Fusion Energy, APPLE-GT-Story
- **Conclusions**

Personal Introduction of Hans J. Scheel

20 Years ETH Z+L
15 Years IBM

1958 Invitation Prof. Paul Karrer (retired 1959)

Chemical Institute, University of Zurich

1959-1968 Prof. Fritz Laves

Institute of Crystallography, Mineralogy, Petrography ETH Zurich (&University ZH)

1968-1982 Invitation Dr. K.A. Müller

IBM Zurich Research Laboratory (50% crystal service, 50% own projects)

1983 Invitation to University of Sao Paulo, Brazil (until 1985 Democratization Act)

Institute of Physics and Chemistry of Sao Carlos & INPE Natl. Space Research Institute S.J.dos Campos

1986-1987 Ferrofluidics Nashua N.H. & Leybold Heraeus, Hanau, Germany

Development of crystal growth machines

1987/1988 Invitation to MASPEC Natl. Institute Parma (Dr. Lucio Zanotti)

First large HTSC YBCO crystals grown with Dr. F. Licci

1988 Invitation Prof. Martin Peter (Physics University Geneva)

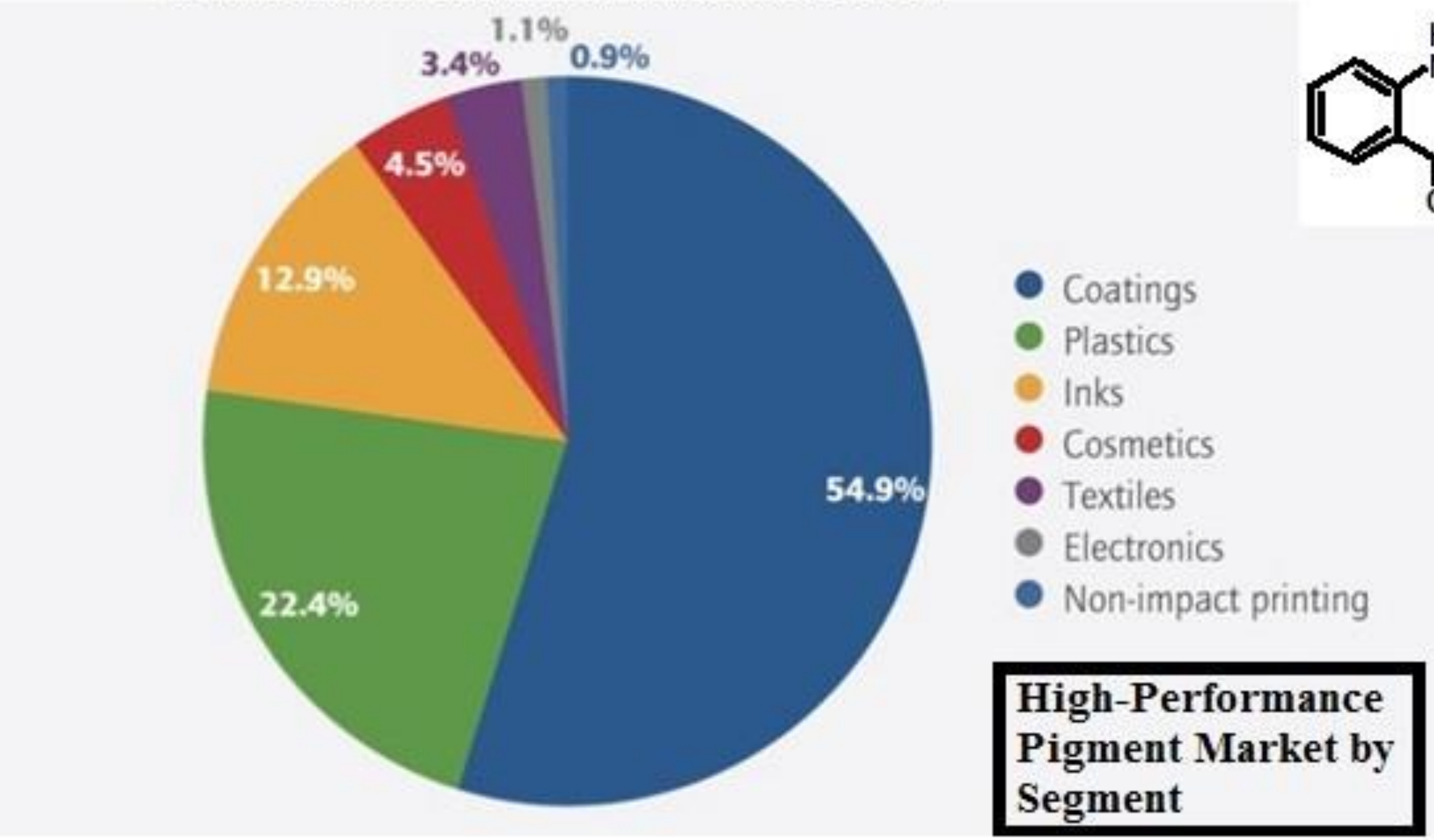
1988-2001 Invitation Prof. E. Mooser & Prof. F.K. Reinhart, EPF Lausanne

Groupe Cristallogenese with support from Thomson-CSF, SNF, DAAD, US Army, NTT, EPFL,etc.

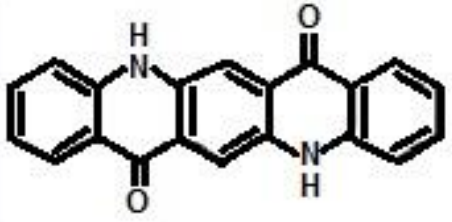
After retirement: visting scholar/professor Osaka Univ. 2002, 2003, 2004, Shandong Univ. Jinan 2005, Tohoku Univ. 2006 --- Now very busy with new company www.general-protection-engineering.ch

Organic Pigment Dye
Quinacridone
(Chinacridon)
Stable against UV and stable at high temperature

COATINGS WORLD: With an overall value of $4.76 billion, the market for high performance pigments is poised for steady growth worldwide. Quinacridone 2016 178.844 tons.
1960: CIBA, Farbwerke Hoechst, DuPond,
now Clariant India & China, AkzoNobel



High-Performance Pigment Market by Segment



MP dec. ~400°C

Unsoluble

⇩

Growth by Sublimation

H. Koyama, F. Laves, H.J. Scheel: Kristallstrukturen organischer Pigmentfarbstoffe I: g-Chinacridon $C_{20}H_{12}O_2N_2$, *Naturwiss. 53(1966)700.*
K. Ogawa, F. Laves, H.J.Scheel: II: 4,4'-Diamino-1,1'-Dianthrachinonyl $C_{28}H_{16}N_2O_4$, *Naturwiss. 53 (1966)700-701.*

Structure Determination in Infrared Microscope!

Lozenge-shape platelets. Hoechst story.

1968 - 1982

Zur Erinnerung an 14 Jahre Forschung im

IBM Labor Rüschlikon

Bob Swendsen

Eric Courtens

M.V. Baumberger

Hildegard Löhner

Marie D'Iorio

W. Schlup

B. Reihl

J.G. Bednorz

W. Stocker

K.R. Müller

Paul Bayer

S. Eigenmann

M. Lang

T. Schneider

D. Widmer

Eberhard Latta

a. diener

BERT OOSENBRUG

Christoph Gerber

Dieter Pohl

Erich Stoll

Alexis Baratoff

Miguel Aguilar

Hartwig Thomas

Peter Dill

Keith W. Blazey

Werner Bächtold

E. Weidel

Heinz Keller

Crystal Growth Activities in Switzerland 1960 – 1980

Commercial Production

Djevahirdjian S.A., Monthey
Swiss Jewel Corporation, Locarno
SADEM, Courtepin
Alusuisse, Neuhausen
Kistler, Winterthur
Mass crystallization in chemical industries

Future: Best Wishes for
Enrico Giannini !

Industry Research Laboratories

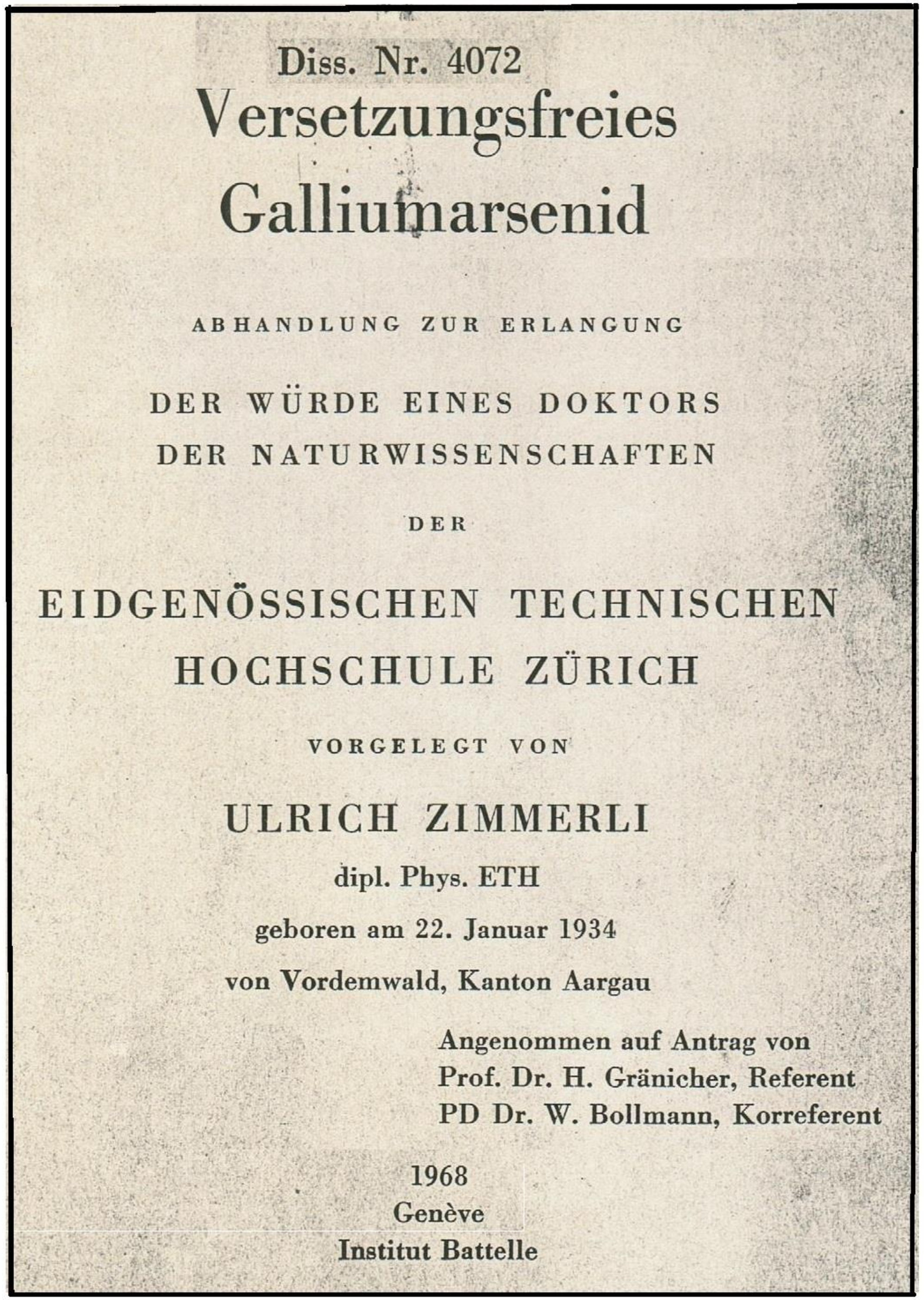
Battelle, Geneva (A. Steinemann, U. Zimmerli, H. Schmid)
Cyanamid, Geneva (E. Mooser, F. Levy)
BBC, Baden (H.U. Beyeler, P. Brüesch, H.R. Zeller)
BBC Dätwyl (C. Schüler)
Balzers (G. Zinsmeister)
RCA Zurich (R. Nitsche, E. Kaldis, H.W. Lehmann, etc.)
IBM Zurich (H.J. Scheel, ACRT)
EIR, Würenlingen
Eastman-Kodak

to be completed

University Laboratories

Geneva (E. Walker, H. Schmid)
ETH Lausanne (W. Kurz, H. Berger, F. Levy)
Bern (F. Hulliger, HU Güdel)
ETH Zurich (N. Ibl)
ETH Zurich (W. Huber, E. Kaldis, J.Karpinski, H. Arend)
ETH Zurich (H.J. Scheel)
Univ. Zurich (H.R. Oswald, J.R. Günter, S. Veprek)
Fribourg (A. von Zelewsky, F.P. Emmenegger)
PSI ?

First International Conference on Crystal Growth and Epitaxy from the Vapour Phase ETH Zurich 23.-26.9.1970
First European Conference on Crystal Growth ECCG-1 ETH Zurich 12-18.9.1976



Diss. Nr. 4072

Versetzungsfreies Galliumarsenid

ABHANDLUNG ZUR ERLANGUNG

DER WÜRDE EINES DOKTORS
DER NATURWISSENSCHAFTEN

DER

EIDGENÖSSISCHEN TECHNISCHEN
HOCHSCHULE ZÜRICH

VORGELEGT VON

ULRICH ZIMMERLI
dipl. Phys. ETH
geboren am 22. Januar 1934
von Vordemwald, Kanton Aargau

Angenommen auf Antrag von
Prof. Dr. H. Gränicher, Referent
PD Dr. W. Bollmann, Korreferent

1968
Genève
Institut Battelle

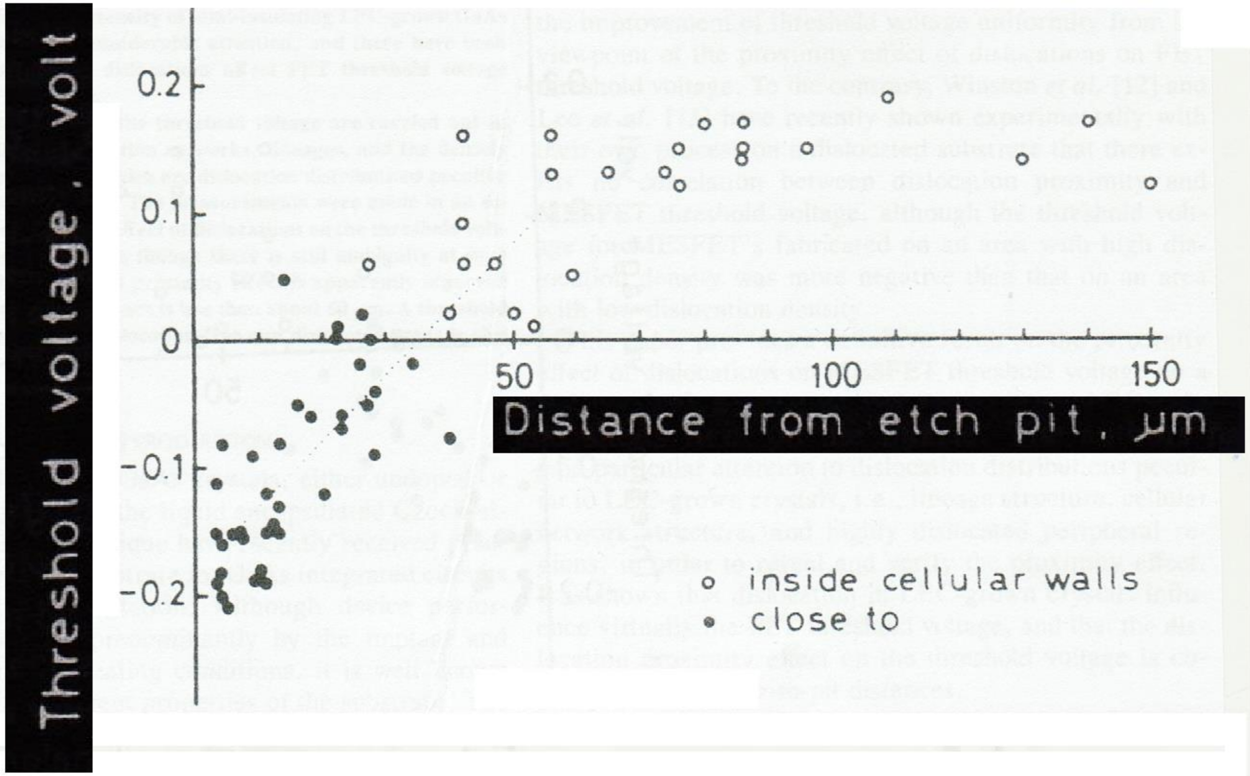
A. Steinemann, U. Zimmerli:
Dislocation-free gallium arsenide single crystals **in**
Crystal Growth, Edit. H.S. Peiser,
Pergamon, Oxford/New York
1967, 81-87

IEEE TRANSACTIONS ON ELECTRON DEVICES, VOL. ED-33, NO. 2, FEBRUARY 1986 **227-233.**

Proximity Effect of Dislocations on GaAs MESFET Threshold Voltage

SHINTARO MIYAZAWA AND FUMIAKI HYUGA

Thanks to S.M.!



The authors are with **NTT** Atsugi Electrical Communication Laboratories, 3-1, Morinosato-Wakamiya, Atsugi-shi, Kanagawa 243-01 Japan.

Masahiro Sasaura

1983/1984

Humanity's Top Ten Problems for next 50 years

According to Richard Smalley
Nobel Prize for Chemistry 1964
Smalley 2003

- **ENERGY**
- WATER
- FOOD
- ENVIRONMENT
- POVERTY
- TERRORISM & WAR
- DISEASE
- EDUCATION
- POPULATION
- DEMOCRACY

2004	6.5	Billion People
2050	~ 10	Billion People

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:

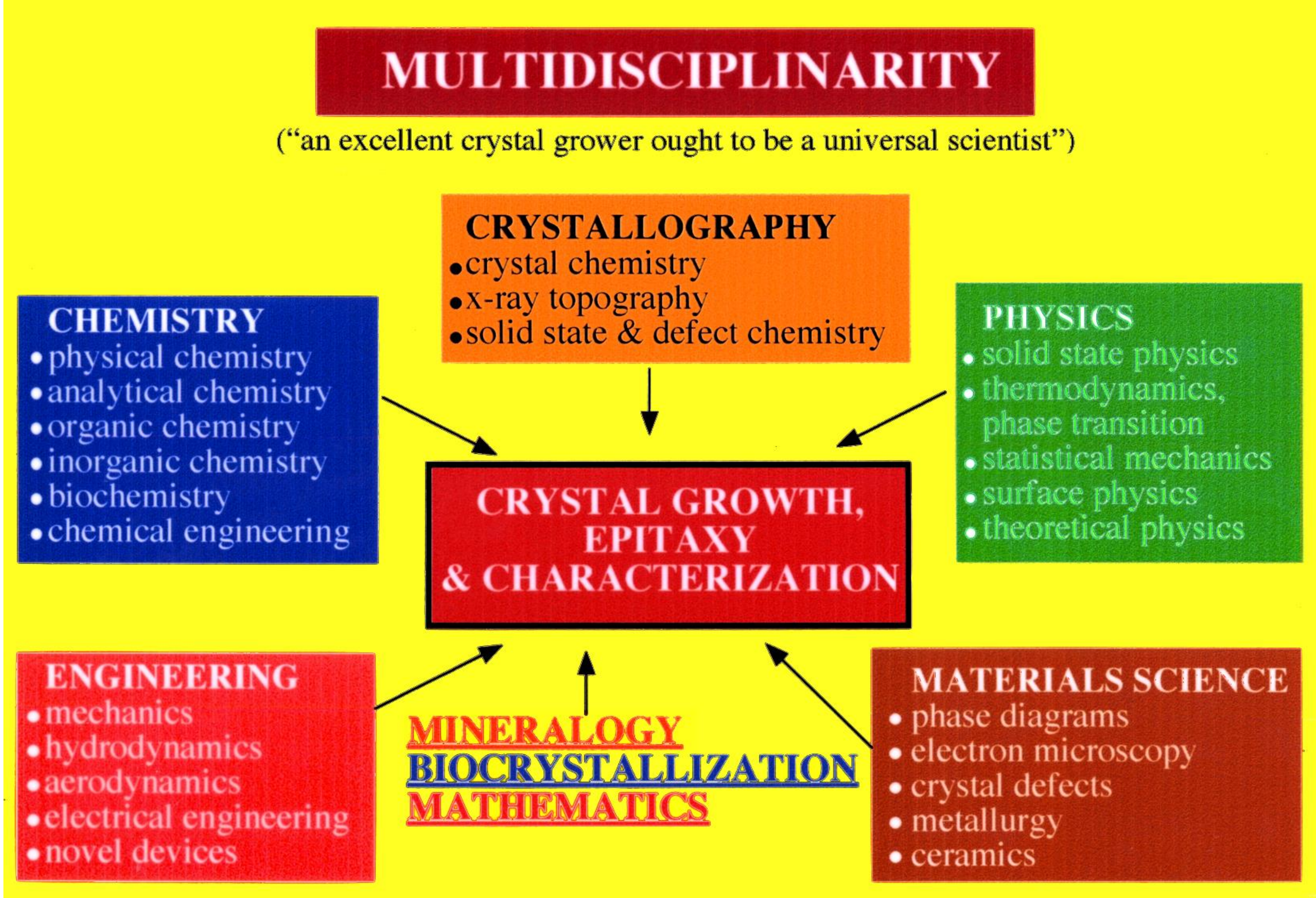
- **New Battery System**
- **HTSC Energy Storage (Flywheel, SMES Superconducting Magnetic Energy Storage)**

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，SQUID**



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

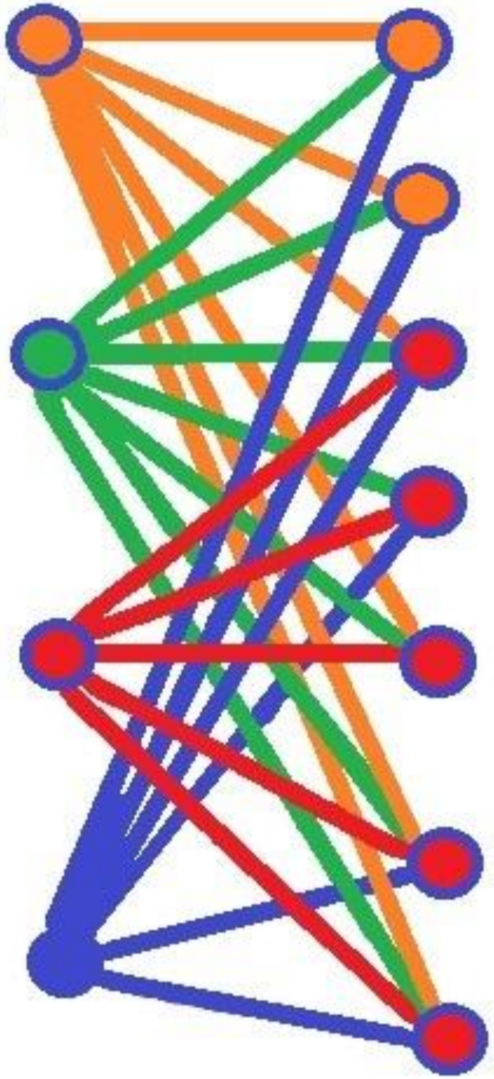
ENGINEERING
- mechanics
- hydrodynamics
- aerodynamics
- electrical engineering
- novel devices

MINERALOGY
BIOCRYSTALLIZATION
MATHEMATICS

MATERIALS SCIENCE
- phase diagrams
- electron microscopy
- crystal defects
- metallurgy
- ceramics

Machine and Process Engineering

Effect of Growth Parameter on Crystal Property



Parameter

Growth Temperature
(from Melt or from Solution)

Supersaturation
⇩
Growth Rate
⇩
Growth Mechanism

Temperature Gradient

Hydrodynamics

Property

Stoichiometry
Equilibrium Defects

Impurities

Homogeneity

Inclusions

Structural Perfection EPD etc.

Facet or Isothermal Surface

Speed & Economy

More than 10 Parameters which have to be Optimized

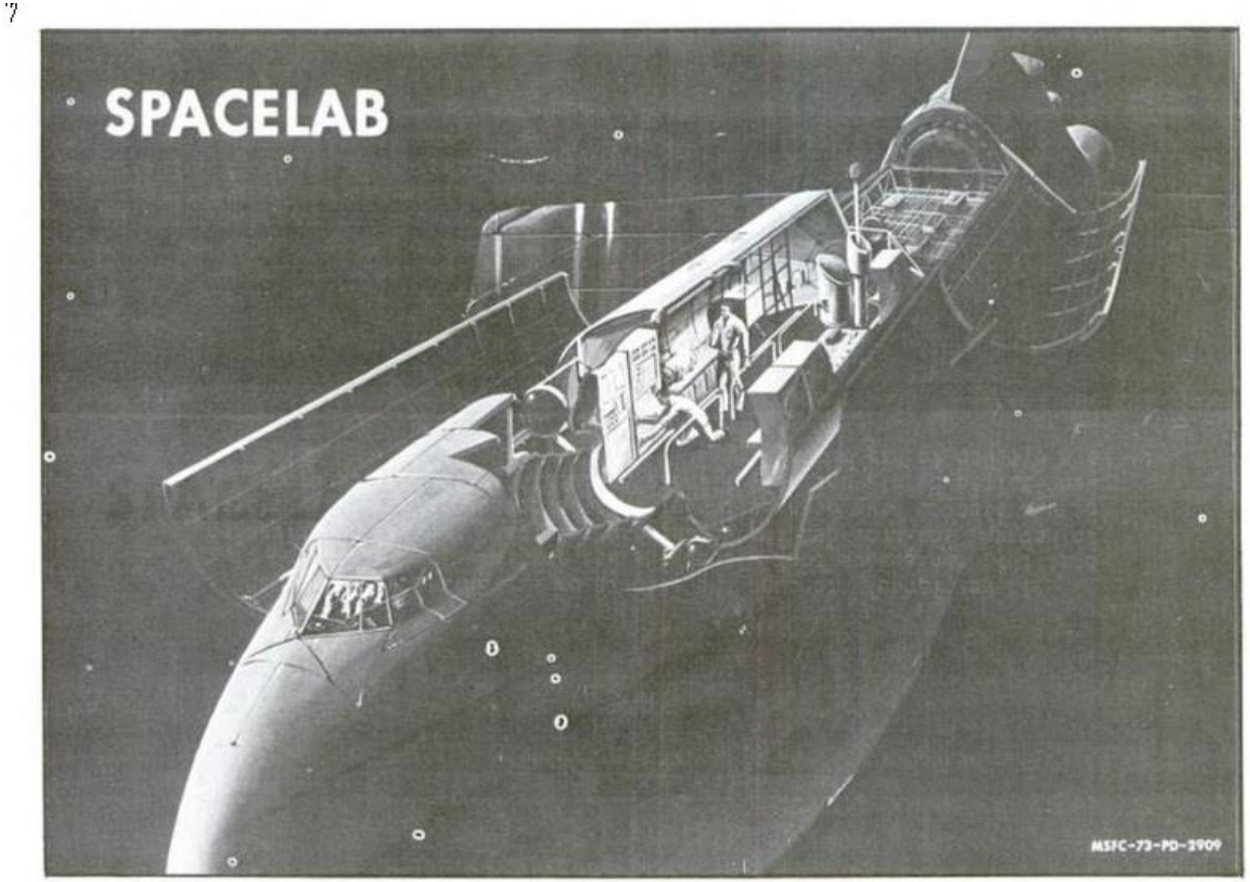
Approach: Trial & Error
Systematic
Intuitive / Empirical
Design of Experiment
Fully Scientific

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

Race to Space



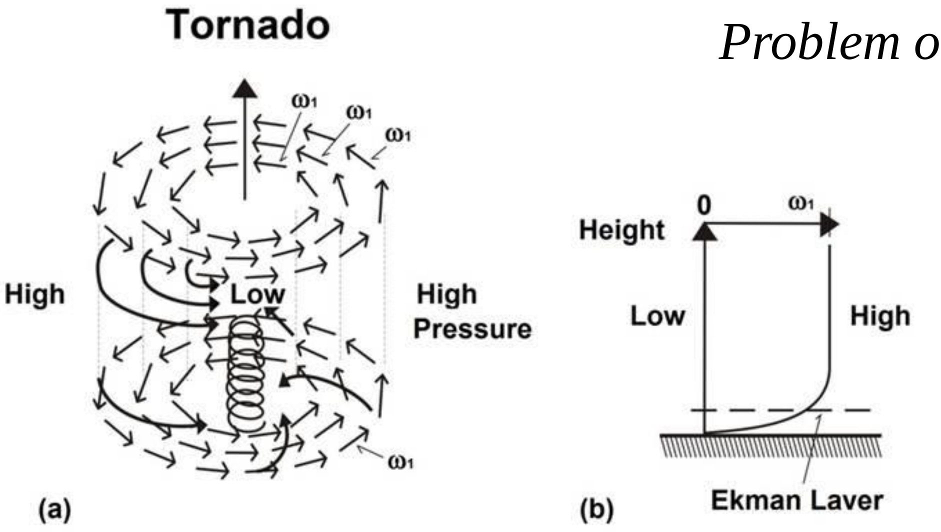
Skylab Flights 1973 – 1978

Spacelab 1983 – 1998 (2008)
22(32) Missions

Fluctuations of Convection cause Growth-Rate Fluctuations: Striations (Growth Bands)
Purpose of the Missions:
Reduction of Convection with «Zero-Gravity» for Growth of Striation-free Crystals

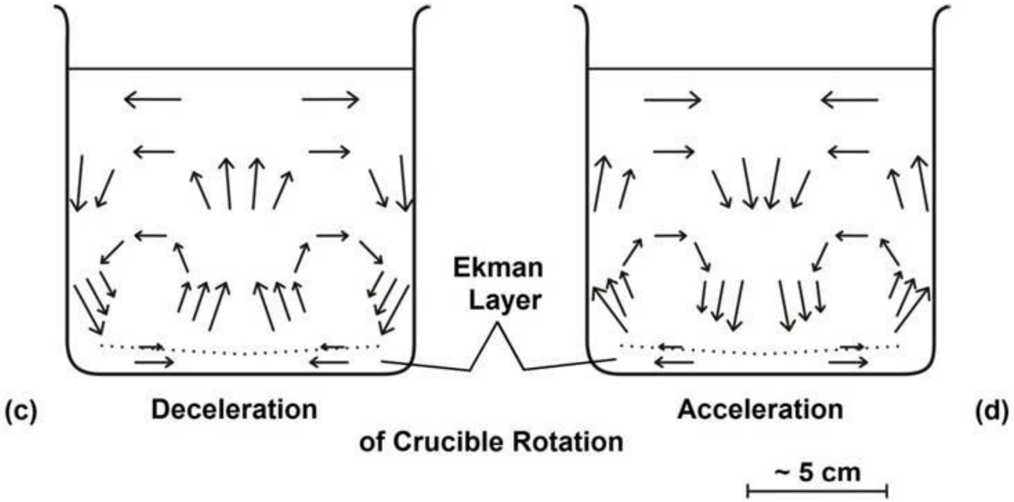
Opposite Approach on Earth: Forced Convection to Homogenize the Melt or Solution

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). With E.O. Schulz-DuBois

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

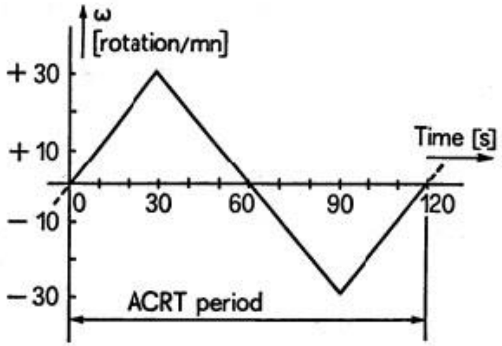


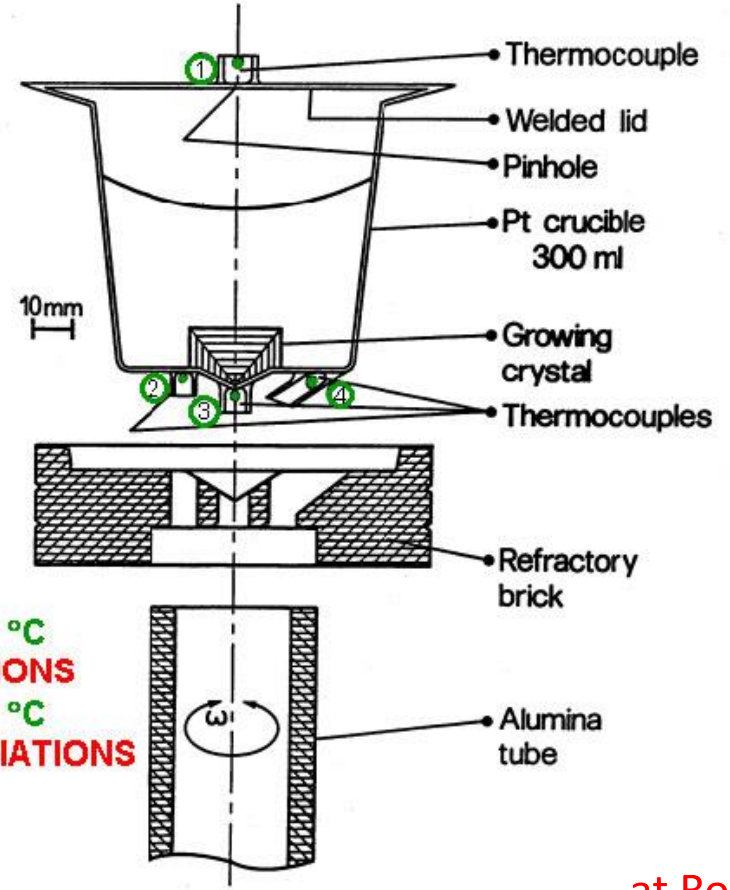
The Ekman Layer Flow occurs also in a circular Container with flat Bottom (c) when its Rotation is decelerated, and the opposite Flow upon Acceleration (d).

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

Accelerated Crucible Rotation Technique ACRT

Demo





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

Temperature Measurement
at Rotating Crucible at high Temperature

- 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.

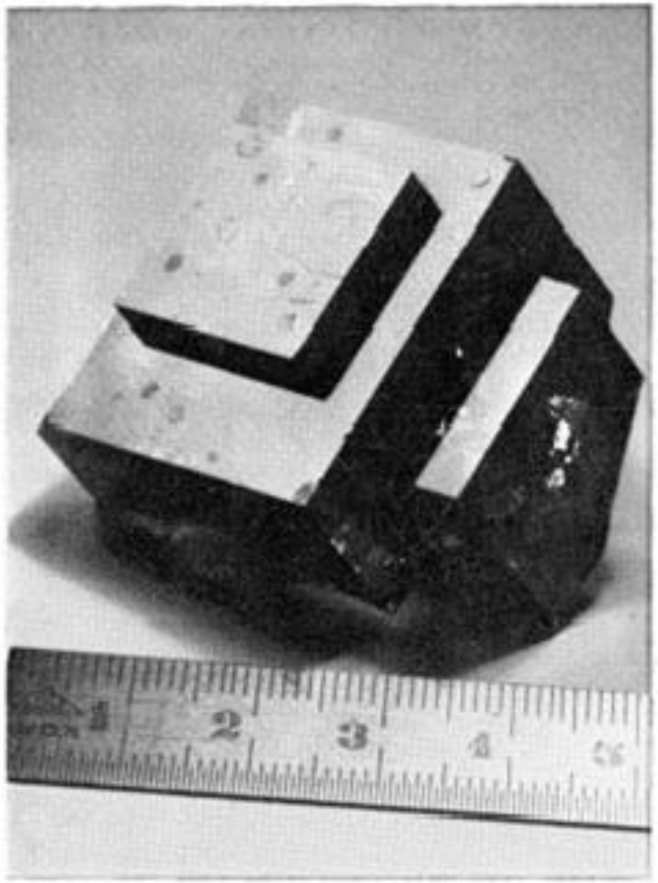
ACRT in Growth from Vapor

- CdS: H.J. Scheel (unpublished)

List not complete

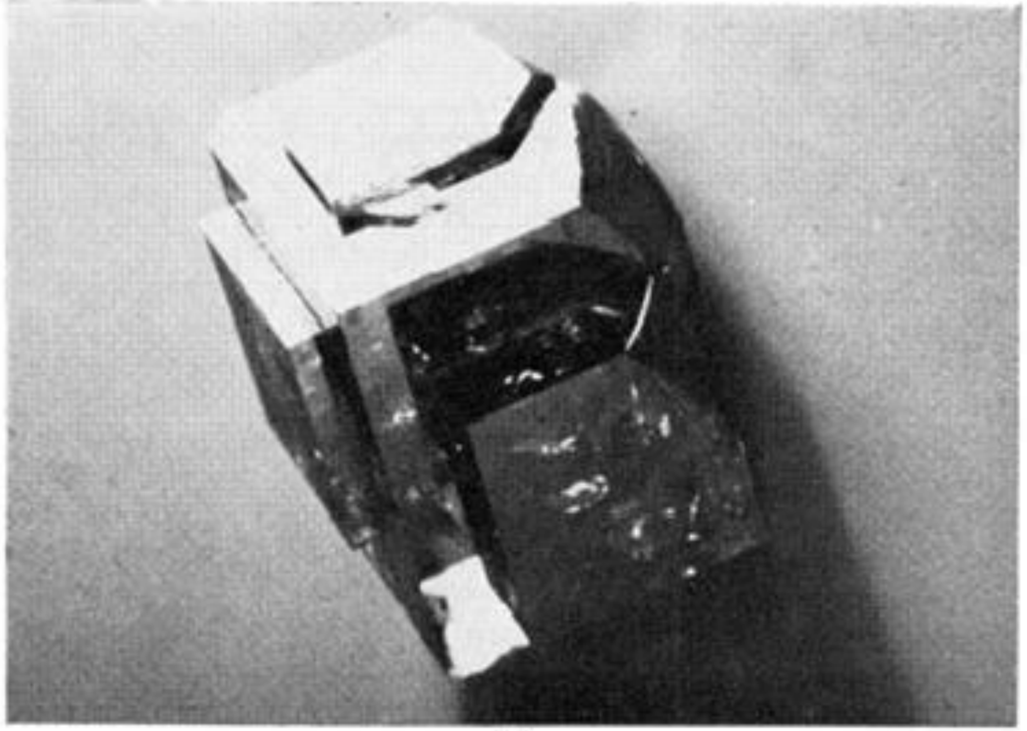
GdAlO3 and Solid Solutions for H. Rohrer / IBM for Magnetic Phase Transitions, Magnetic Phase Diagram.

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



(a)

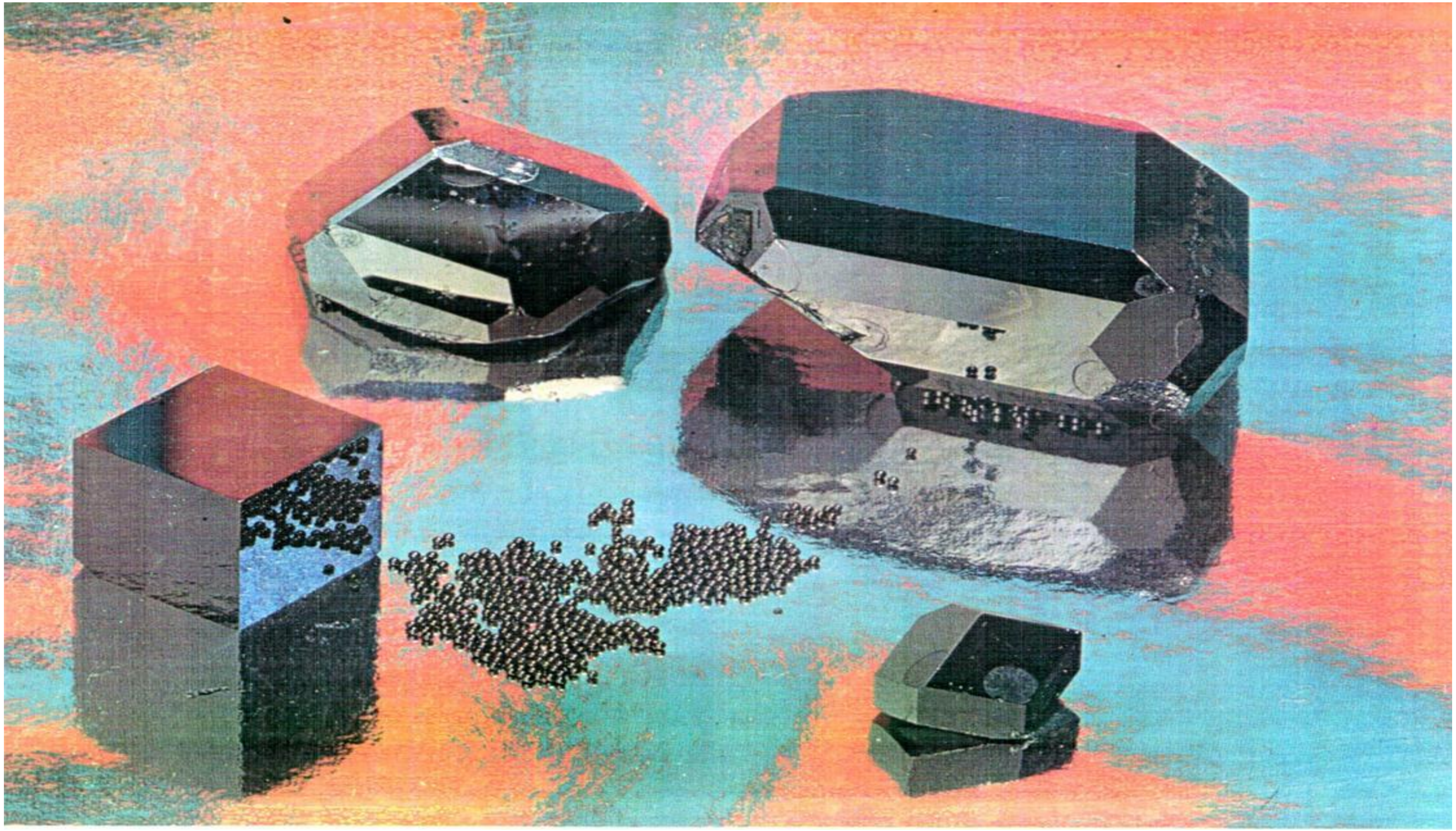
$GdAlO_3$
Perovskite
$Gd_{1-x}La_xAlO_3$
$Gd_{1-x}Y_xAlO_3$
$Y_3Fe_{5-x}Ga_xO_{12}$



(b)

Crystal grown by Accelerated Crucible Rotation Technique (ACRT)

H.J. Scheel, E.O. Schulz-DuBois: J. Crystal Growth 8(1971)304-306.
H.J. Scheel: ICCG-3 Marseille July 5-9, 1971 Proceedings, J. Crystal Growth 13/14(1972)560-565.



YIG ($Y_3Fe_5O_{12}$) Garnet Crystals grown by ACRT at Philips Research Laboratory Hamburg: W. Tolksdorf, F. Welz: J. Crystal Growth 13/14(1972)566-570.

Example $SrTiO_3$

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 Growth, Crystal Machining, Epilayer Growth, and Characterization
- ▶ Workshops and Schools on Crystal Technology
  →IWCGT-3 Sept. 10 -18, 2005 Beatenberg, Switzerland

Results:
- ▶ Saving of more than 90% of Development Costs for Crystals and Epilayers, of Resources, and of Energy
- ▶ Enhanced Developments of Solid State Sciences and of Technologies

Flame-Fusion (Verneuil) Growth

Nakazumi; National Lead: no information
Master Thesis of J.G. Bednorz with H. J. Scheel:
J.G. Bednorz and H.J. Scheel: J. Crystal Growth 41(1977)5-12.

EPD: >> 1’000’000/cm2

Top-seeded Solution Growth (TSSG)

V. Belruss, J. Kalnajs, A. Linz, R.C. Folweiler: Mat. Res. Bull. 6(1971)899-905.

EPD: 10 - 100/cm2

High-Temperature Solution Growth
(Flux Growth)

H.J. Scheel: Z. Krist. 143(1976)417-428;
H.J. Scheel, J.G. Bednorz, P. Dill: Ferroelectrics 13(1976)507-509.

EPD: 0 – 100/cm2
Trace impurities from flux

IBM Zurich Research Laboratory (HJS 1968-1982)

Device Department: Si- and GaAs-MESFET, then Josephson Devices

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

Crystal Growth: 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

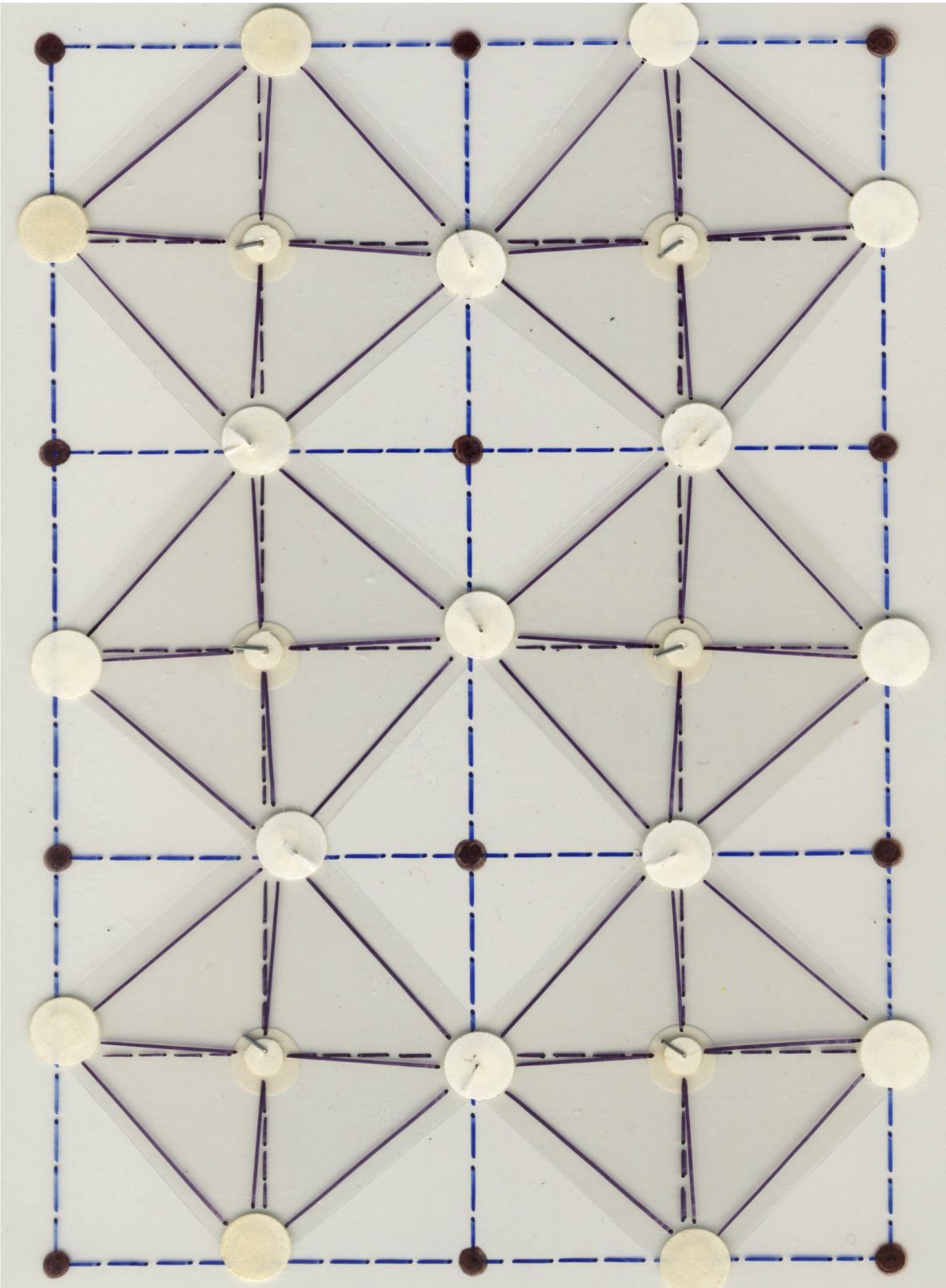
$n_D = 2.41$, $n_F - n_C = 0.108$, $H = 6 – 6.5$

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

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

Crystal Grower (HJS)	**Physicist (KAM)**
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!***

Characterization is important!



CCCritical Phenomena at the Structural Phase Transition of $SrTiO_3$

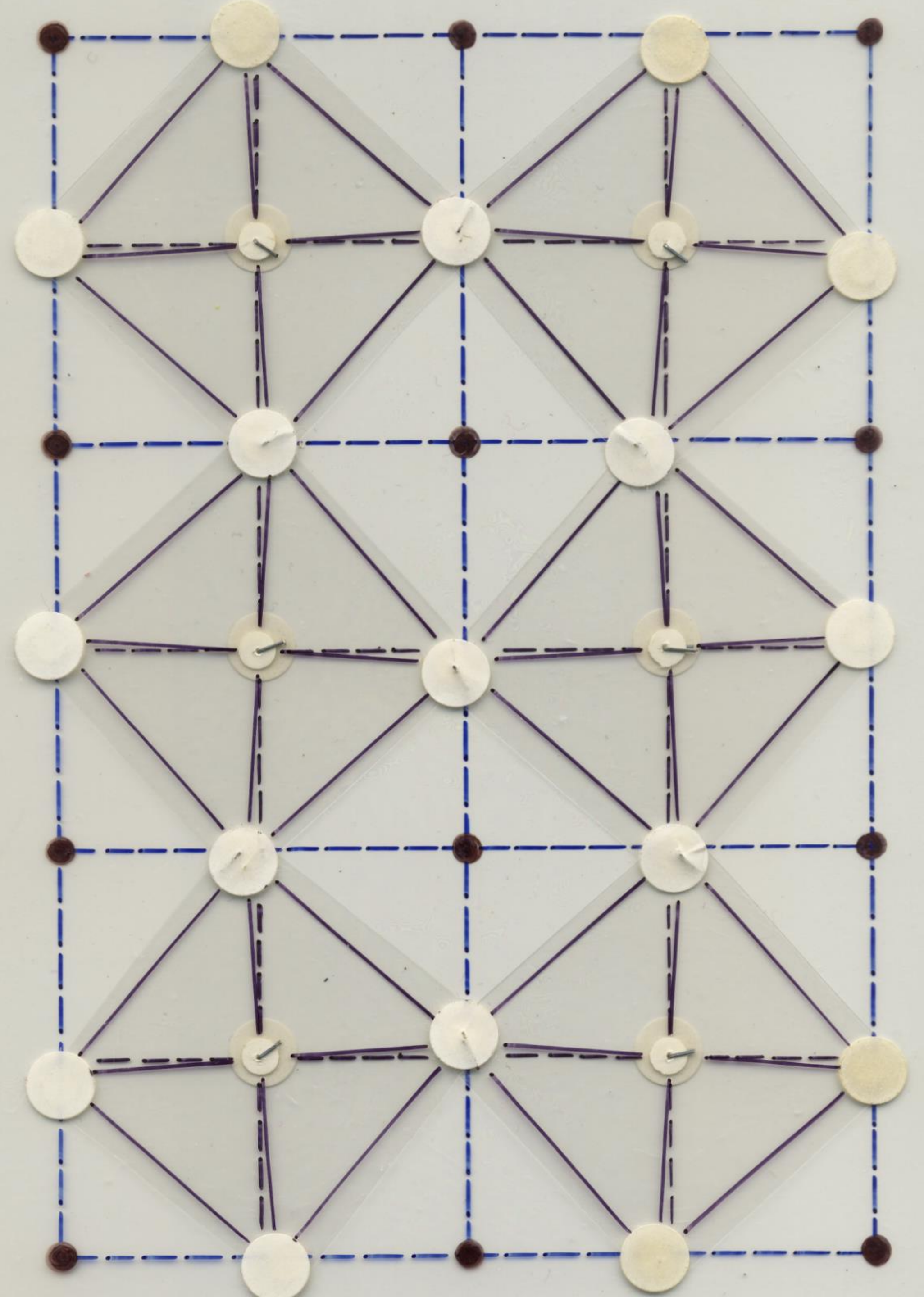
Pm3m > 105 K > I 4/mcm
Cubic Tetragonal

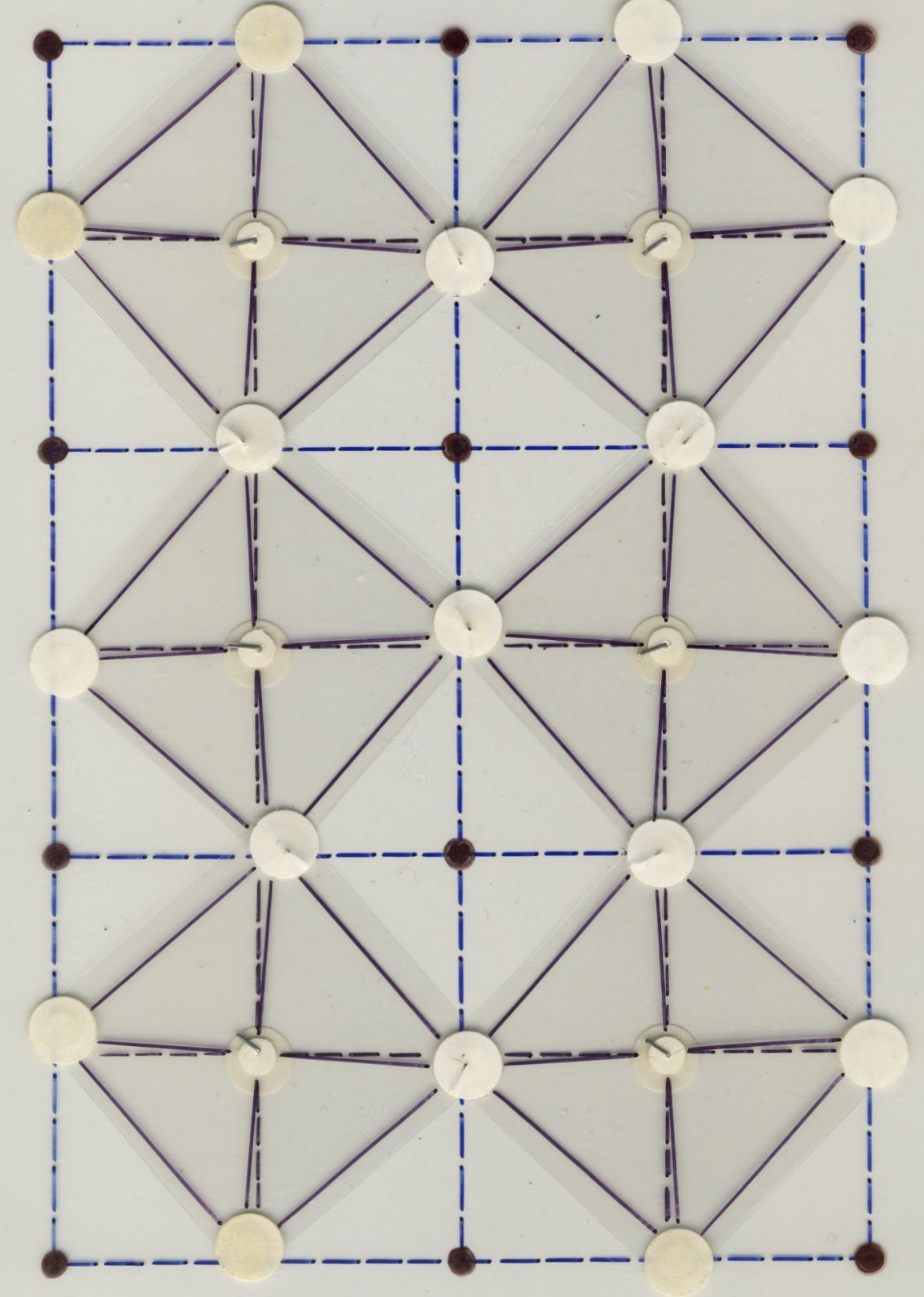
Effect of Defects/Impurities on Central Peak:
B.I. Halperin and C.M. Varma: Phys. Rev. B 14(1976)4030-4044

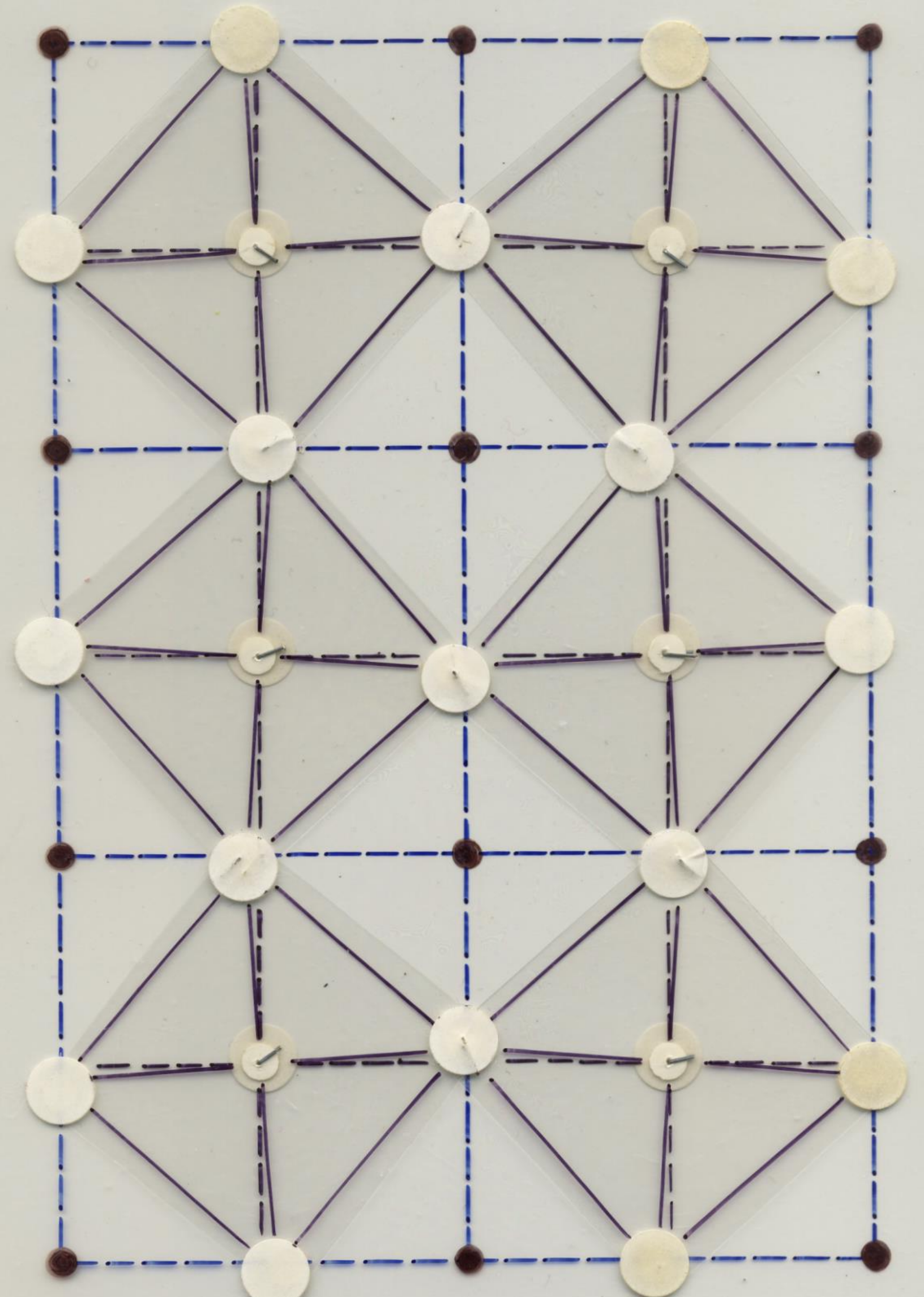
Effect of Dislocations by Growth of Dislocation-free Crystals: **H.J. Scheel: Z. Krist. 143(1976)417-428; H.J. Scheel, J.G. Bednorz and P. Dill: Ferroelectrics 13(1976)507-509; J. Hutton, R.J. Nelmes and H.J. Scheel: Acta Cryst. A37(1981)916-920 (extinction corrections)**

Crystal Growth by Flame-Fusion (Verneuil) Method: **J.G. Bednorz and H.J. Scheel: J. Crystal Growth 41(1977)5-12.**

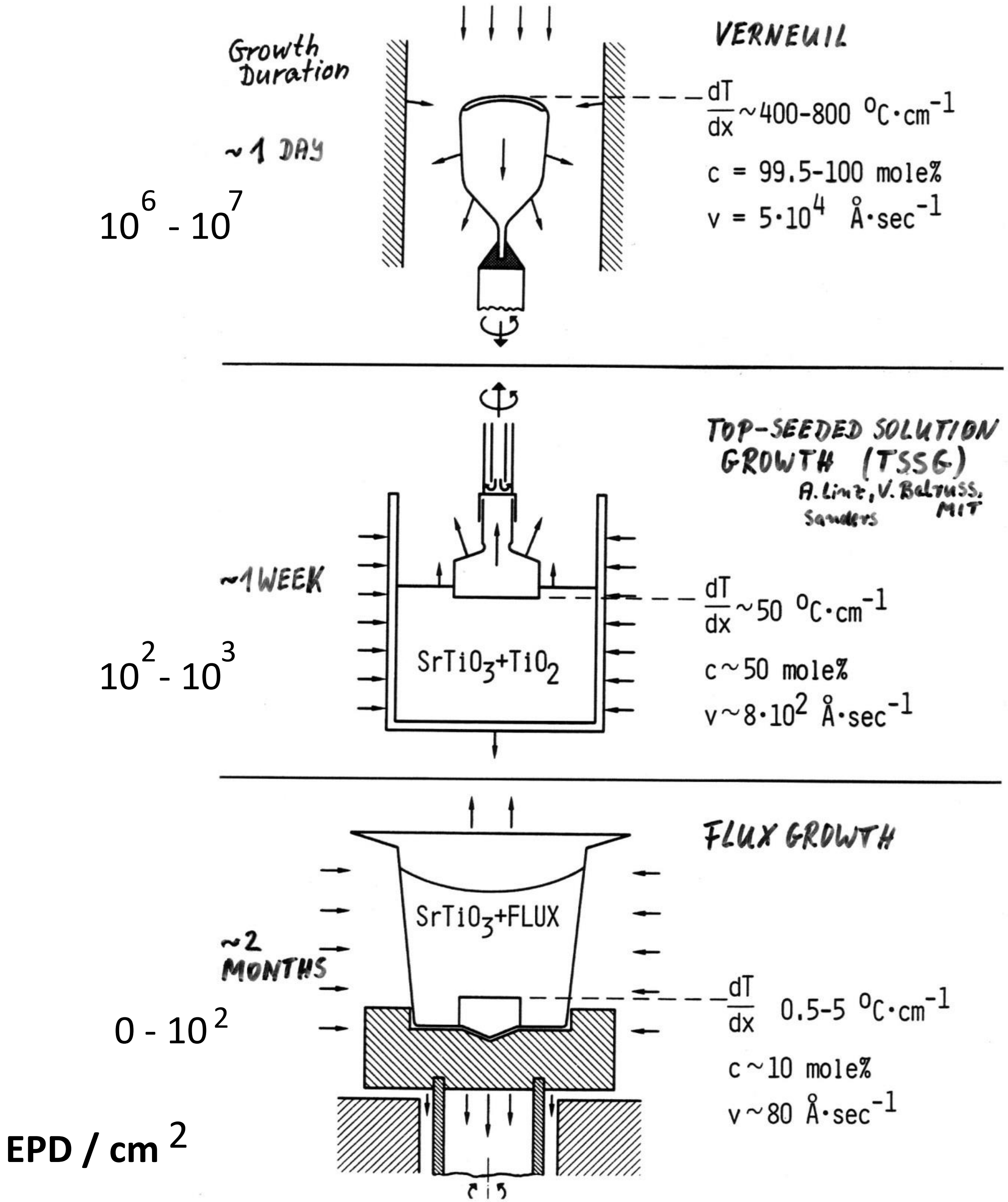
<< Model of Dr. Daniel Rytz







Model Daniel Rytz



$10^6 - 10^7$

$10^2 - 10^3$

$0 - 10^2$

EPD / cm ^{2}

Dislocations & Temperature Gradient

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

SrTiO3

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

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

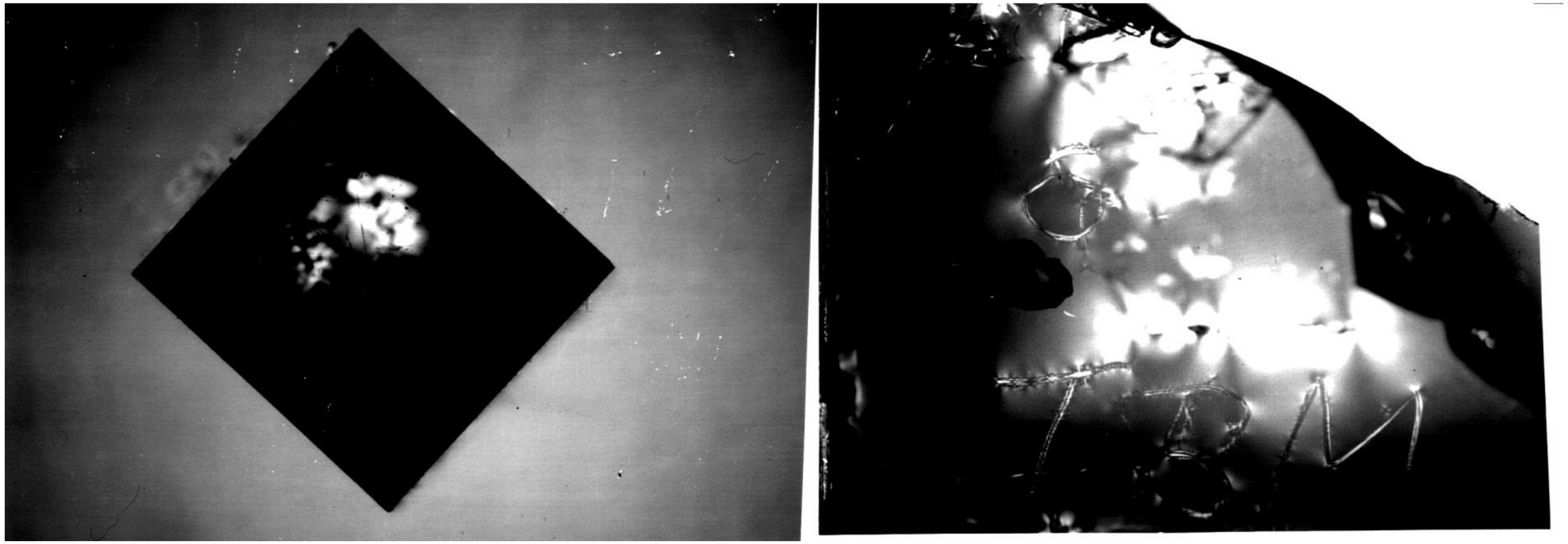
X-Ray Topography & Pol.Microsope

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

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:

- **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.**

First did not believe and had the crystal checked

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

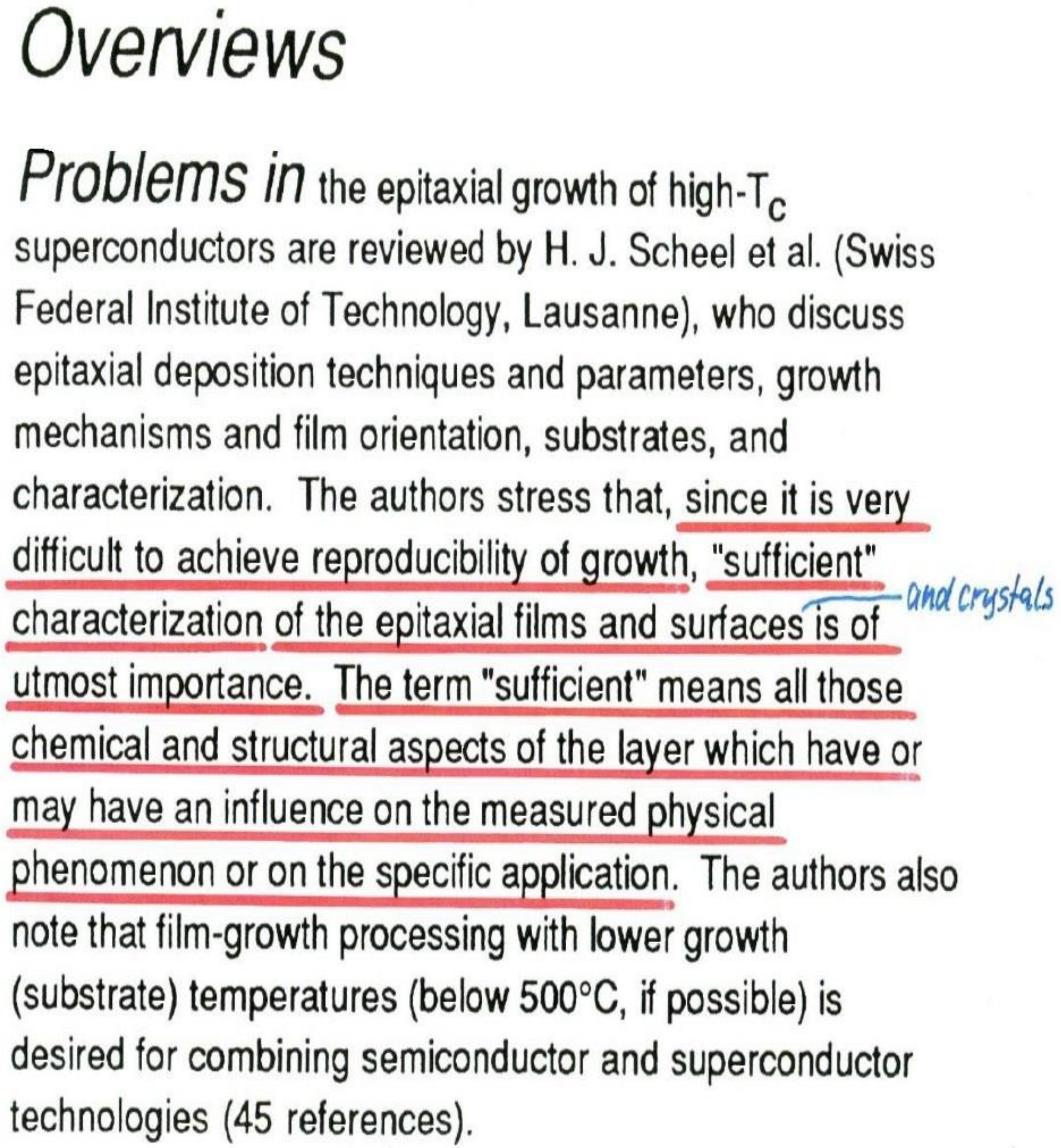
Conclusion:

"Sufficient" Characterization is required

for reproducible high-quality Solid State Physics!

"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!

USO ?

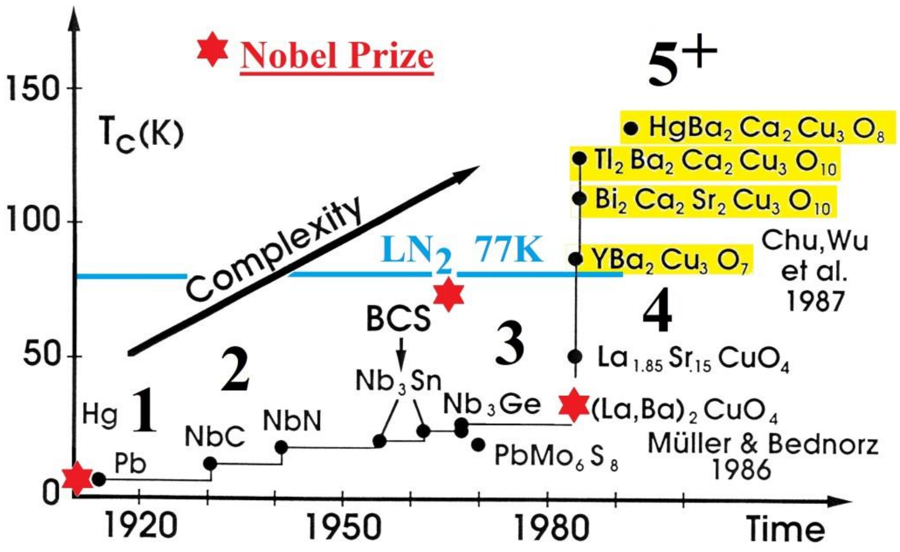
3 mixed Ba-La-Cu-O phases
Possible Tc about 30K
J.G.Bednorz & K.A. Müller
Z. Phys.B 64(1986)189

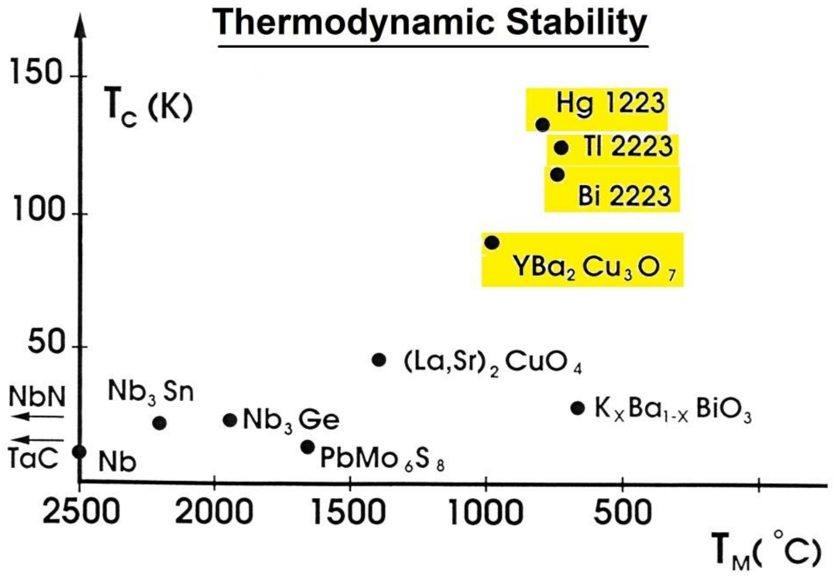
Multible phases Y-Ba-Cu-O
Show Tc (>80K) at 93K.
M.K. Wu and C.W. Chu et al.
Phys. Rev. Lett. 58
(1987)405, 908-910,
Science 235(1987)567.
Pressure ?

Identifikation of phase
K.Kitazawa et al.
Jap.J.Appl.Phys. 26L1(1987)1.
La-Sr-Cu-O (K2NiF4-Typ)
Tc 48.6K: K.Kitazawa et al.
and R.J. Cava et al.:
Phys.Rev.Lett. 58(1087)408.

Nobelpreisträger K.A. Müller und J.G. Bednorz in ihrem Labor 1987

High-Temperature Superconductivity





Increasing Complexity

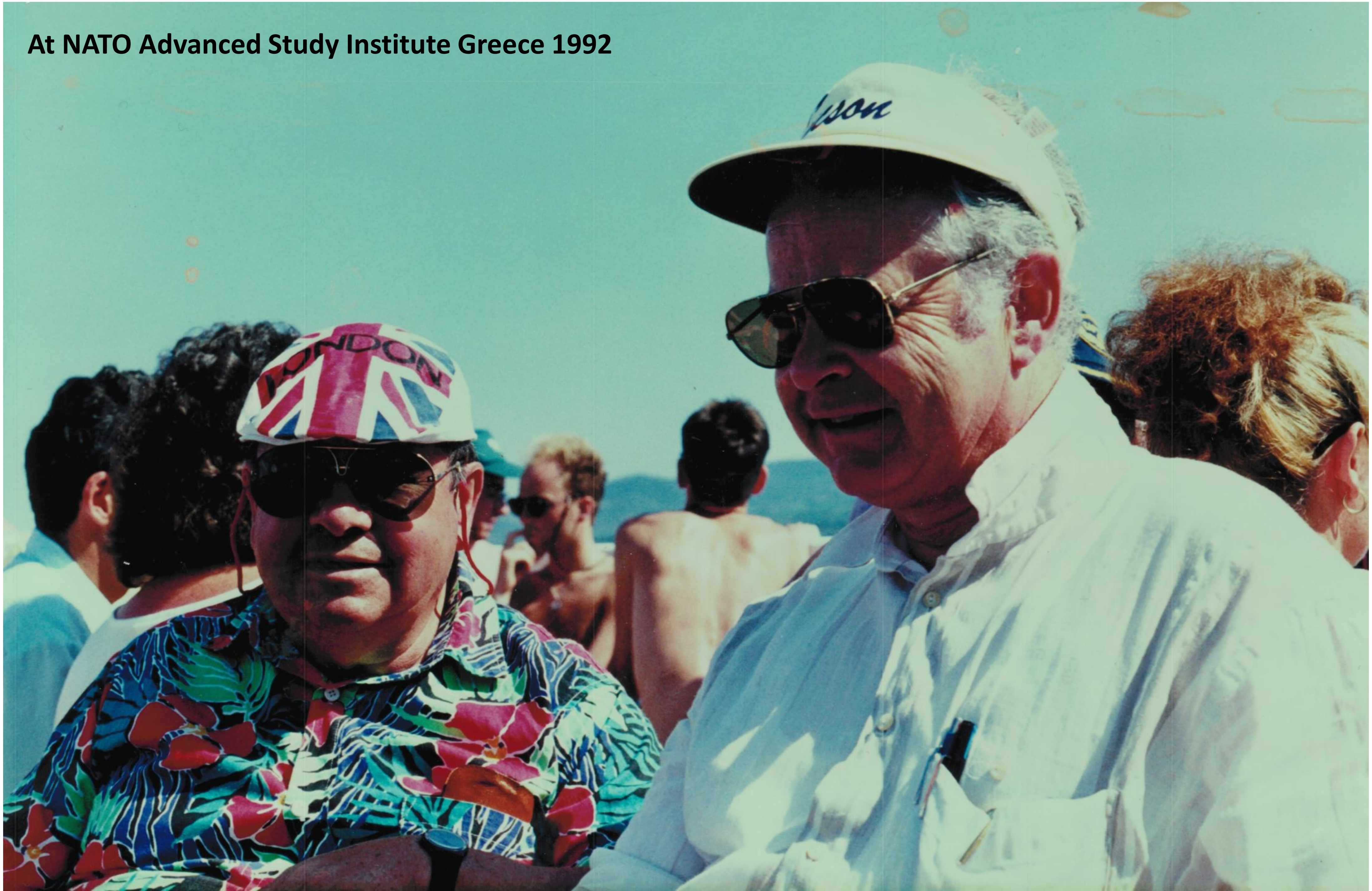
Decreasing Stability

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.

At NATO Advanced Study Institute Greece 1992



Vereshchagin Institute for High Pressure Physics
Russian Academy of Sciences

Now S.M. Stishov-Institute

Address: HPPI RAS, 142190,
Troitsk, Moscow, Russia
Phone: 7-495-8510582
Fax: 7-495-8510012
E-mail: mailto:hpp@hppi.troitsk.ru

Director 1988-1991
Acad. A.A. Abrikosov

Visit July 4, 1989

(21.6.-4.7.1989)

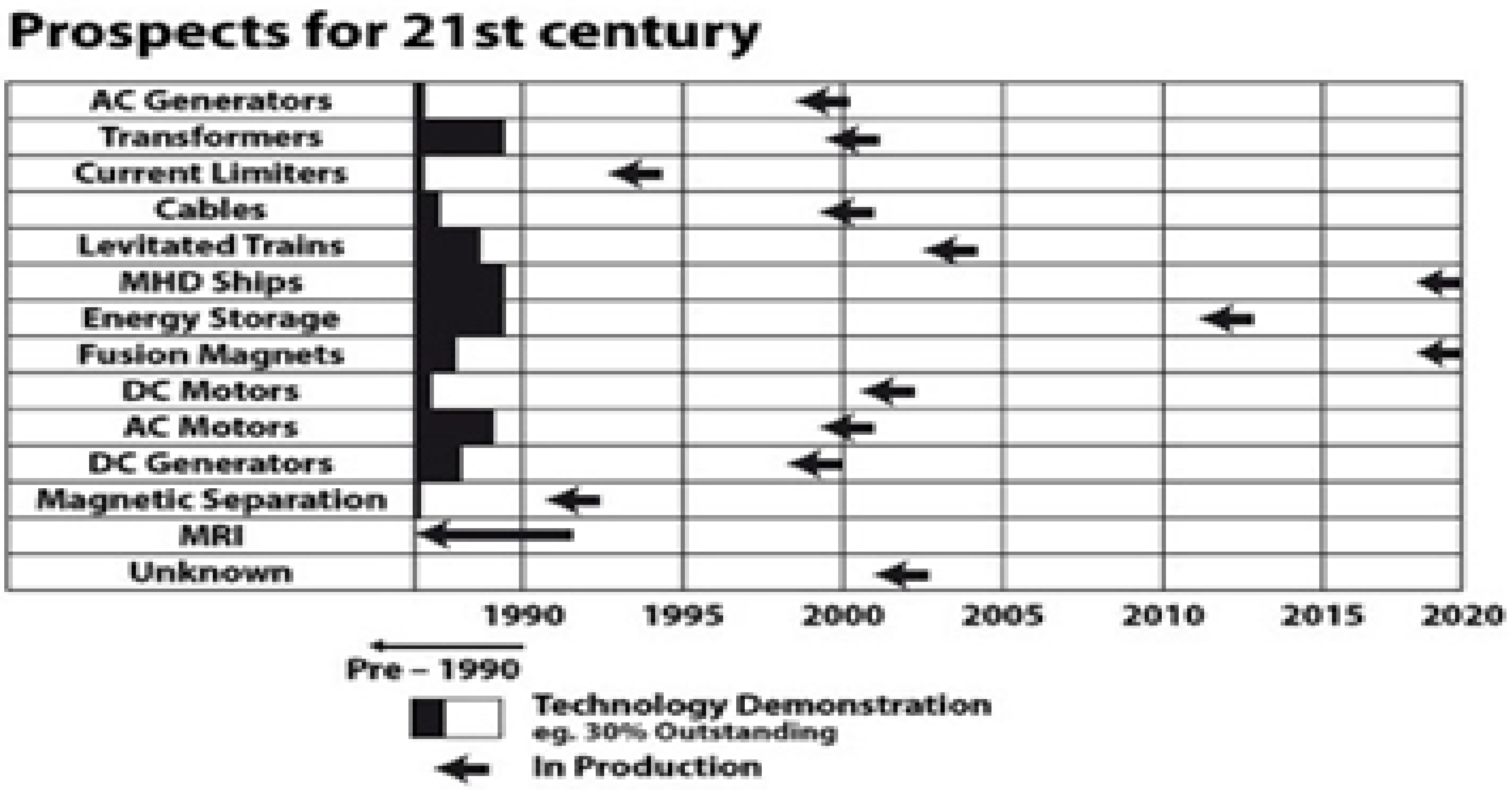
Offer not accepted

The Institute, founded by Academician L.F. Vereshchagin in 1958, received international status in the beginning of 1960's due to the successful synthesis of diamond and cubic boron nitride. The original equipment and technologies, developed in the Institute, formed the basis of diamond industry in the USSR .

1961 Sergey M. Stishov synthesized Stishovite (SiO_2 rutile-type)

Expected Applications of High-Temperature Superconductivity

After A.D. Appleton at NATO Advanced Study Institute Greece 1989/1992


Prospects for 21st century

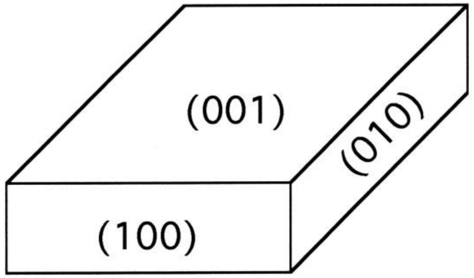
SQUID ------

The EU- HTSC-SQUID-Project with A.I. Braginski (KFA Jülich), MPI Stuutgart, Cristallogenese EPFL, etc. and Project Leader Prof. Dieter Wohlleben (Physik Uni Köln) stopped with his car-accident 13.7.1992.

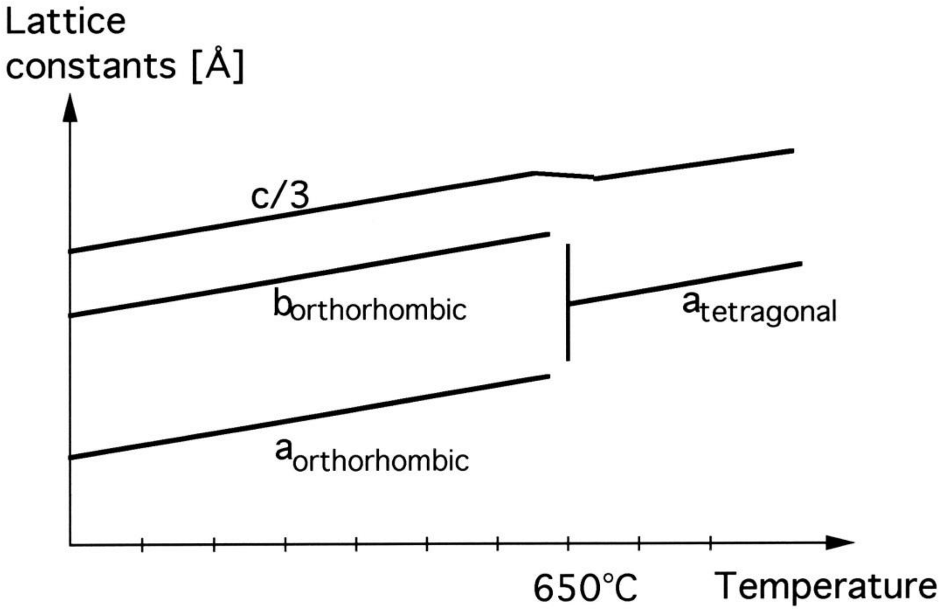
Oxidation and Epitaxy Problems with High-Tc Superconductors

$$YBa_2Cu_3O_7 \xleftarrow[<650°]{[0]} YBa_2Cu_3O_6$$

orthorhombic   tetragonal



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



Thermal
Expansion
Measurements
of potential
substrates
at PSI

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 technologists in collaboration with physico-chemists, mechanical engineers, structure engineers.

Synthesis below 650°C ?

The Failure of High-Temperature Superconductivity (HTSC)

- Complex Composition and Structure, many possible Defects

- Limited Thermodynamic Stability (P_{O2} – dependent)

- Phase Transition with large Change of Lattice Parameters:

from synthesized non-superconducting tetragonal $YBa_2Cu_3O_6$
to superconducting orthorhombic $YBa_2Cu_3O_{\sim6.85}$ with Tc 92K

The Development of Physics and Applications of HTSC is limited by Crystal-Material-Chemical-Mechanical and Crystallographic Problems, not by Physics!

Therefore, in 1988, the Crystal Grower proposed Minimum 50% Funding for Material Development.

- First Internatl Conf. InterlakenFebruary/March 1988 : Leading Physicist rejected

- Third Internatl. Conf. 1991 Kanazawa, Japan: Leading Physicist rejected again

- Problem: In CH- and EU-Committees only physicists, no chemist or material scientist

Sorry, last chance for an old responsible scientist to discuss these problems which bothered me for years

No Success due to Crystal- / Material- Problems

Magnetic-Bubble-Memory / Data Storage for Computers

Invented by Andrew Bobeck at Bell Labs 1967: Magnetic bubble domains move in **thin films of extreme perfection**: Substrates, epitaxy > liquid phase epitaxy, contacts, write/read technology: not achievable in production (HJS). Large efforts at Bell Labs., Konami, Texas Instruments, IBM Research San Jose, Intel etc.

Replaced by hard disc with faster data speeds, more storage, and cheaper production costs.

Now: CD > Memory Sticks >

Production of Homogeneous Crystals in Zero Gravity (Space)

Wikipedia: *Kristallwachstumsversuche, die auf der Erde aufgrund der Erdbeschleunigung scheiterten, konnten erfolgreich durchgeführt werden (Skylab 1973).*[1] Now forced convection to homogenize melts & solutions on earth.

Reduced convection versus forced convection on earth:
Accelerated Crucible Rotation Technique ACRT (H.J. Scheel 1971)

Josephson Junction Computer & SQUID Detectors

Cooper electron pairs tunnel at 4K between Pb superconductor contacts through a nm Pb – PbO - Pb Josephson junction, later Nb - AlO_x - Nb edge junctions at IBM, stopped 1983. Replaced by Si bipolar technology. Now Quantum computers with high-temperature superconductors, see below. Chance without crystal technologists?

Fusion Energy (TOKAMAK) with Magnetic Inclusion of Plasma

Magnetic inclusion of 100Million degree corrosive plasma and fast neutrons require a first wall which has not been found. Wall problems are reduced with inertia technology, laser fusion energy. This requires large radiation-hard Laser and nonlinear-optic crystals, to be solved by **well-educated crystal technologists.**

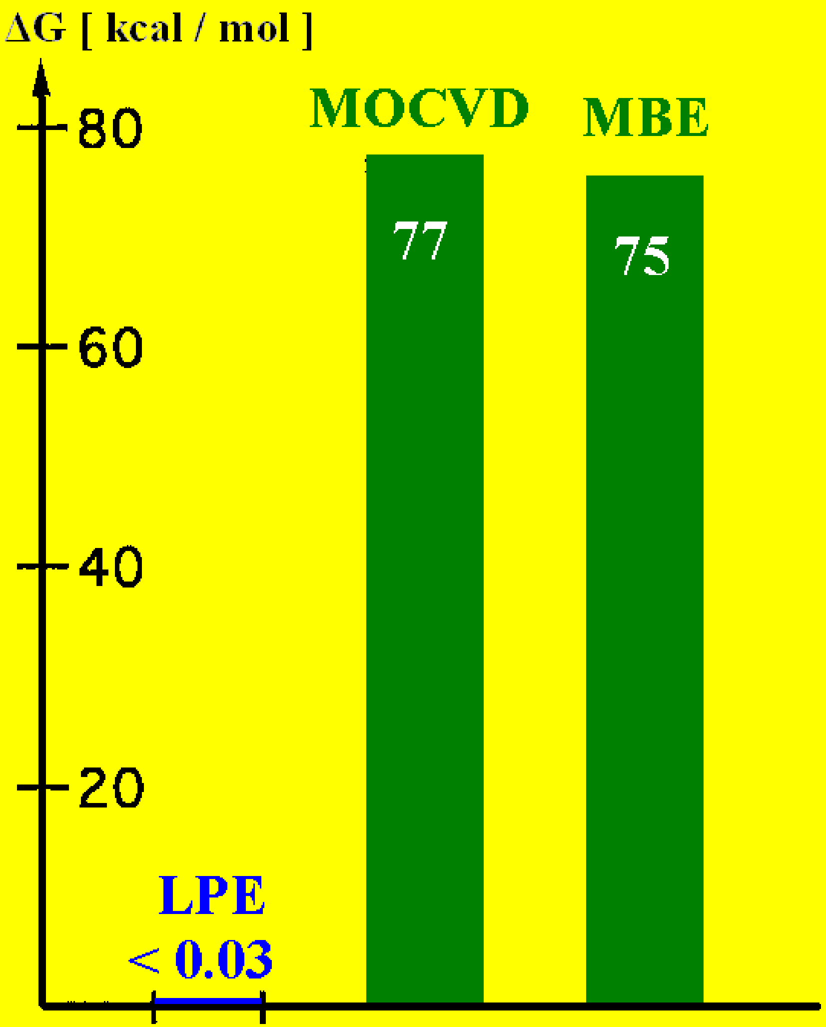
Sapphire Windows for iPhone for APPLE

2013 Apple invested 439M USD, GT 900M USD to build factory for 700 employees in Mesa/Arizona for 2036 HEM furnaces for 262kg sapphire boules, to be machined by Meyer Burger saws. Failure with cracks etc. October 2014 bankruptcy of GT. **No educated crystal technologist yet in USA.**
Now MONOCRYSTAL Inc. (Stavropol, Russia) announced 350kg sapphire boules grown by Kyropoulos technique. **(without contact of growing crystal with crucible wall)**

High-Temperature Superconductivity

Special story starting with $SrTiO_3$ at IBM Zurich Research Laboratory.

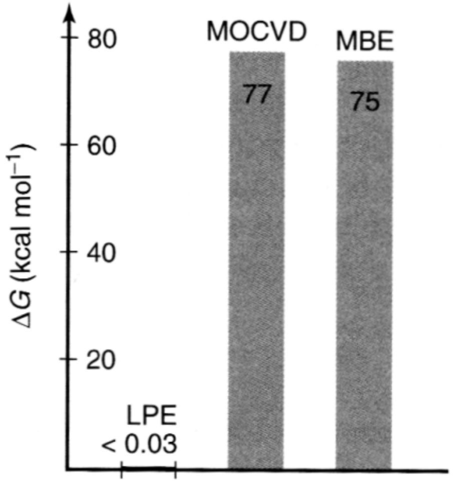
Gibbs Free Energy Difference between Reactants & Products (Layers, Crystals)



The estimated thermodynamic driving forces for LPE (ΔT < 6 K), MOCVD (TMGa + arsine) & MBE (Ga + As_4) of GaAs at 1000 K.

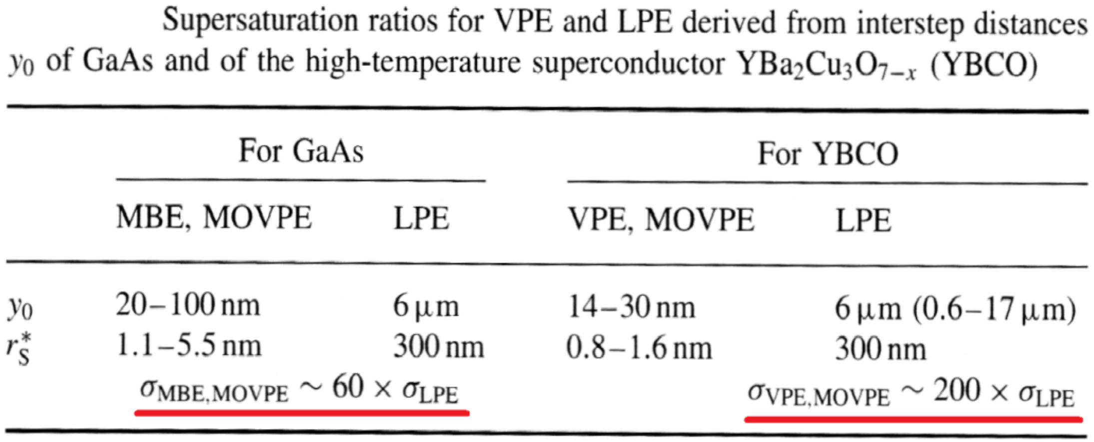
After G. B. Stringfellow, J. Crystal Growth 115 (1991) 1.

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
	$\sigma_{\mathrm{MBE,MOVPE}} \sim 60 \times \sigma_{\mathrm{LPE}}$			$\sigma_{\mathrm{VPE,MOVPE}} \sim 200 \times \sigma_{\mathrm{LPE}}$

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

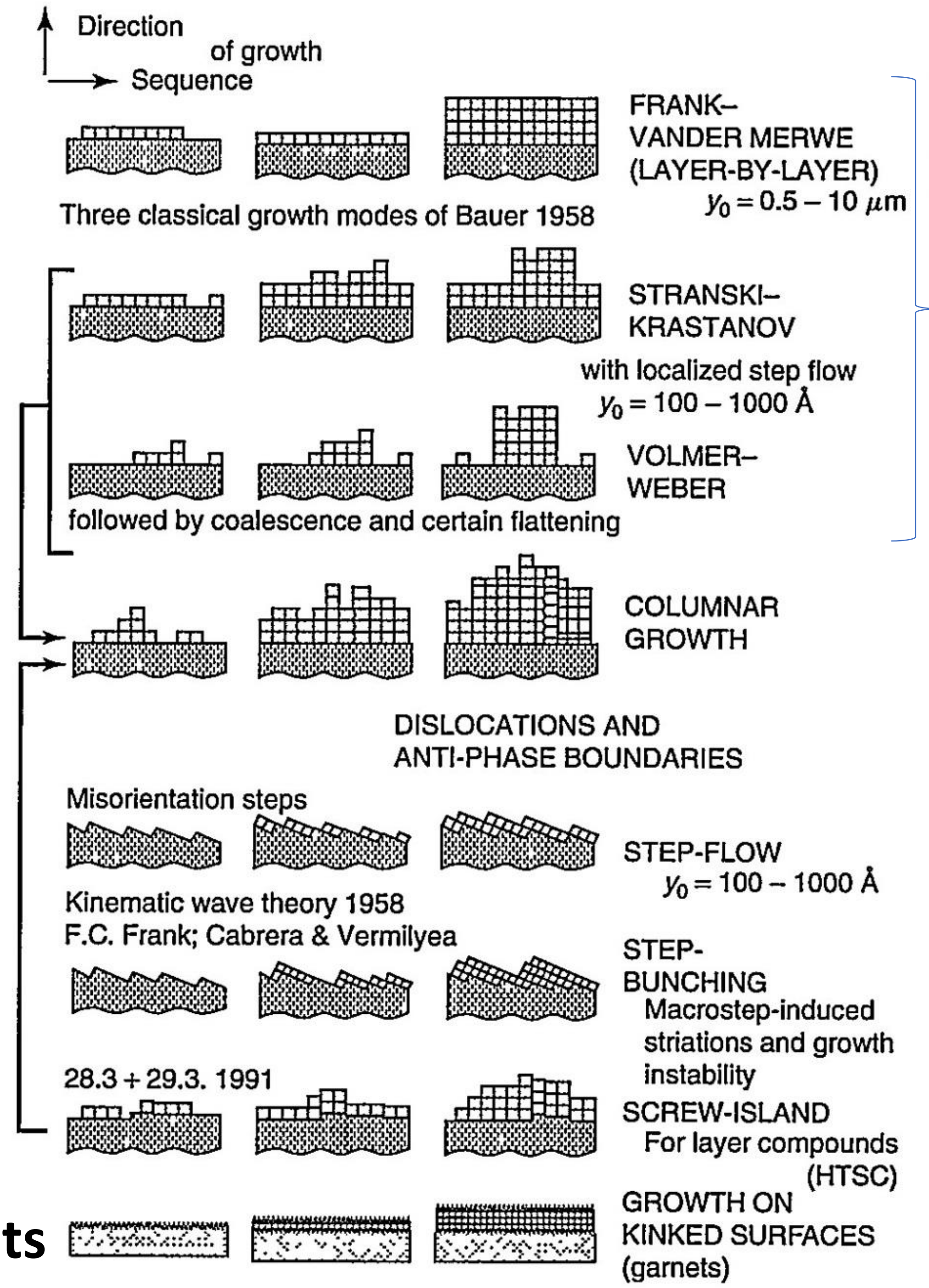
See also P. Clapper & M. Mauk: *Liquid Phase Epitaxy*, Chapter 1: H. J. Scheel

Liquid Phase Epitaxy

Gas Phase Epitaxy

Reduction of Growth Islands

LPE Magnetic Garnets



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

< 3 Classical Growth Modes

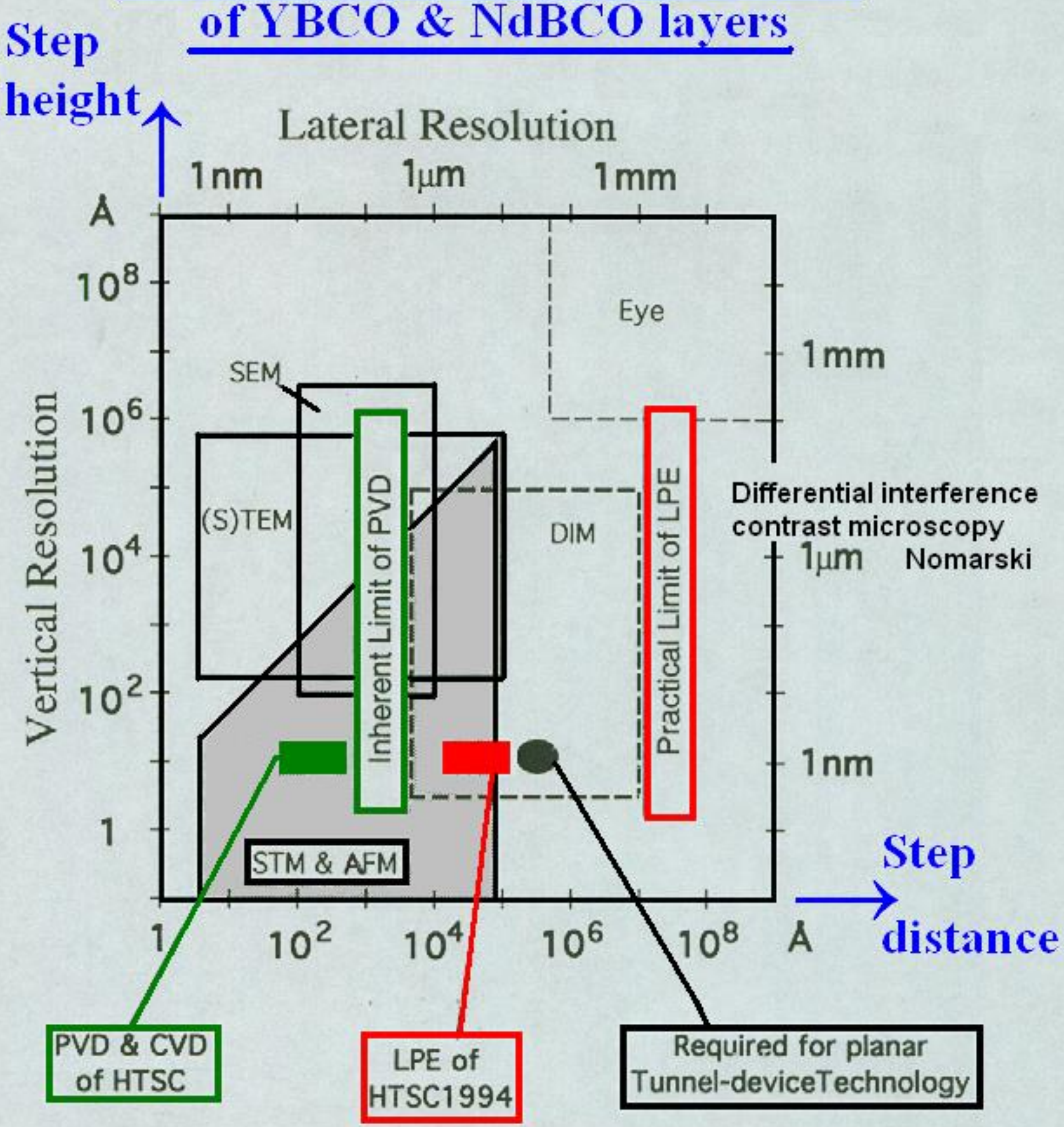
In «Liquid Phase Epitaxy of Electronic, Optical and Optoelectronic Materials»
Eds. P. Capper & M. Mauk
Wiley 2007.
Chapter 1: Hans J. Scheel

YBCO films grown by Liquid Phase Epitaxy

(Scanning Force Microscopy, derivative image)

H.J. Scheel, C. Klemenz, F.–K. Reinhart, H.P. Lang, H.–J. Güntherodt
Appl. Phys. Lett. 65 (1994) 901.

Step heights & interstep distances of YBCO & NdBCO layers



PVD & CVD of HTSC

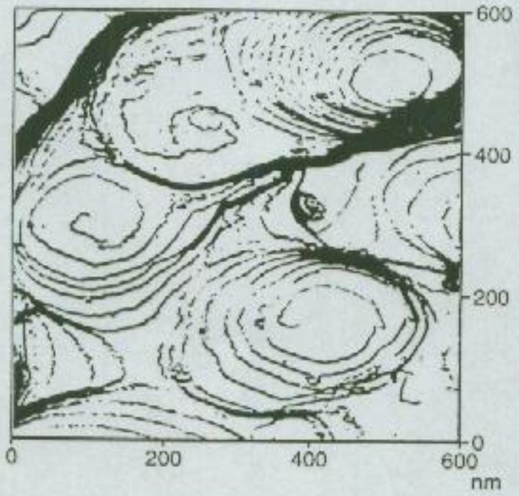
~ 1000 groups

LPE of HTSC1994

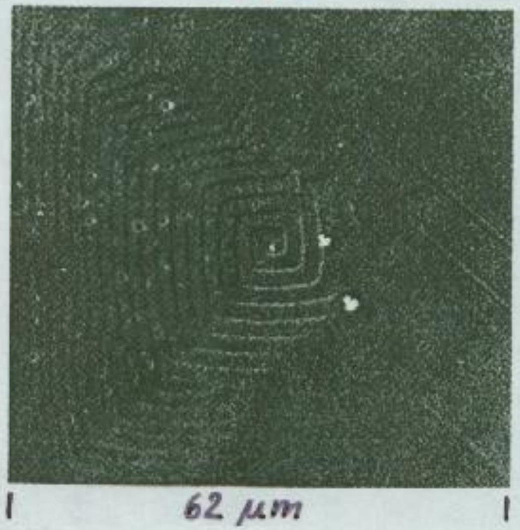
~ 10 groups

Required for planar Tunnel-deviceTechnology

MOCVD



LPE

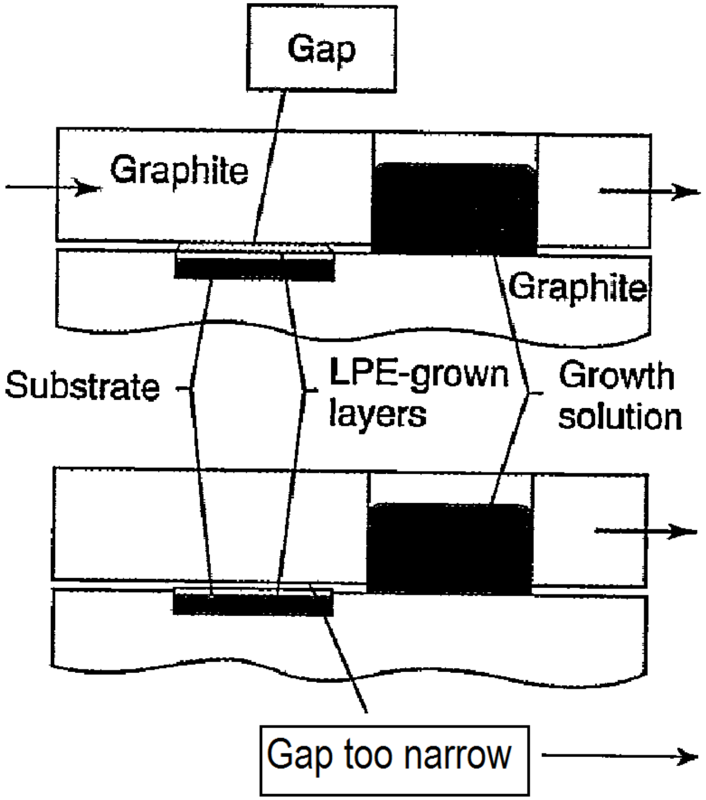


H. J. Scheel , MRS Bulletin Sept. 1994

? Optimum Growth Technology?

Liquid Phase Epitaxy

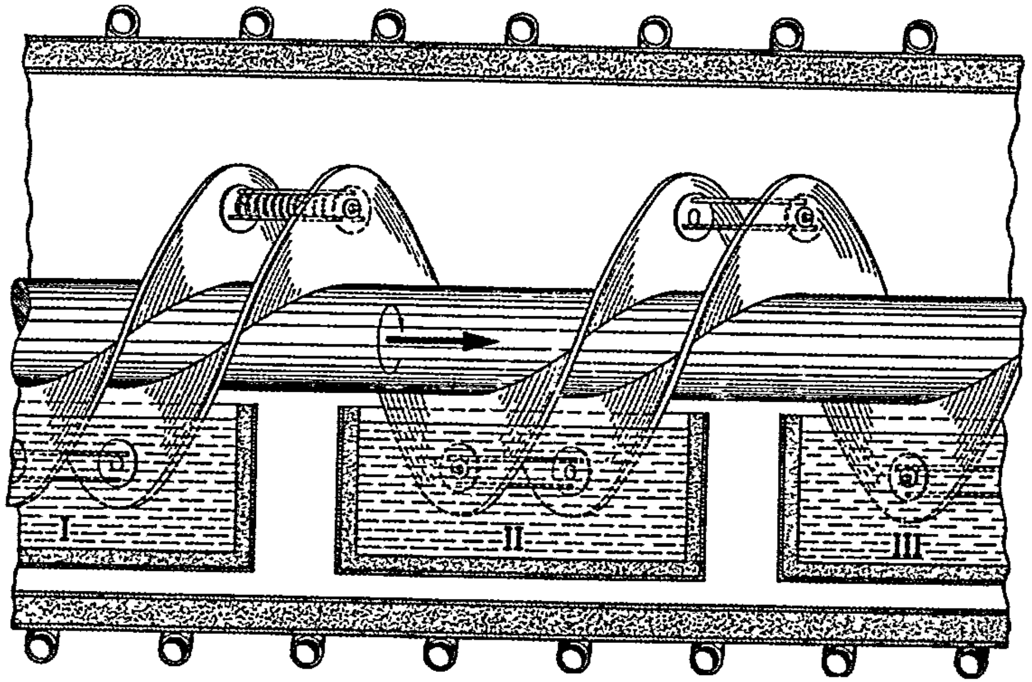
Problems in Slider Technology



Gap too wide:
Aftergrowth
Mixing with next Solution
Raised Edge
Thickness Limitation
Scaling-up difficult

Scratching of LPE-grown Layers

Sliding-free Technology for Mass Production

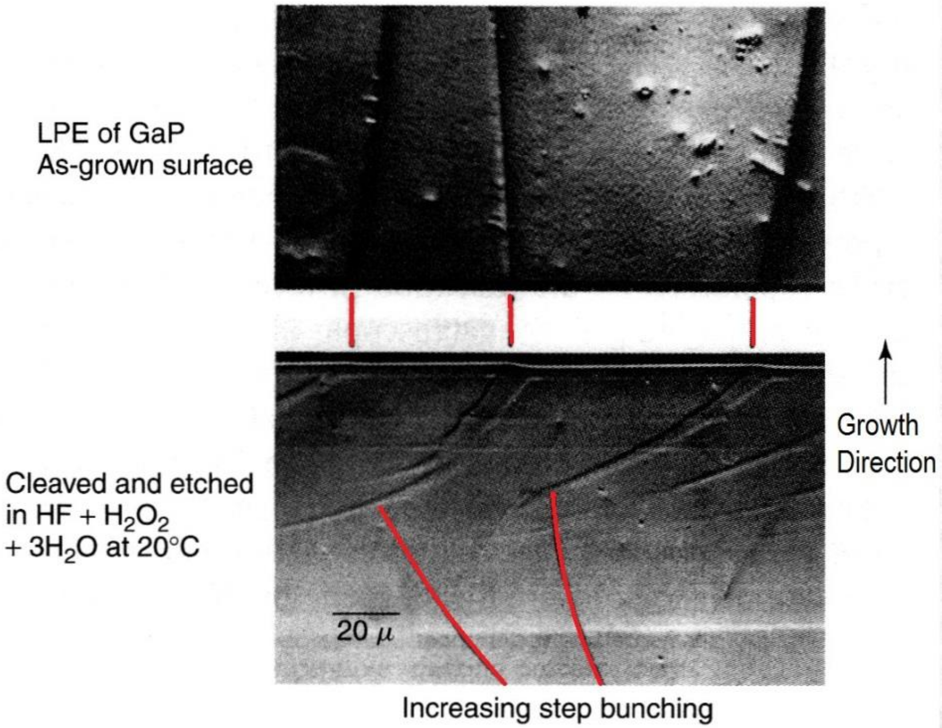


US Patent 3,858,553 (Jan.7, 1975, H.J.Scheel /IBM,
J. Crystal Growth 42(1977)301 - 308 (ICCG-5 Boston).

LPE of Semiconductors in Laboratory:
Double-Archimedian Srew in Graphite Block

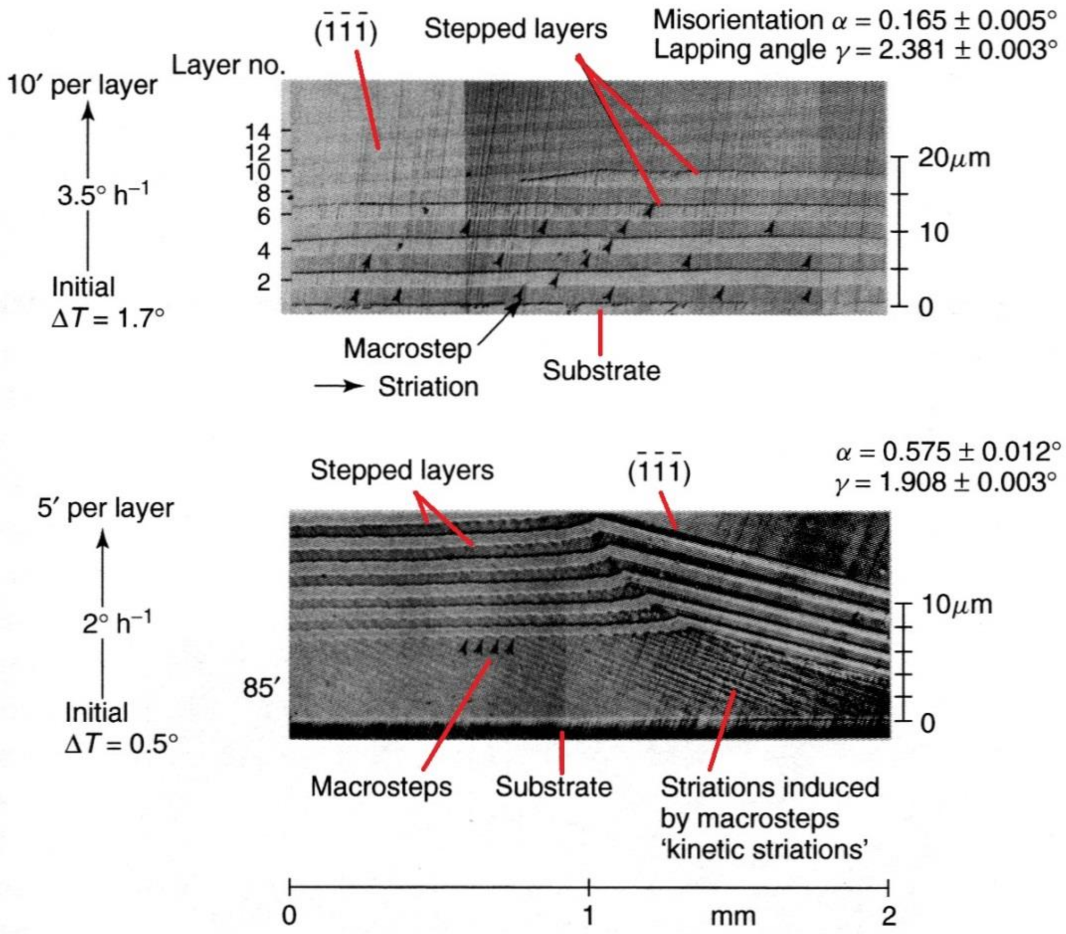
MultiLPE with Double-Screw Device

Macrostep-Induced Striations



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

Transition to Faceting in Multilayer LPE

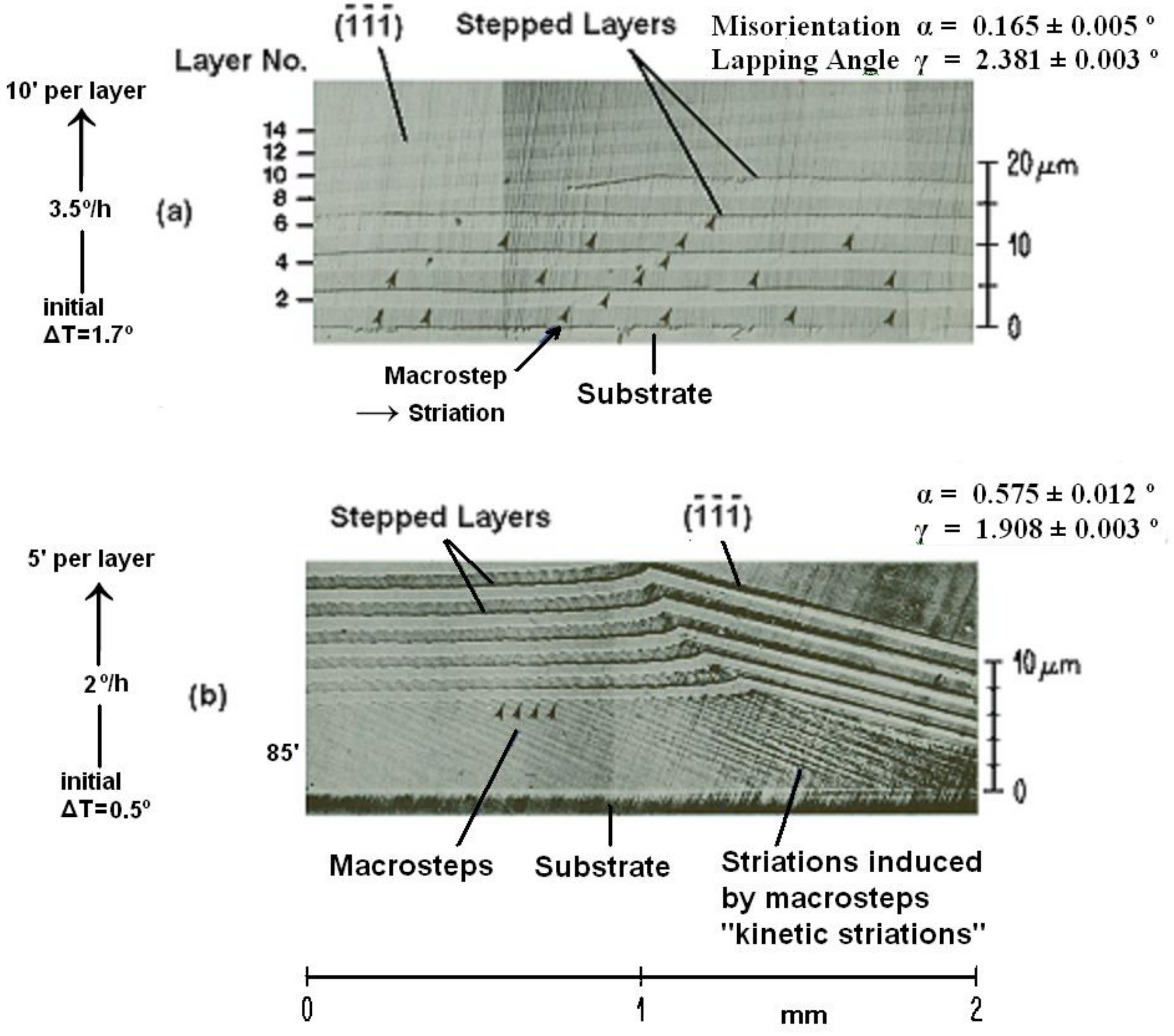


Appl. Phys.Letters 37 (1980) 70-73, H.J.Scheel

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

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

A. Chernov

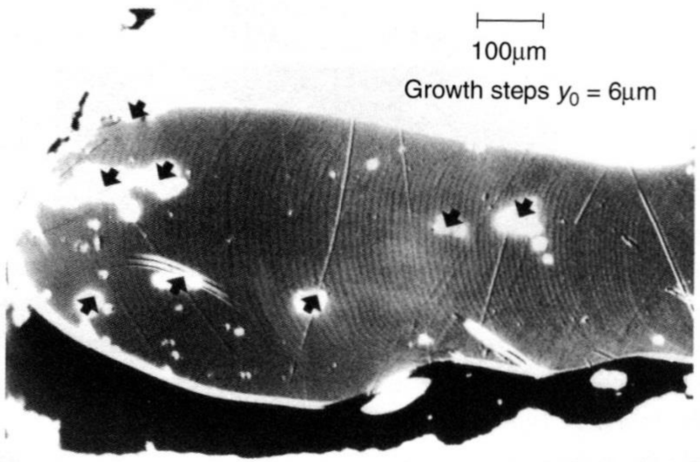


H.J. Scheel , "Transition to faceting in Multilayer LPE of GaAs"
Appl. Phys. Lett. 37 (1980) 70 - 73

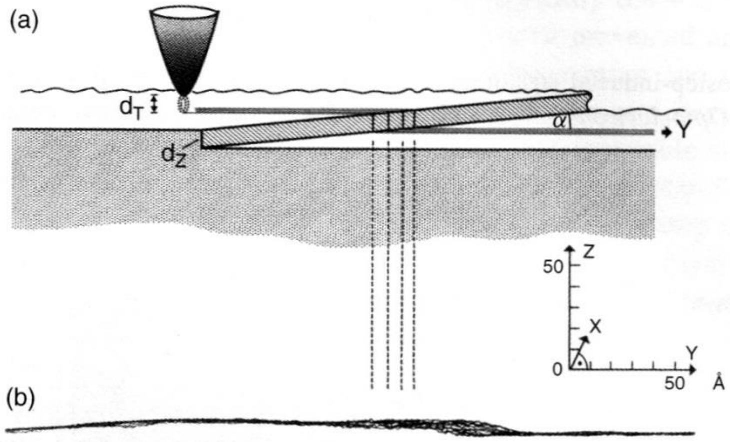
Liquid Phase Epitaxy for

- **low dislocation density**
- **flat p-n-junctions**

gives highest-performance electronic and optoelectronic devices



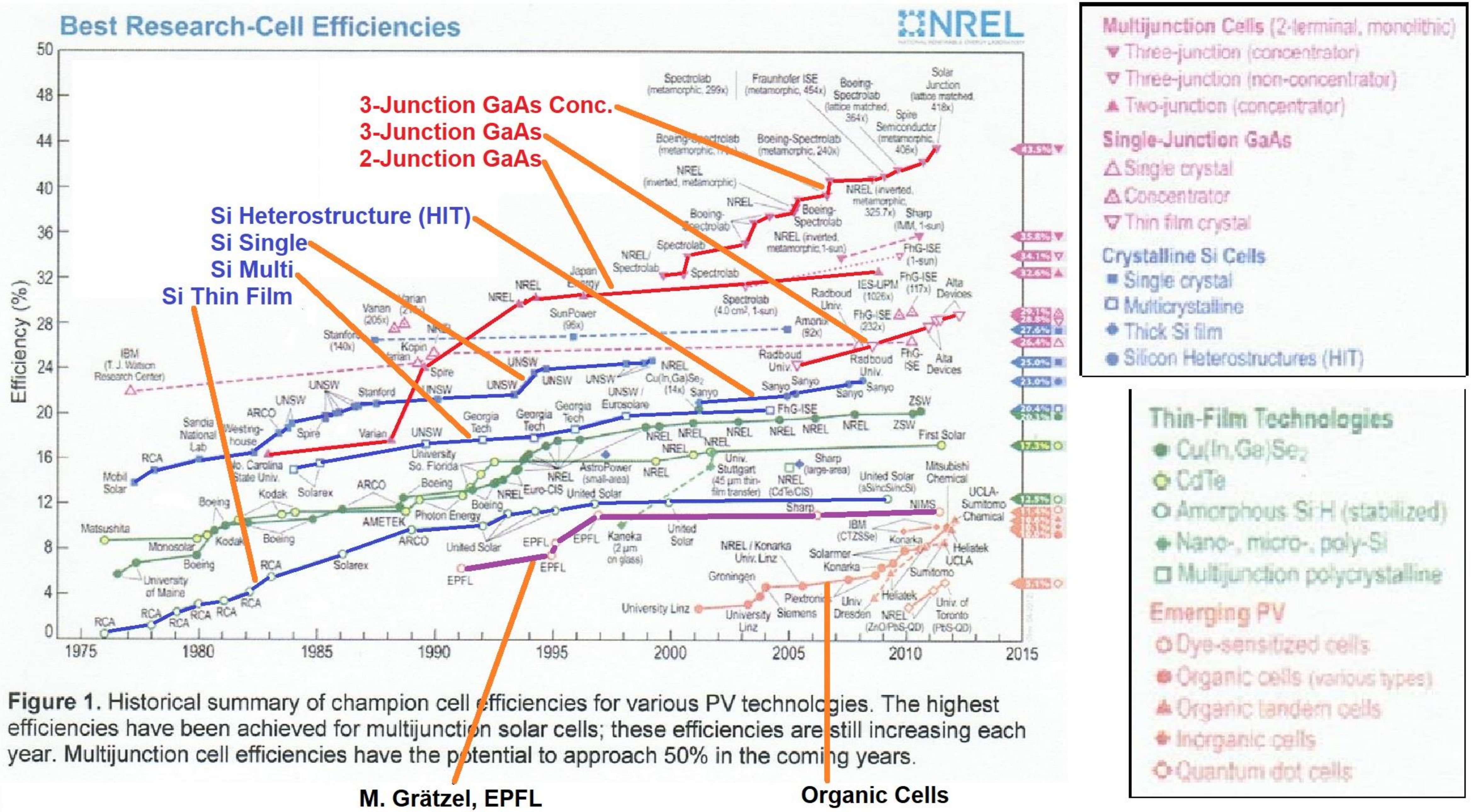
Differential interference contrast microscopy (Nomarski) of GaAs (111) facet. Step distances of 6 µm are visible.



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.

G.H. Binnig ca. 1980



3-Junction GaAs Conc.
3-Junction GaAs
2-Junction GaAs

Si Heterostructure (HIT)
Si Single
Si Multi
Si Thin Film

Figure 1. Historical summary of champion cell efficiencies for various PV technologies. The highest efficiencies have been achieved for multijunction solar cells; these efficiencies are still increasing each year. Multijunction cell efficiencies have the potential to approach 50% in the coming years.

M. Grätzel, EPFL

Organic Cells

After Sarah Kurtz, NREL TP-5200-43208

Growth Technologies for Silicon Solar Cells

Czochralski crystal pulling
Directional solidification
Casting
Heat-exchanger method (HEM) (Crystal Systems, F. Schmid, Chandra Khattak), > GT > APPLE
Vertical sheet pulling
Dendritic sheet pulling
Horizontal sheet pulling (on graphite: J. Grabmaier/Siemens, terminated)
(HJS & DH) Octagon-cylinder sheet pulling (Tyco-Mobile, Mass., >ASE Germany, LASAG roboter saws, terminated)
Thin-Film deposition/mass production

10th International Workshop on Crystalline Silicon for Solar Cells (CSSC-10)

Sendai, Japan April 8 – 11, 2018: New technologies

Continuous Czochralski CCZ with silicon feeding
Kyropoulos mit top seeding
Dendrite cast method
Non-contact crucible method
NeoGrowth technique with feeding liquid Si, crucible-free, up to 450mm diameter
Silicon ribbons from thin liquid zone heated with electric currents or laser
Granulate crucible method (up to 60mm diameter)

The Nobel Prize in Physics 2014

Nagoya University
to
Meijo University

Photo: A. Mahmoud

Isamu Akasaki

Photo: A. Mahmoud

Hiroshi Amano
(Nagoya-Meijo-Nagoya)

Photo: A. Mahmoud

Shuji Nakamura

Nichia Company Japan
to
University Santa Barbara

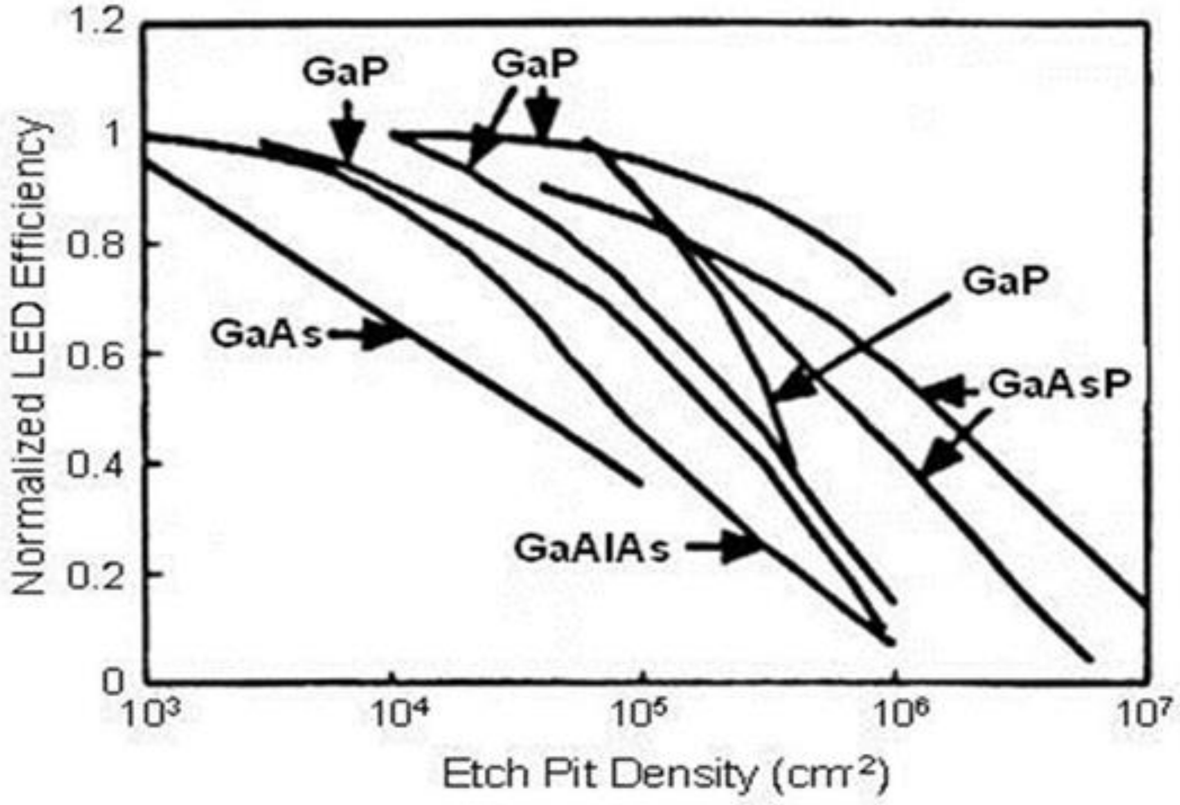
"For the invention of the blue light-emitting diode which has enabled bright and energy-saving white light sources"

Low-temperature buffer layer
+ p-type doping, MOCVD

GaN and Solid Solutions

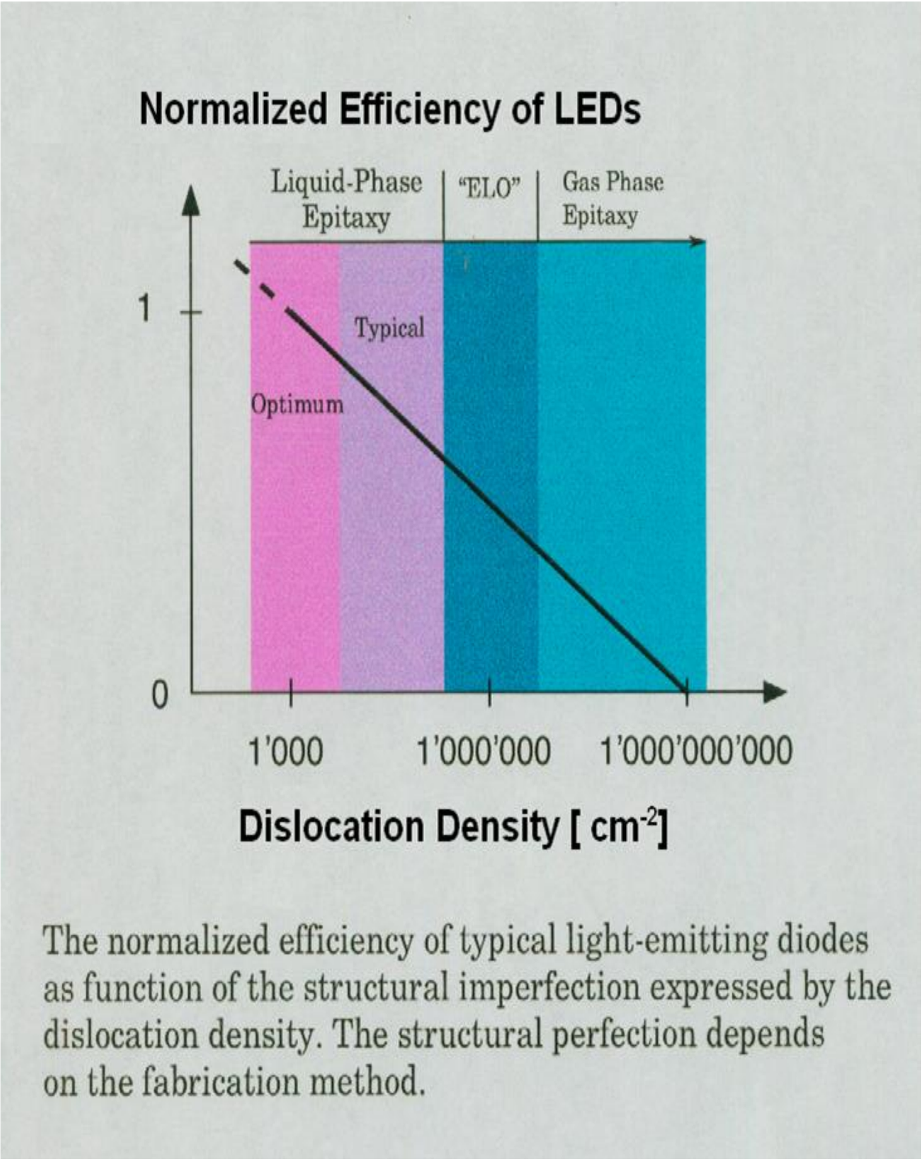
White LED, fabrication process

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

EDUCATION OF CRYSTAL TECHNOLOGISTS

For optimum Growth Technology for Solid State Physics Research

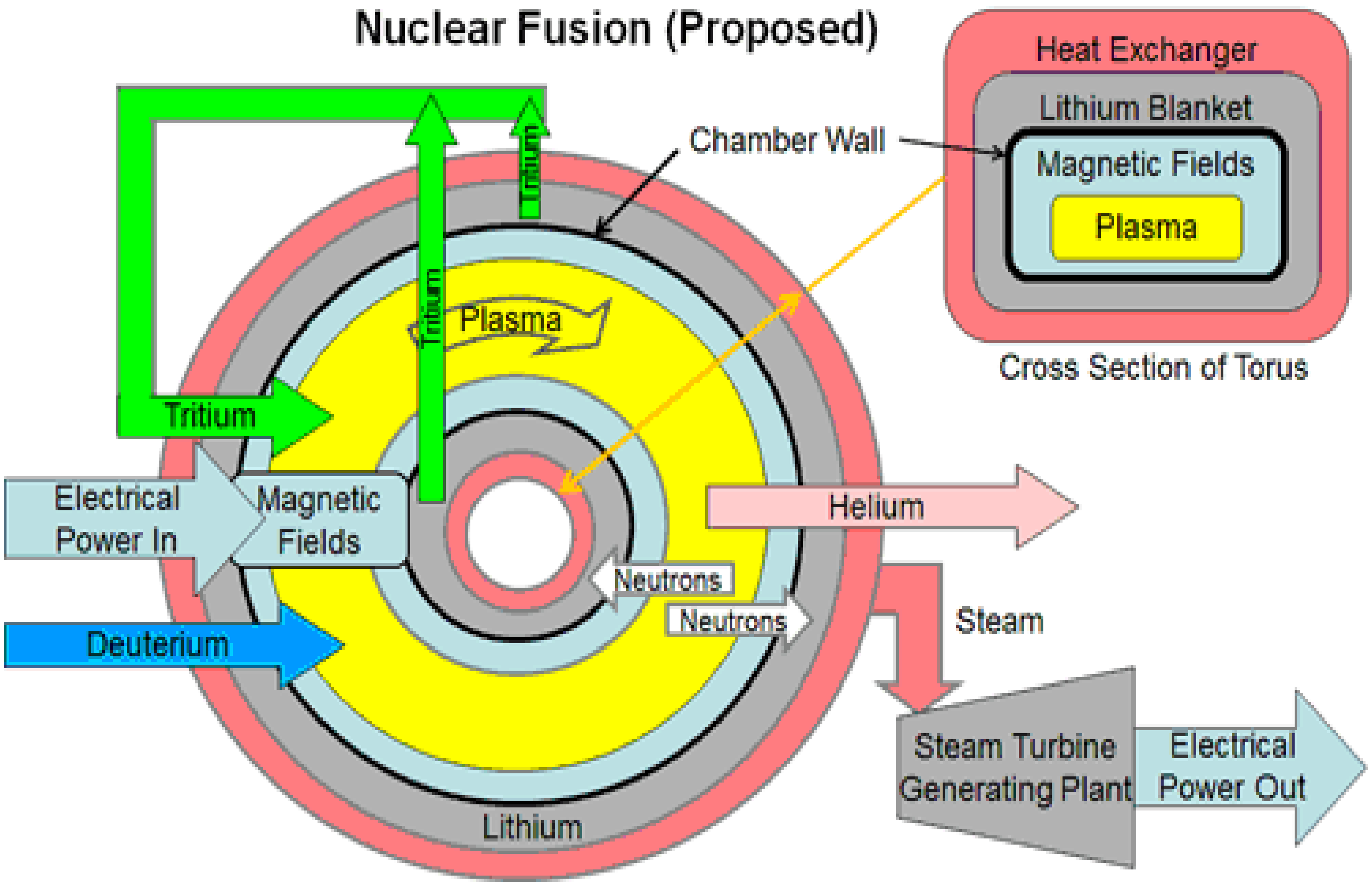
For economic PV Solar Cells with increased Efficiency

For Light-emitting Diodes (LEDs) with improved Luminence

For Electric Power Devices with increased Efficiency

For Development of High-Temperature Superconductivity

For Laser-Fusion Energy



Magnetic Confinement

Plasma

> 100’000’000 °C

Hot Neutrons

Main Problem:

First Wall

Material, Lifetime

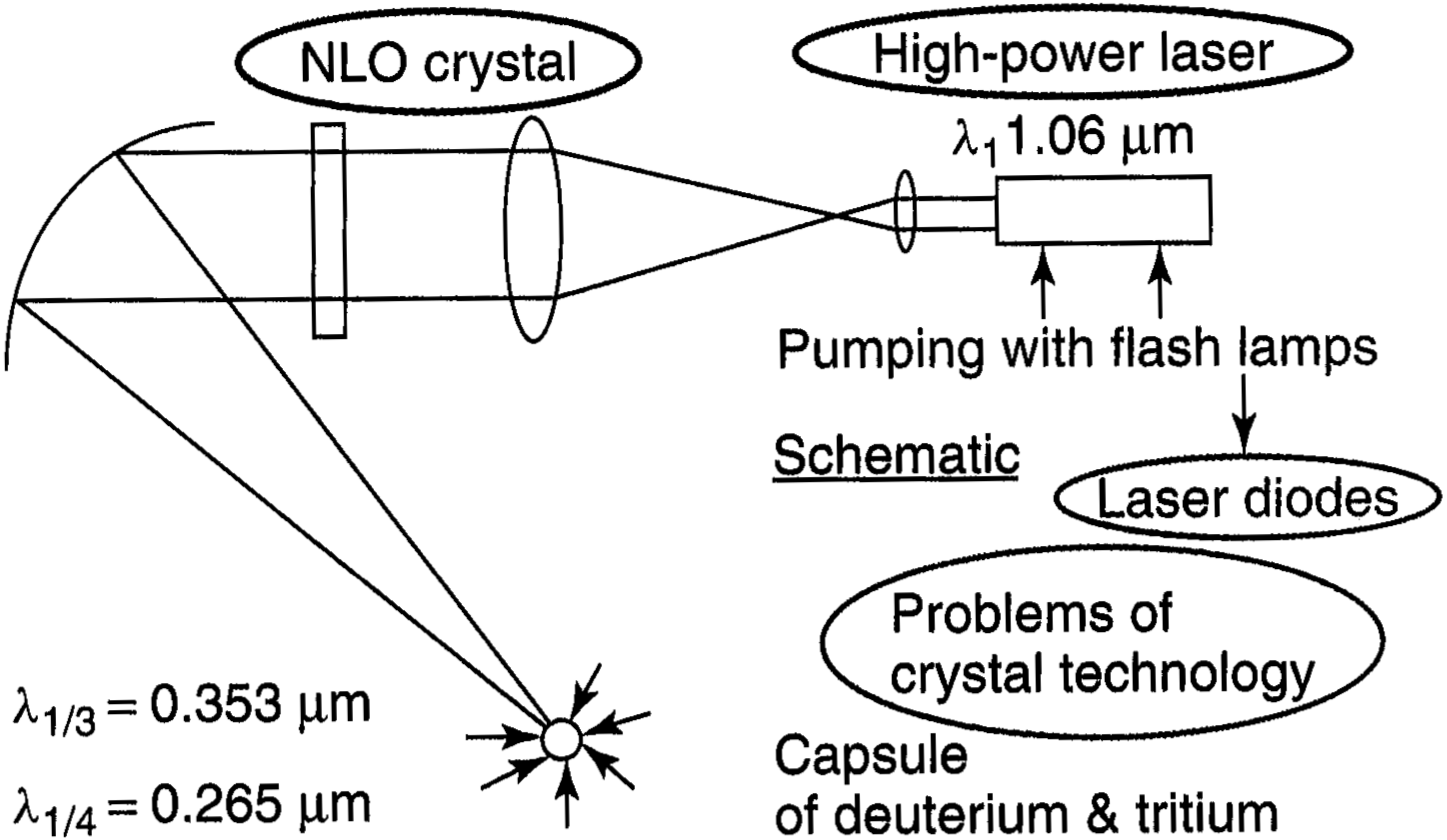
Alternative:

Inertial Confinement

Laser Fusion Energy

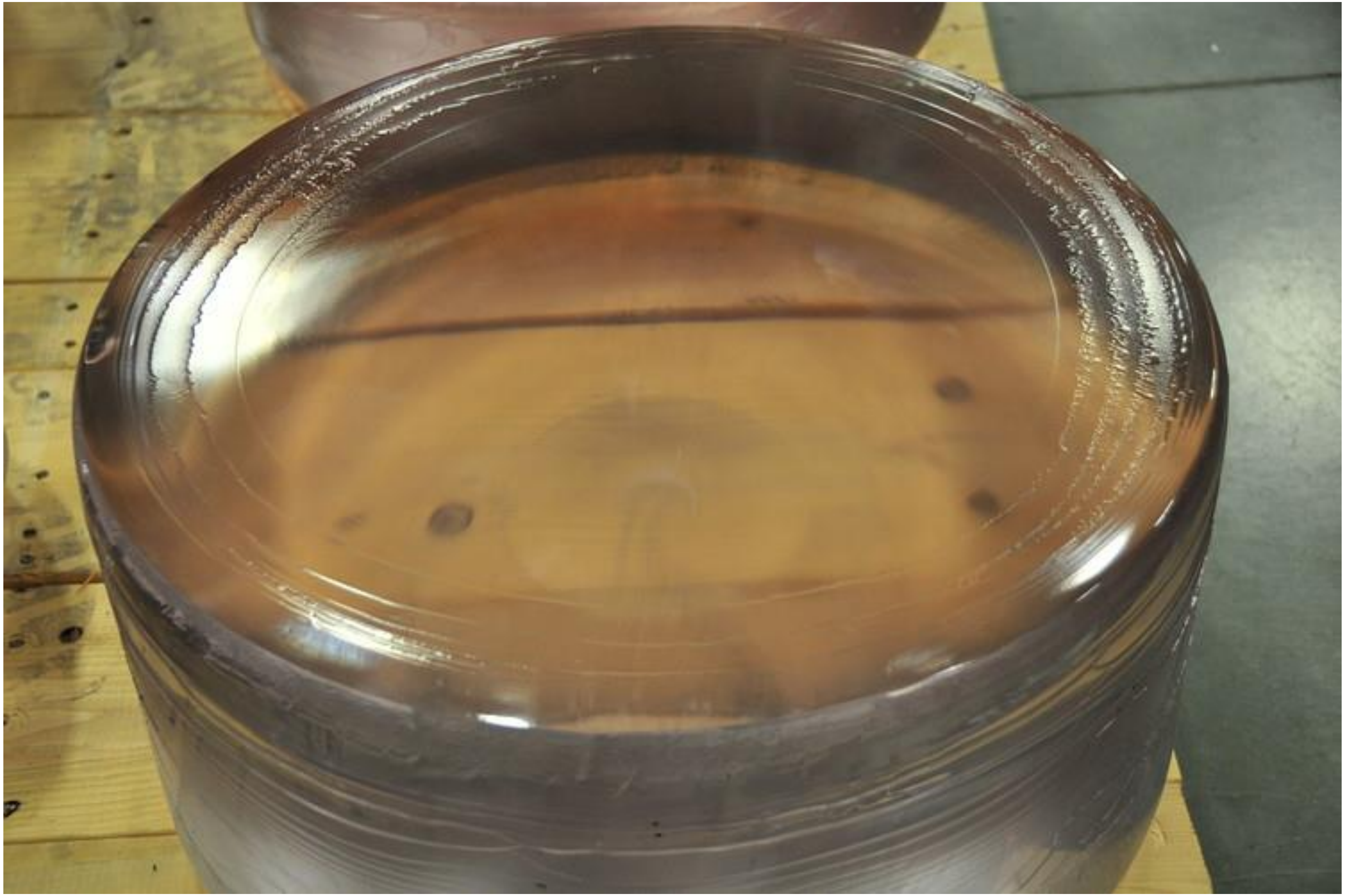
Has Fusion Energy by Magnetic Inclusion (Tokamak) a Chance as long as the Problem of the "First Wall" is not solved?

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 University GEKKO XII with 12 beams . **LMJ 2 tons KDP crystals, 300 tons Nd-glass laser**. (Bordeaux)

Future!



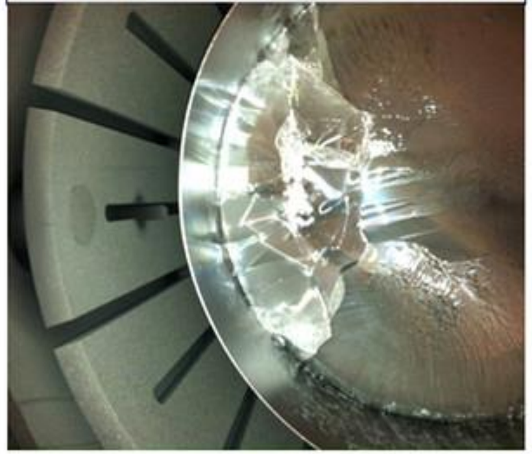
GT – APPLE
Sapphire
boule 2014

Poly on top

Crack initiated from seed

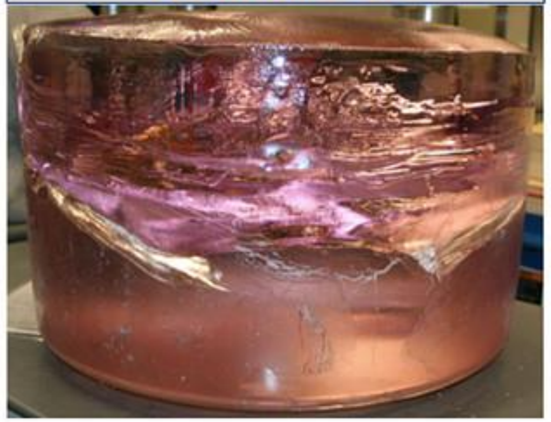
Thermal crack in cool down

Crack from blackbody



Spiral crack

Horizontal crack



For iPhone 4S and iPad 2 screen
APPLE & GT

New Factory in Mesa, AZ: 500M$
700 employees
2038 HEM furnaces 578 M$
For Sapphire boules 262 kg

GT bankrupt
Wallstreet Journal Nov. 20, 2014

Crystal Machining Sawing, polishing etc.: Meyer Burger Thun (Diamond Materials Tech)
Colorado Springs CO, USA
70 employees
Now sold to China

Not the Optimum Technology and Process Development!

Crystal Technologists are needed!

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.

See WHITE PAPER Project 16 in www.general-protection-engineering.ch

Propsals to

- **Materials Dept. ETH Zurich 1998**
- **Rector & President ETH Zurich 2013**
- **Technikum Winterthur 1999/2000**
- **Arizona State University 2000**
- **Univ. Wisconsin at Madison WI 2000**
- **State Univ. New York/Stony Brook**

- **4 International Workshops on Crystal Growth & Crystal Technology**

in Beatenberg BE 1998, 2005, 2008 & Mount Zao, Japan 2000 (with T. Fukuda)

International Discussion Meeting Greece May 2012 >> WHITE PAPER

There are 2 different worlds, crystal growth for research and industrial crystal and layer production, but in both cases crystal technologists are needed

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!

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**

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

Role of Crystallography!

Achievements: In Reproducibility

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**

Potential for Crystallography and for Crystal Technologist

The development of crystals, epilayers, fibers, cables, coils from an optimum HTSC compound is

- allowed by thermodynamics,
- probably a technologically solvable problem.

Necessary steps (with theoretical support) with

1. Establish **one** optimum HTSC compound (1.2.3?) with
   - Tc > 90K
   - sufficient thermodynamic stability
   - minimum problem from phase transition
   - develop conditions of synthesis: temperature-P(O_2) program, gas pressure, mechanical pressure,
2. Develop substrate for epilayer (surface structure, surface layer, phase transition)

6th German-French Workshop on Oxide, Dielectric, and Laser Crystals 2017
September 14 – 15, 2017 Bordeaux, France

Perfect Crystals and Epitaxial Layers: Proposed Education of Crystal Technologists

Hans J. Scheel

General Protection Engineering GmbH
Bromattenweg 2, 3805 Goldswil b. Interlaken, Switzerland
hans.scheel@bluewin.ch +41 79 542 0078   www.hans-scheel.ch

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

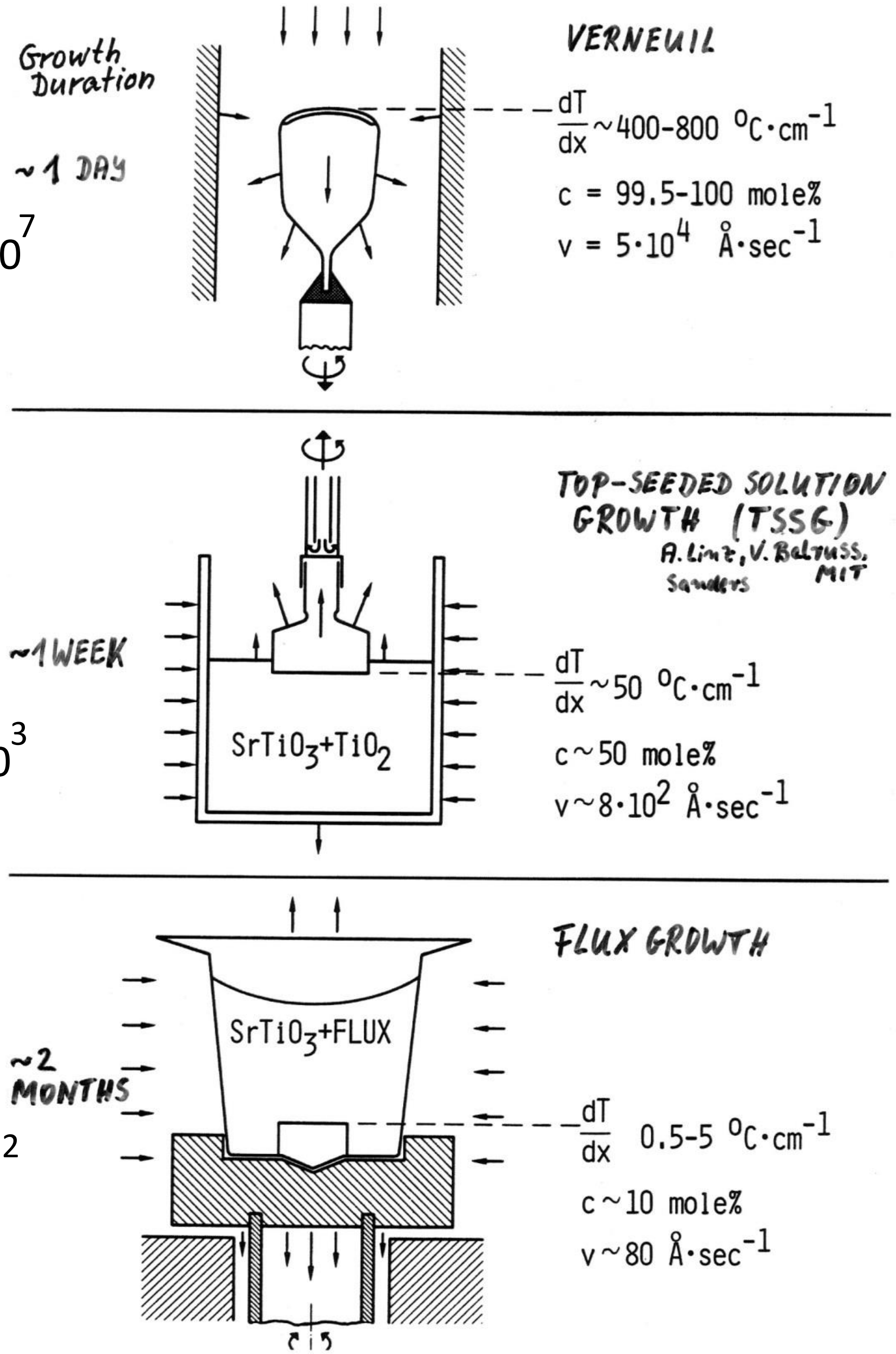
Complexity of Optimized Crystal Fabrication

Education of Crystal Technologists

Conclusions

Dislocations & Temperature Gradient

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



$10^6 - 10^7$

$10^2 - 10^3$

$0 - 10^2$

EPD / cm^2

SrTiO3

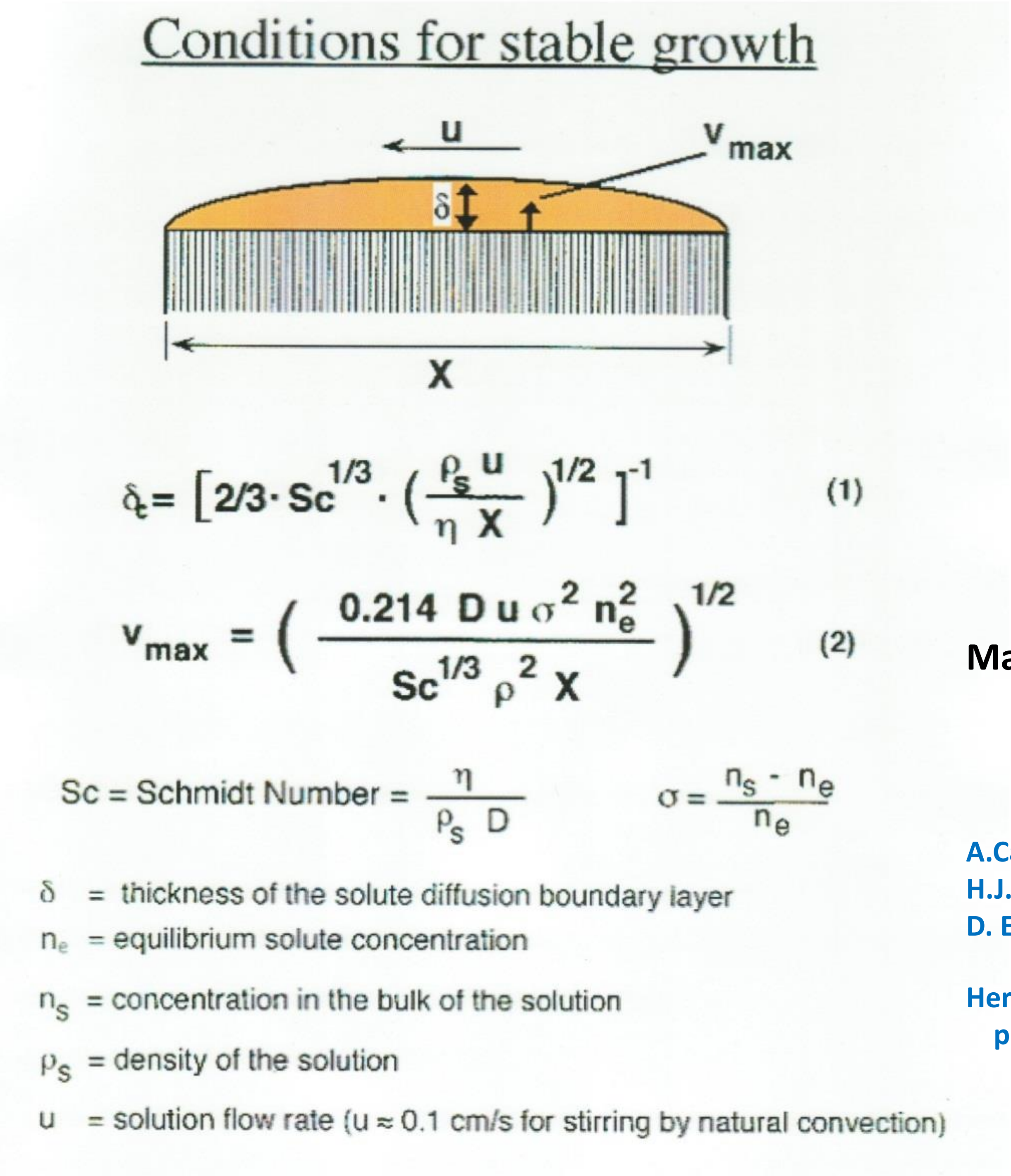
V. Belruss, J. Kalnajs, A. Linz
Mater.Res.Bull . **6**(1971)899-906

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

Growth of Inclusion-free Crystals



Conditions for stable growth

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

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

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

δ = thickness of the solute diffusion boundary layer

n_e = equilibrium solute concentration

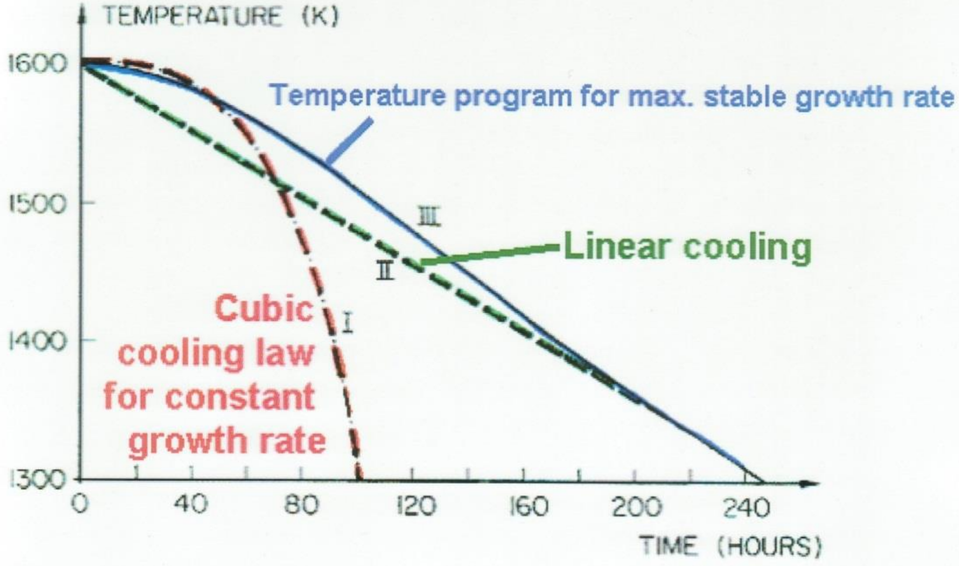
n_s = concentration in the bulk of the solution

ρ_s = density of the solution

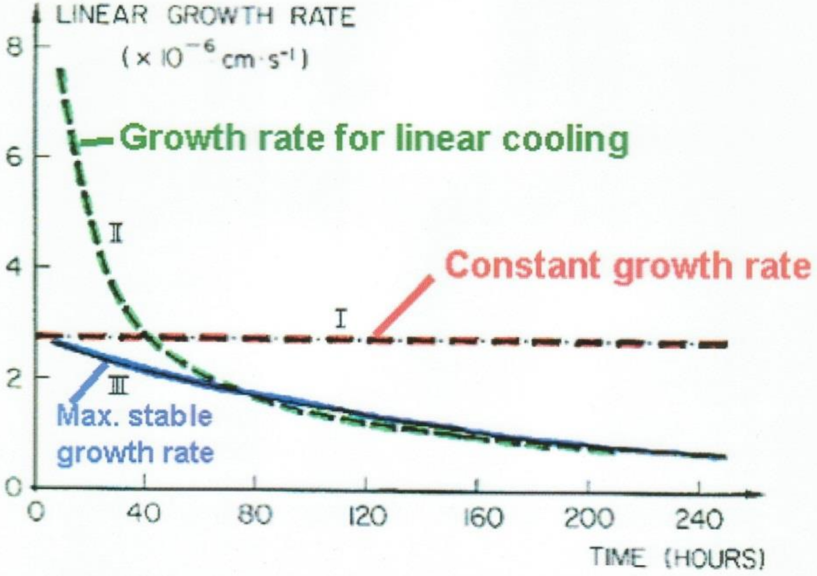
u = solution flow rate ($u \approx 0.1$ cm/s for stirring by natural convection)

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

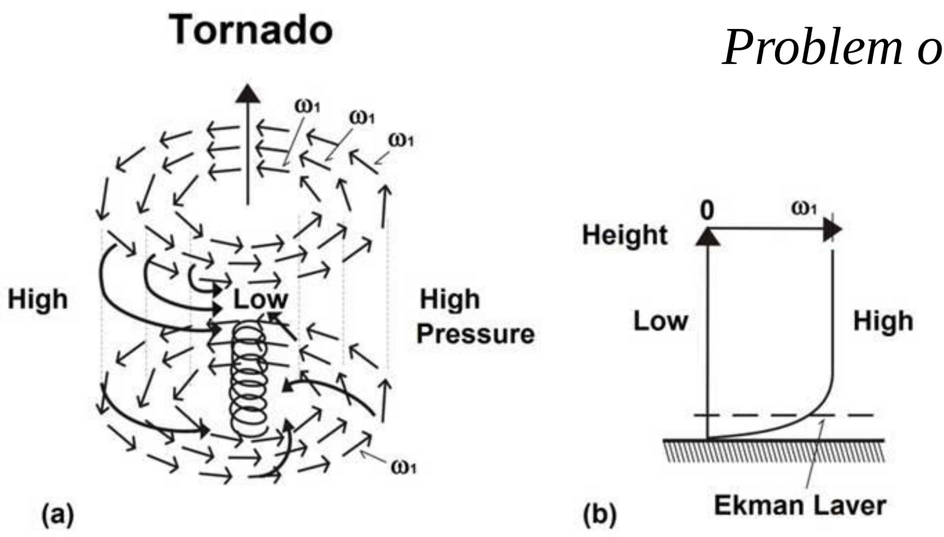
Observed Maximum Stable Growth Rates

(For 1cm crystals)

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

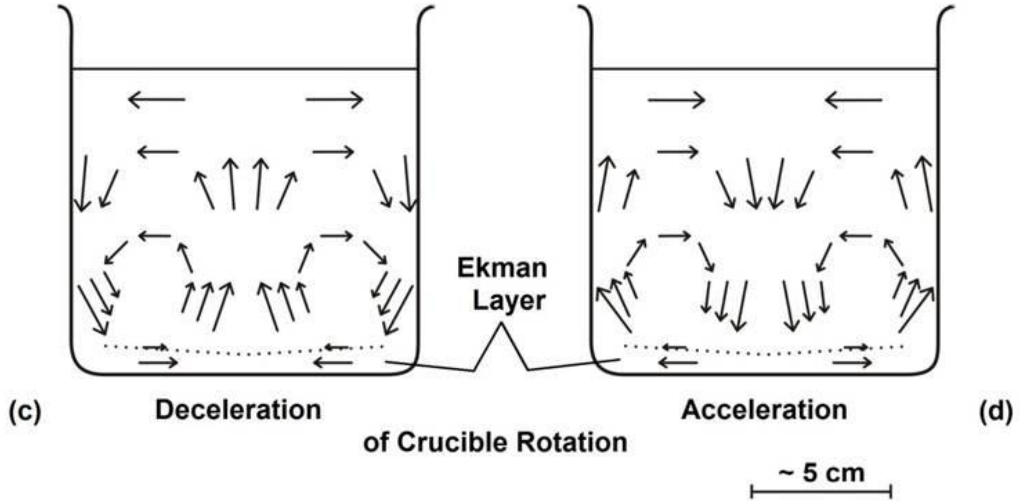
* 600 g ADP in 1l solution at 60ºC (~40%) and flow rate >10 cm s^{-1}, cooling rate 2 - 3° / day, growth rate ~11 - 15 mm / day

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).

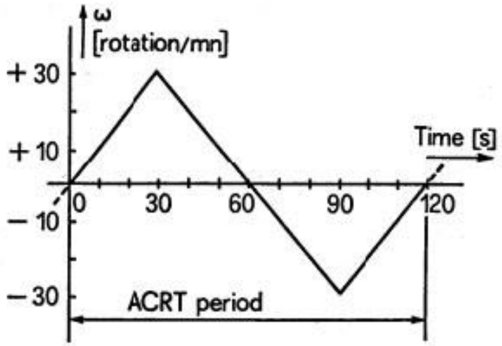
Spiral-Shear Flow and Ekman-Layer Flow, Movie at ICCG Marseille 1972

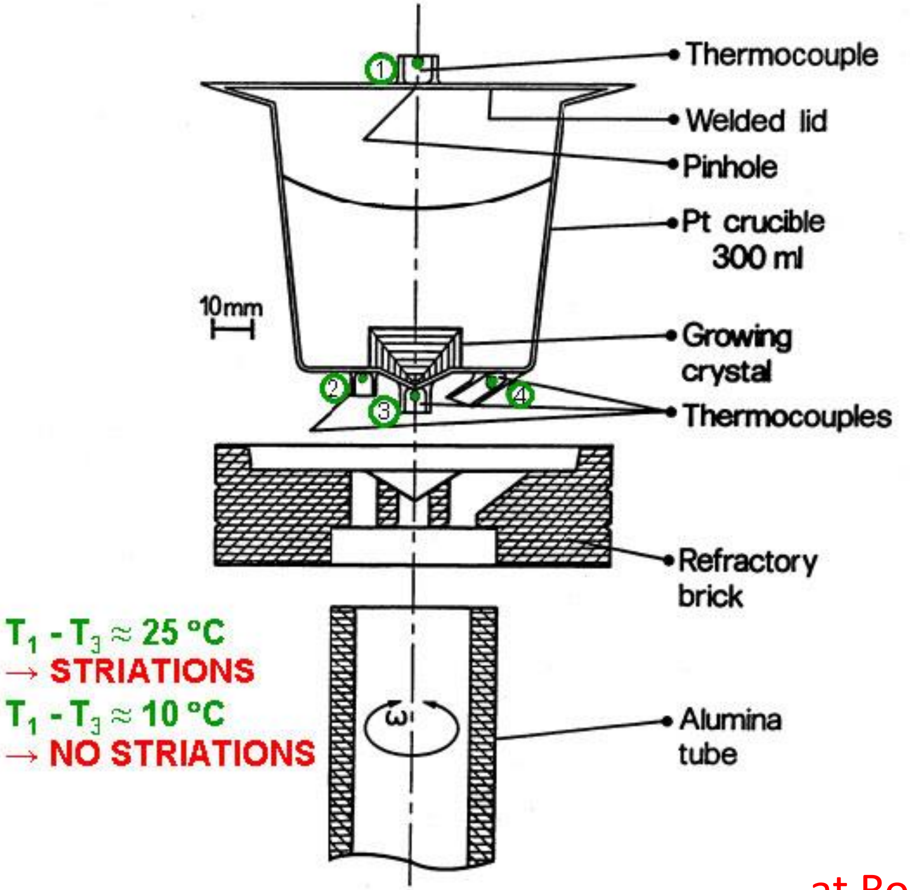


The Ekman Layer Flow occurs also in a circular Container with flat Bottom (c) when its Rotation is decelerated, and the opposite Flow upon Acceleration (d).

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

Accelerated Crucible Rotation Technique ACRT





Temperature Measurement
at Rotating Crucible at high Temperature

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

<u>ACRT in Growth from High-Temperature Solutions</u>

- $GdAlO_3$ & 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.

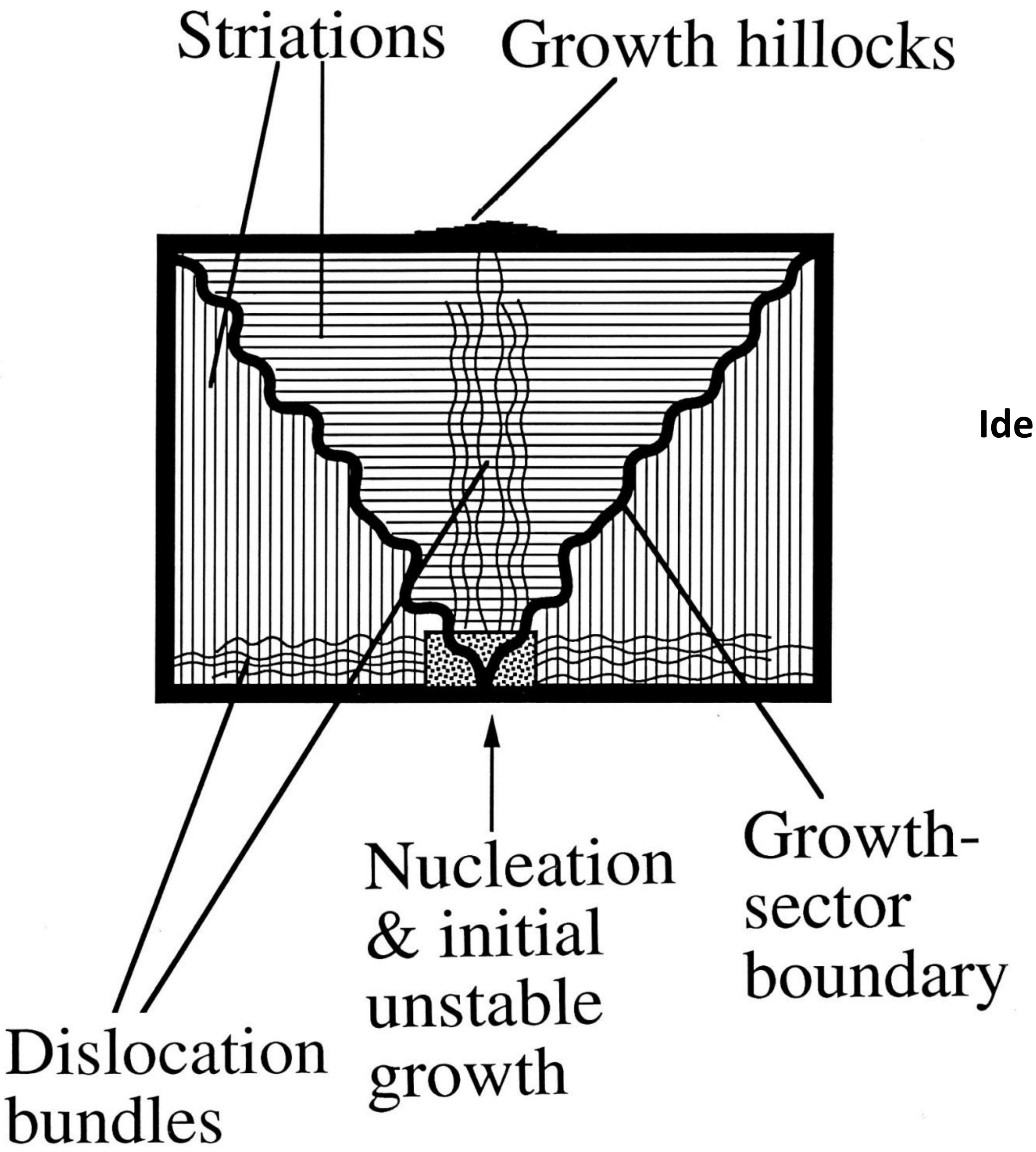
<u>ACRT in Bridgman Growth</u> (> flat growth surface)

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

<u>ACRT in Growth from Vapor</u>

- CdS: H.J. Scheel (unpublished)

List not complete



Idealized Cross Section

PhD Thesis at ETH Lausanne IBM Zurich Research Laboratory

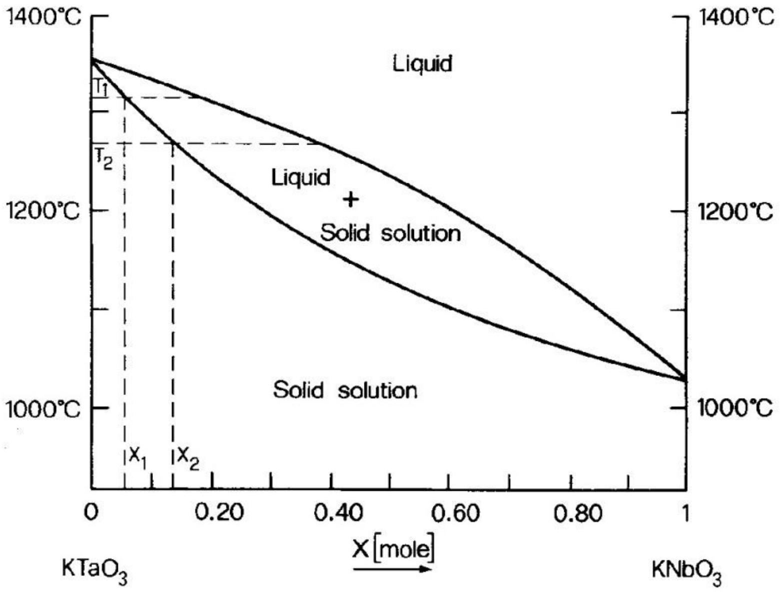


Fig. 2. Schematic solid-solution phase diagram (after ref. [5]). Growth starts at temperature T_1 with an initial concentration x_1, and ends at temperature T_2 with a final concentration x_2.

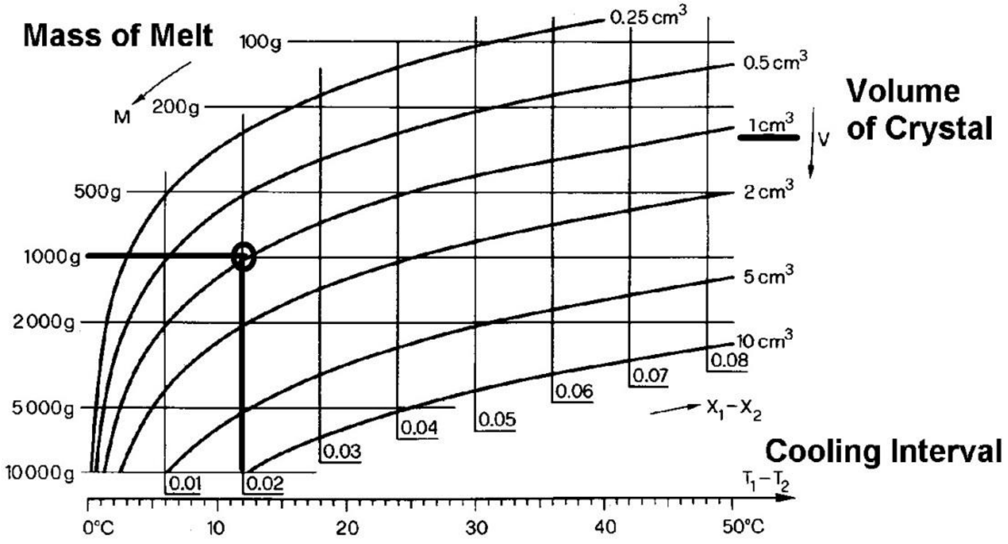
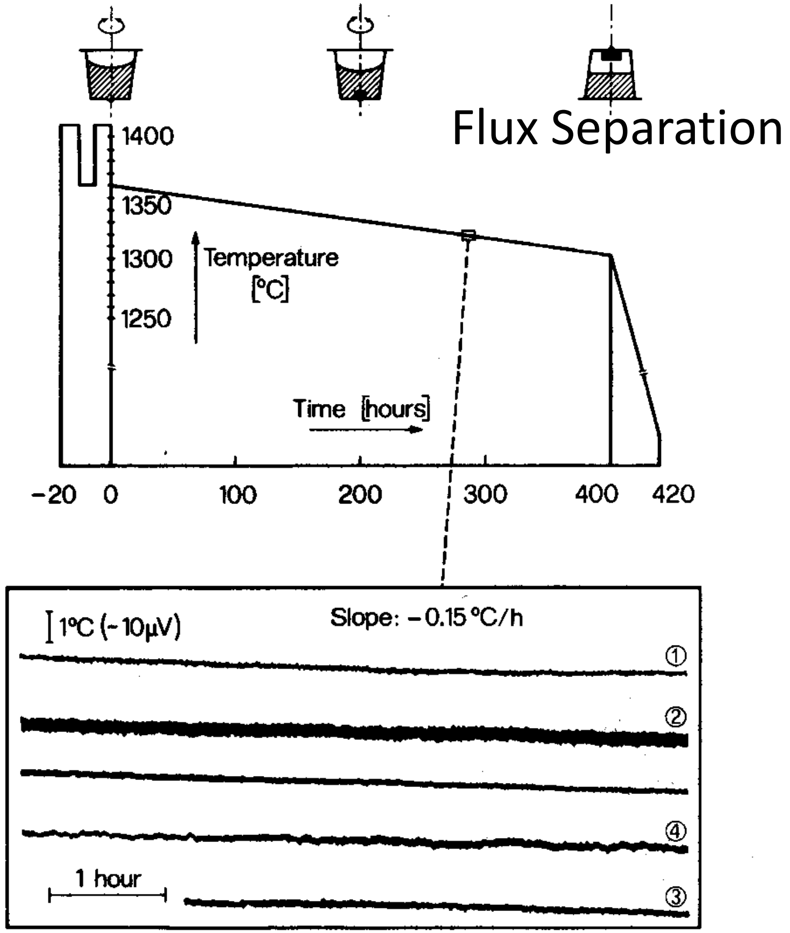


Fig. 3. Plot of crystal size V and inhomogeneity $x_1 - x_2$ as a function of experimental parameters (mass of melt M and cooling interval $T_1 - T_2$). A numerical example is detailed in the text.



Flux Separation

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.

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

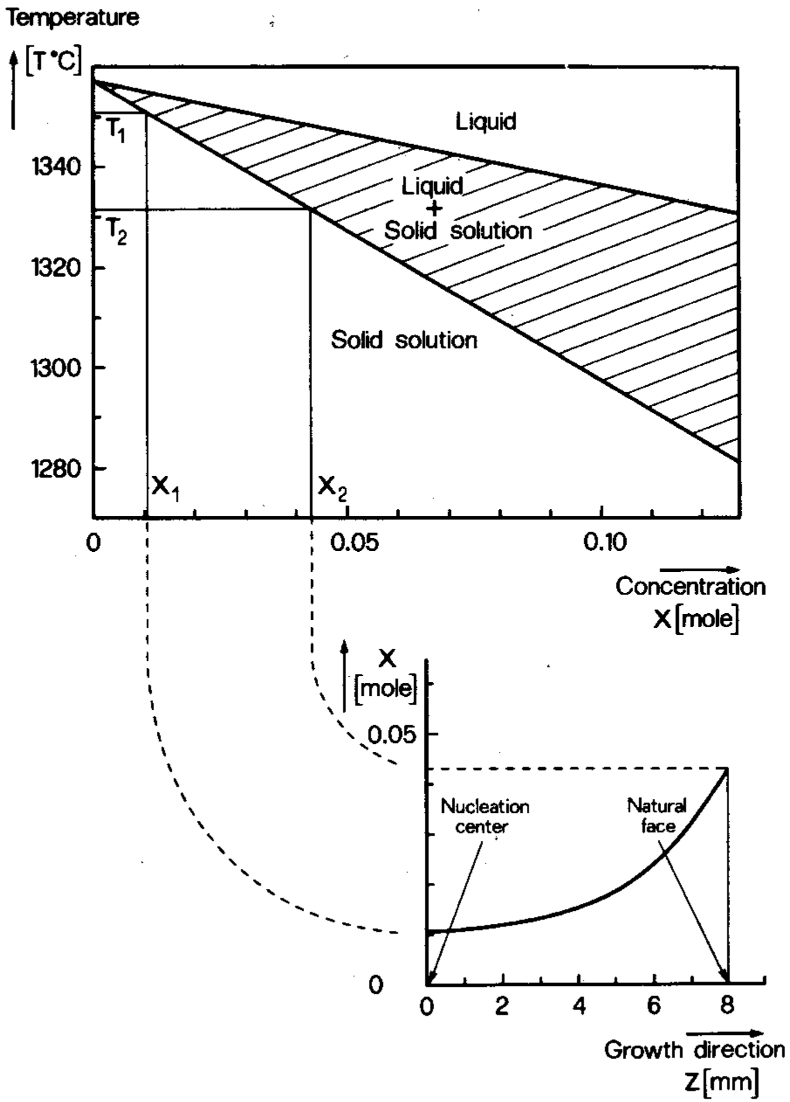
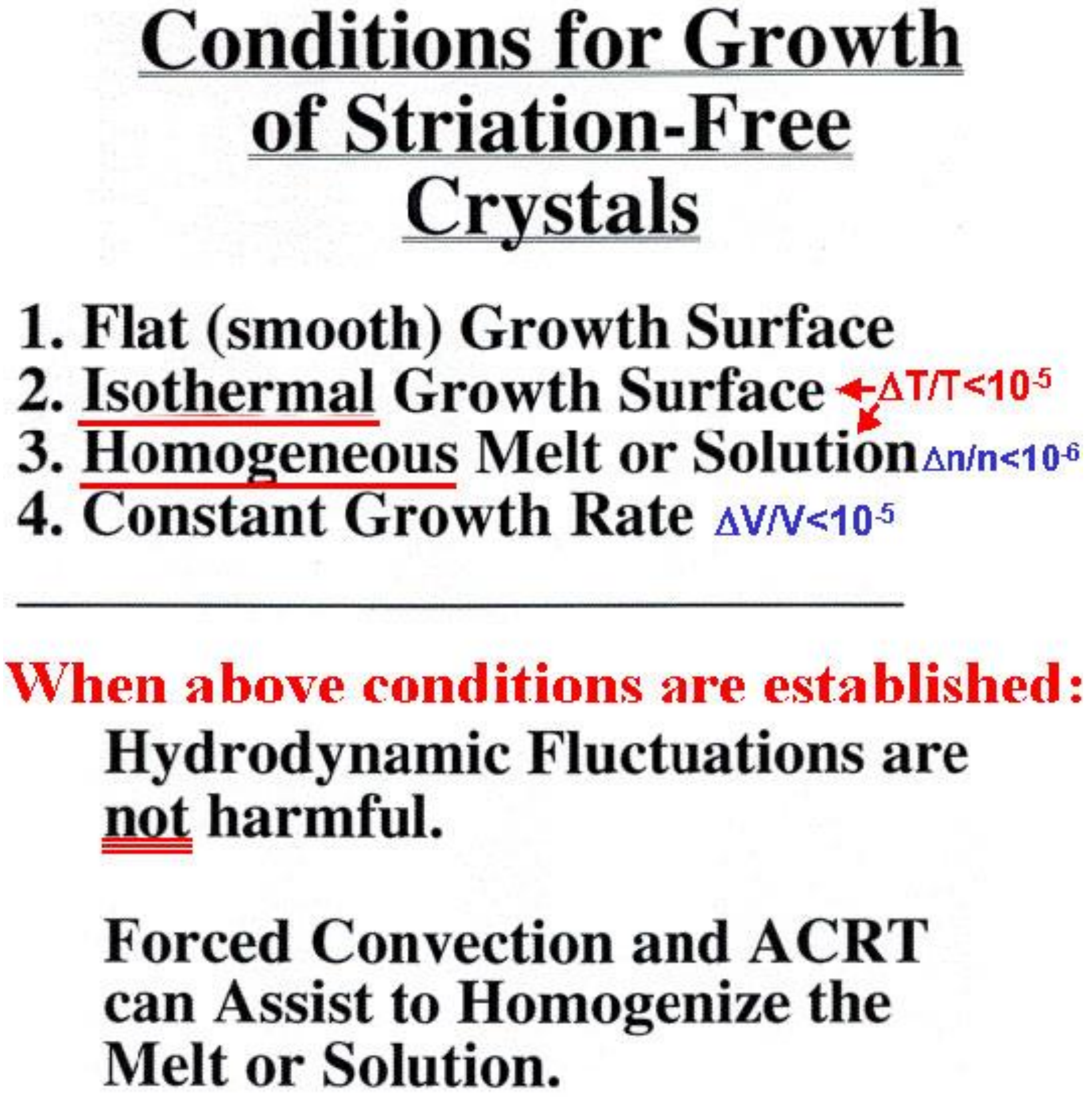


Fig. 4. Schematic phase diagram of $KTa_{1-x}Nb_xO_3$ and spatial variation of the concentration x along the growth direction z. The inherent bulk concentration gradient induced by the slow-cooling method is clearly shown. (The numerical values $T_1-T_2=20°C$, $x_1-x_2=0.03$ and $V\sim 8\times 16\times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



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.

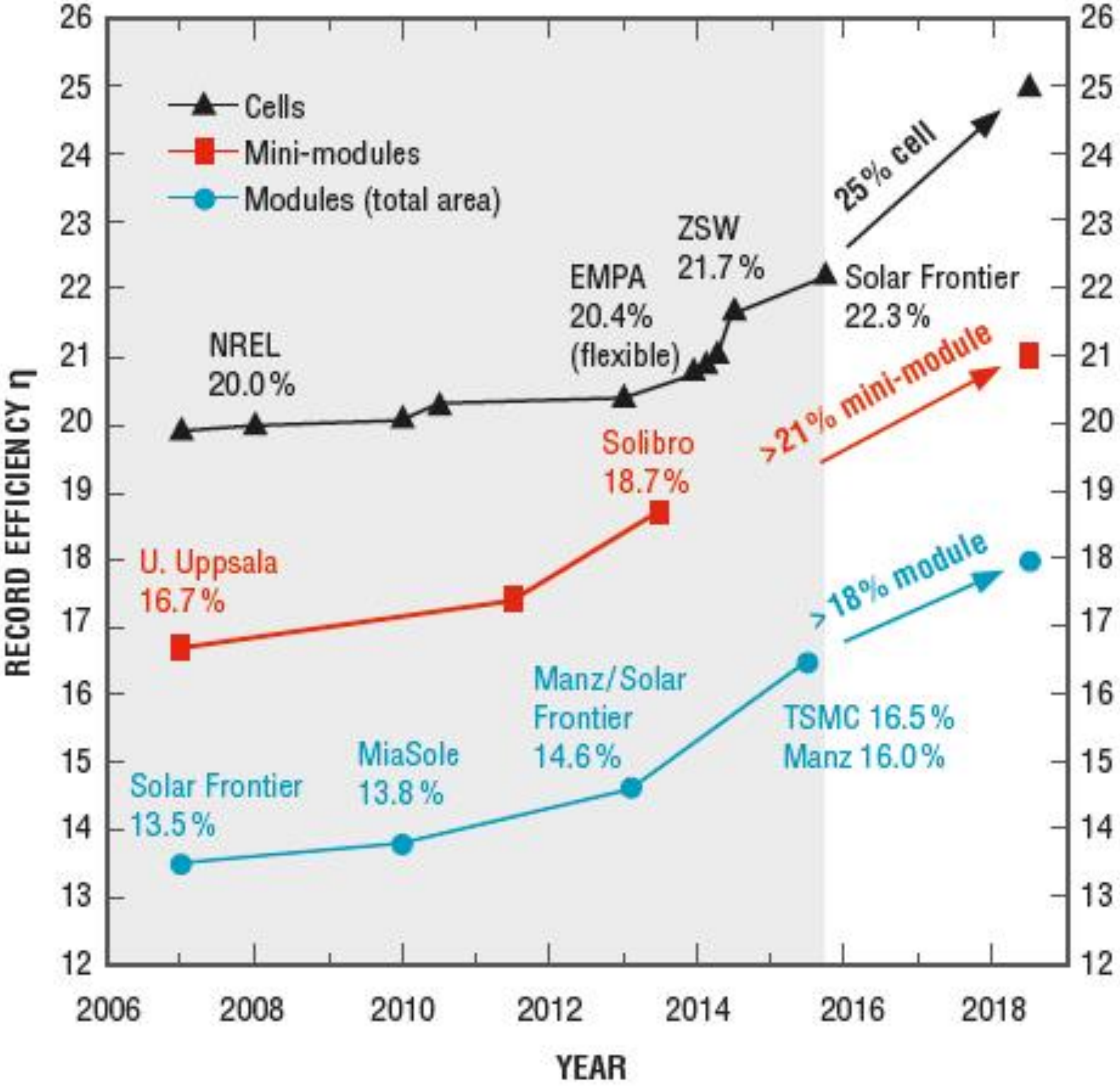
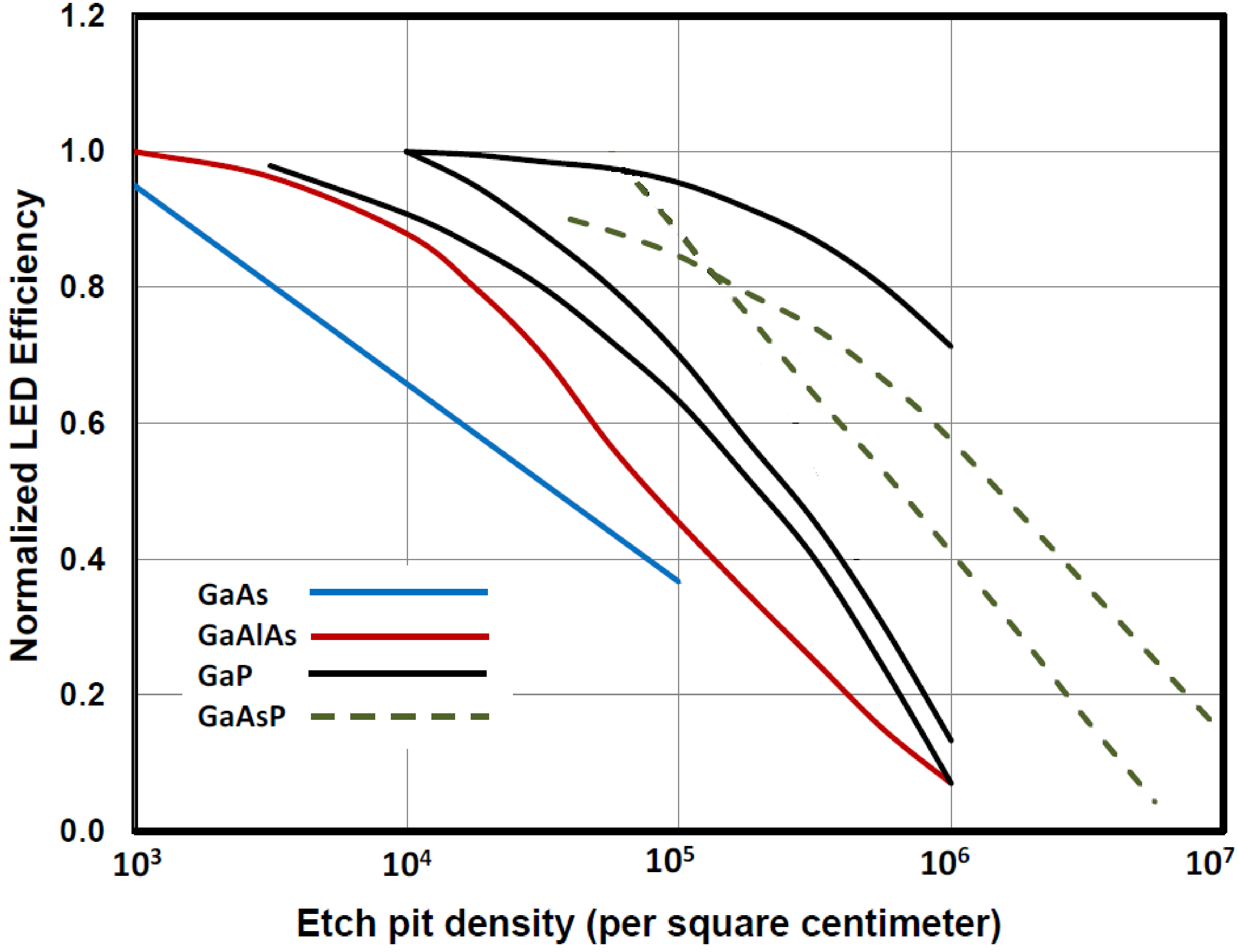
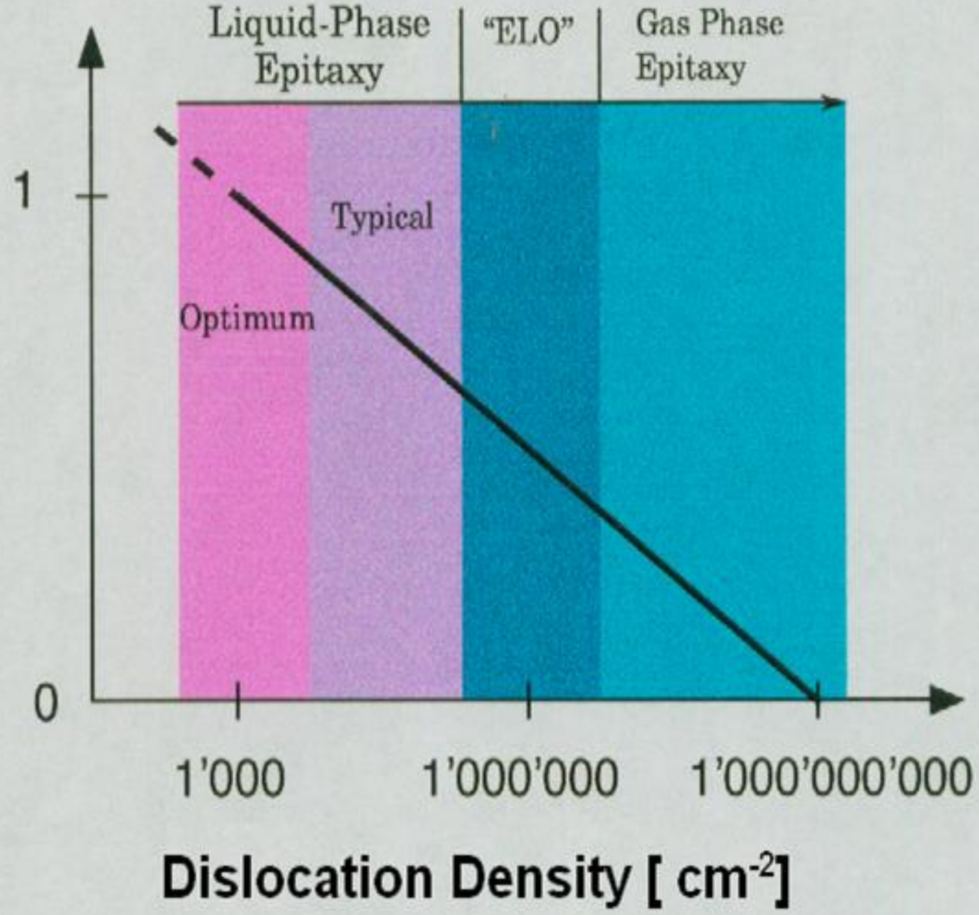


Fig. 1: Evolution of record efficiencies highlighting a steeper increase since 2014; 2016–2019 projections based on current R & D projects.



LED efficiency as a function of decreasing crystal quality (here shown as increasing dislocation density) for several types of compound semiconductor devices after S.D. Lester, F.A. Ponce, M.G. Craford, D.A. Steigerwald: Appl. Phys. Lett. 66(1995)1249-1251.

Normalized Efficiency of LEDs



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.