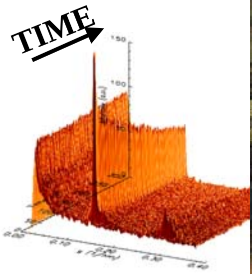
SAXS Under Extreme Conditions

H.Amenitsch



Layout of Presentation

Time-Resolved Measurements:
- -How to Trigger the Reactions
- -Biological Samples
  - Muscle, Proteins, Phospholipids
- -Material Science
  - Nanoparticles
  - Mesoporous Materials

Grazing Incidence Small Angle Scattering (GISAXS/GISAD):
- -Theory
- -Surface Diffraction Lipids
- -Mesoporous Materials
- -Nanoparticles/Nanocrystals

Why?

What is extreme?

- -Temperature: mK, 10^3 K, 10^6 K
- -Time scales: years,s, ms, µs
- -Pressure: MPa, GPa
- -Chemical potential
- -Non equilibrium states => Transitions

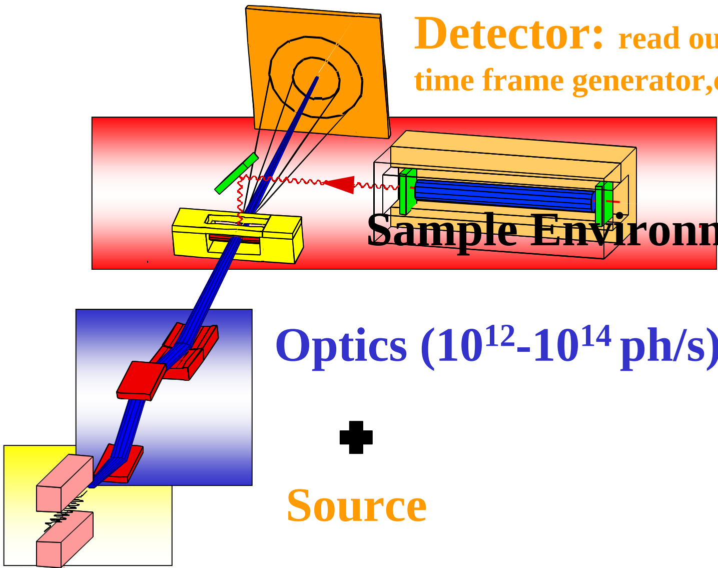
Scientific Case:

Function – Structure – Dynamics – Energy

Biology and Biomedicine:
-understand molecular and cellular function
-find ways to cure diseases

Material Science:
-understand macro- and supramolecular assembly
-find new, purpose-designed materials

What do you need?



Detector: read out times, time frame generator,cps, efficiency

Sample Environment!!!

Optics (10^{12}-10^{14} ph/s)

+

Source

How to trigger transitions?

-T-jump (heating): Erbium Glass Laser (ms)
"heat exchanger"
-T-cool jump: "heat exchanger" (s)
-p scans (jumps): High pressure cells (ms)
-hydrostatic pressure
-diamond anvil cells
-Stopped-flow cells, jet-cells (μs-ms)

-M.C.Ramachandra et.al. Biophysical Journal 74, (1998), 2714
-Segel DJ et.al. , JOURNAL OF MOLECULAR BIOLOGY, 288, 489, (1999)
-Pollack L et.al., PNAS, 96,10115, (1999)
-Akiyama S et.al., PNAS, 99,1329, (2002)
-Rössle M et.al. *Biomacromolecules*, *4*, 981-986, (2003)

-Batch reactor (s)
-Magnetic field
-Shear experiments
-Mechanical stretch (μs-ms-s)

How it all began - Muscle Contraction

September 1970: DESY
Rosenbaum,Holmes & Witz, Nature (1971), **230**,434

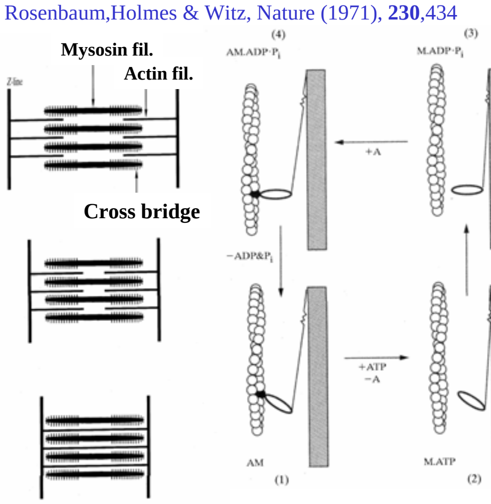


Fig. Muscle Contraction thick (myosin)-, thin-(actin) fibers are interdigitating
K.C.Holms Acta Cryst. **A54**, (1997), 789

Fig. Lymn-Taylor cycle. (Lymn, Taylor Biochemistry, (1971)10, 4617 Mysoin-cross-bridge is bound in rigor (1) ATP binds->quick dissociation (2) ATP->ADP + P (hydrolysis) binding of myosin to actin 90 up (3) release of components, rowing to (1)

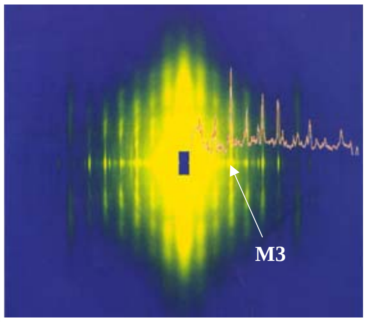
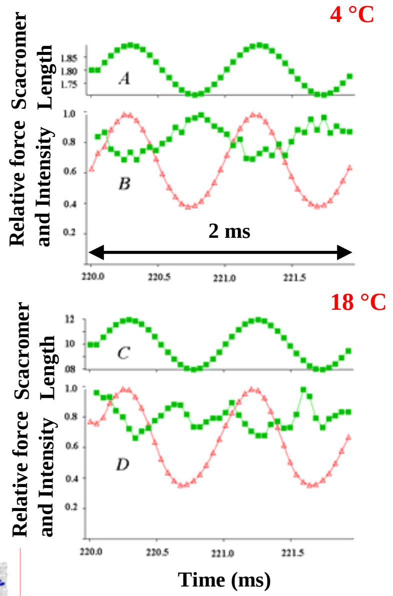


Fig. Diffraction pattern of life skeletal frog muscle Cover page: Yagi, et.al. J.Synchrotron. Rad (1996), 3,247

How it all began - Muscle Contraction



Rana temporaria **(tibialis anterior fibers)**
Frequency: 1 kHz
Time resolution: 50 µs

Frequency: 3 kHz
Time resolution: 16 µs

Literature:

Bagni MA, et.al., BIOPHYSICAL JOURNAL **80**, 2809, (2001)

Griffiths P J, et.al. PNAS, **99**, 5384, (2002)

Piazzesi G, et.al. NATURE **415**, 659, (2002)

Reconditi M, et.al. NATURE **428**, 587, (2004)

Biomechanics on Human Aorta: Motivation

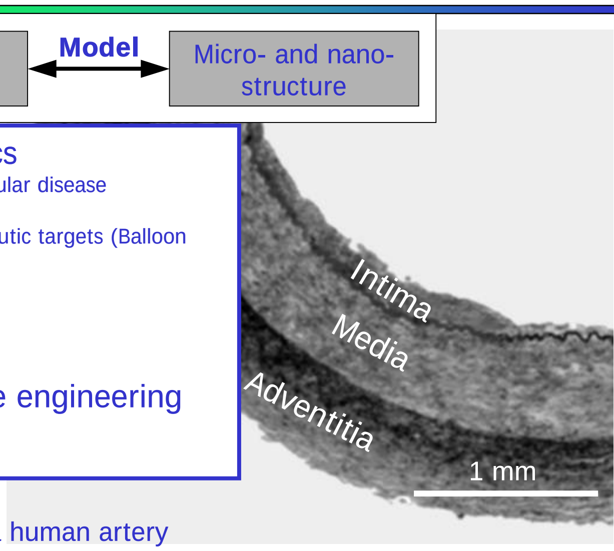
Macroscopic response ⟷ **Model** ⟷ Micro- and nano-structure

Pathology, Clinics
Characterization of vascular disease
Effects of aging
Identification of therapeutic targets (Balloon Angioplasty)

Graft design
Biomimetic materials

Functional tissue engineering

Mechanobiology

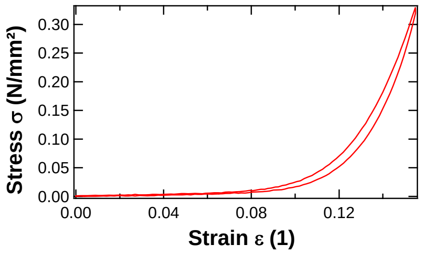


Cross section of a human artery

Human Aorta: Mechanical Parameters

Macroscopic

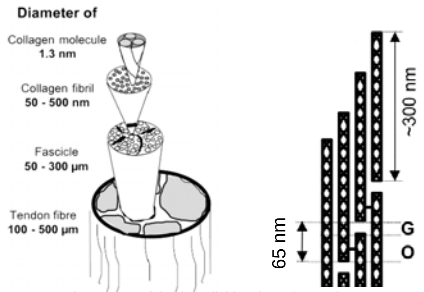
- geometric deformation
- stress
- strain



Nanoscopic

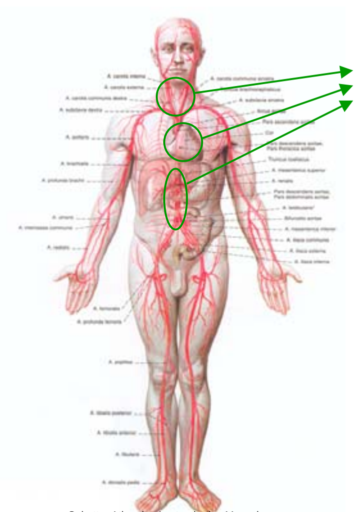
- fiber – matrix composite
- fiber alignment
- fiber strain

Collagen - The most abundant protein

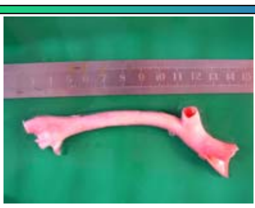


P. Fratzl, Current Opinion in Colloid and Interface Science, 2003

Human Aorta: Sample Preparation

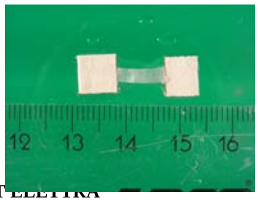


Sobotta, Atlas der Anatomie des Menschen, Band 2, 20. Auflage, S.14, Abb31



An artery, cleaned from surrounding tissue

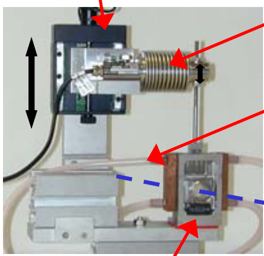
After dissection into its major layers



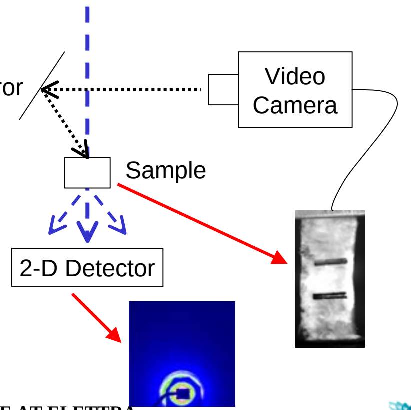
The final sample

Human Aorta: The Sample Stage

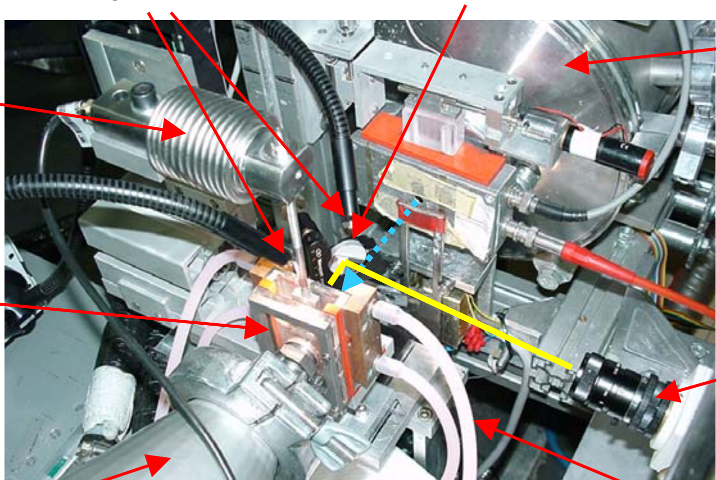
Stretching and mechanical data acquisition device



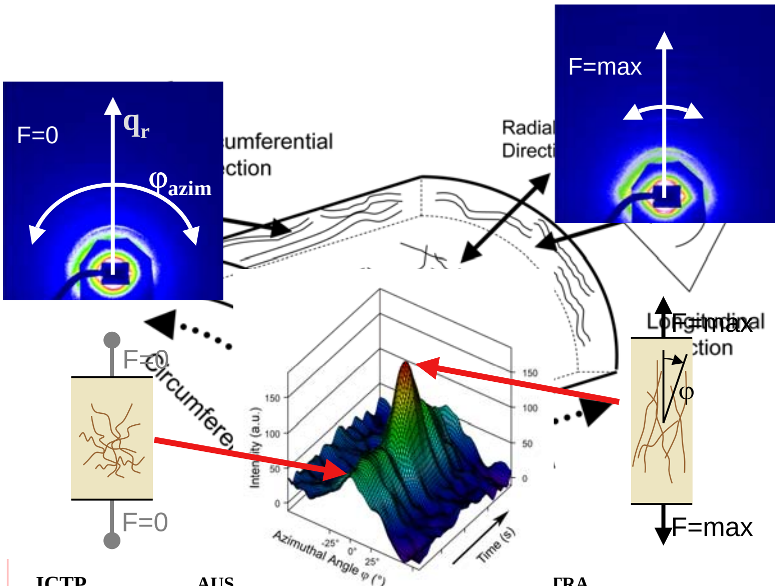
Recording geometrical changes during stretch; Top view



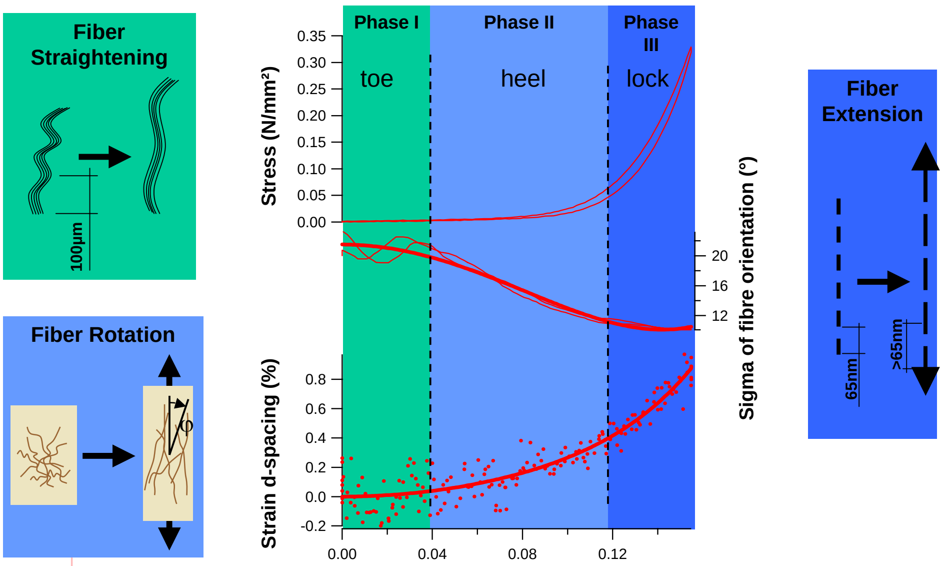
The Setup @ Beamline



Human Aorta: Collagen Fiber Orientation

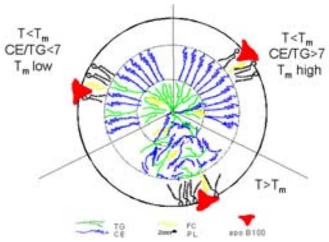


Nano – Macro Coupling



F. Schmid et al., J. Synchrotron
2005, in press

T-jump on Low Density Lipoprotein



Sketch of the LDL lipo-protein in the 3 different states:
-core liquid crystalline state
-core isotropic state TG, CE, FC, PL denotes triglycerides, esterified cholesterol, unesterified cholesterol, phospholipids.

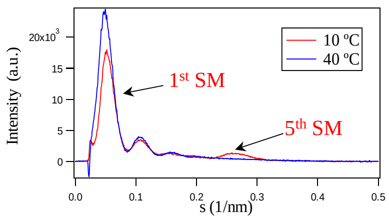


Fig. Static diffraction pattern at different temperatures

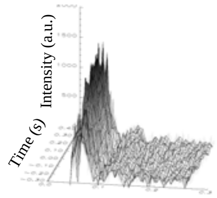
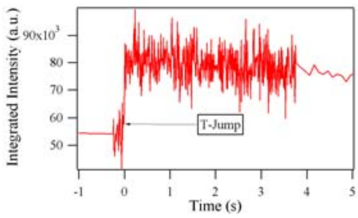
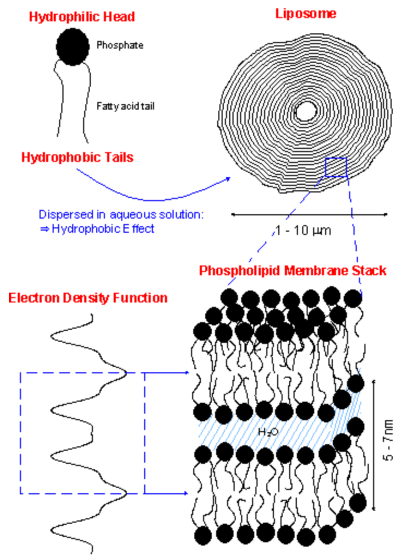


Fig. Time-resolved diffraction pattern during the T-jump left pattern – right integrated intensity 1st side maximum



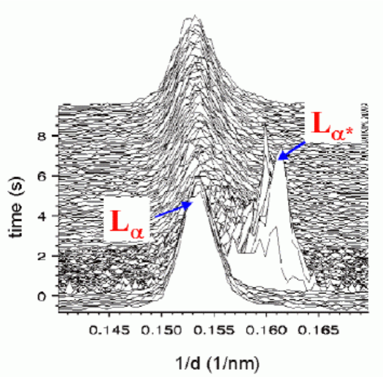
Prassel R. et.al. (2005)

T-jumps: Phospholipid Phase Transition



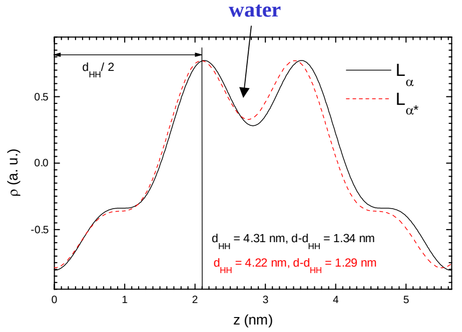
The formation of a phospholipid membrane. Phospholipids aggregate spontaneously into ordered supra-molecular structures in the presence of water. This can be explained in simple terms by the fact that phospholipids feature a hydrophilic headgroup (attracting water) and hydrophobic hydrocarbon-chains. The average 1- dimensional repeat distance d, i.e., bilayer plus water layer of the depicted liquid crystalline phase (L_α) is in the range of 5-7 nm. The electron density distribution of a bilayer (bottom left corner) has maxima in the headgroup regions and a minimum at the methyl terminus of the hydrocarbon-chains. The dashed rectangle marks the part of the electron density distribution shown in the fig below.

T-jumps: Phospholipid Phase Transition

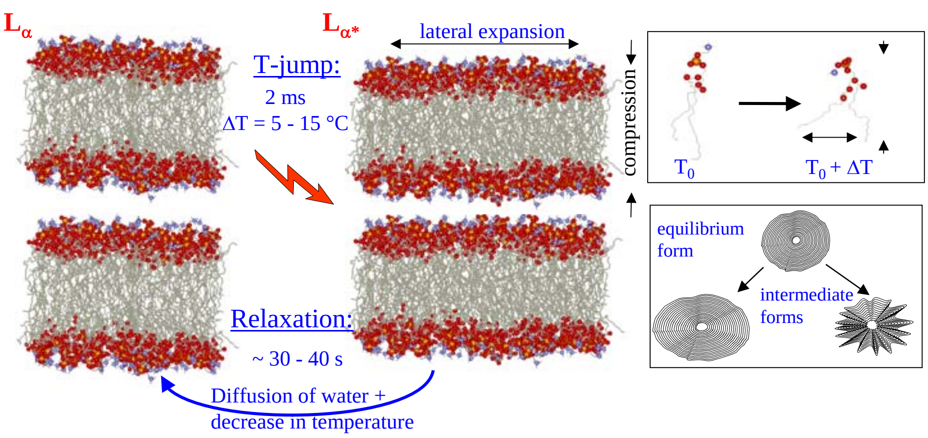


The first order diffraction peaks of a phospholipid sample during a T-jump experiment (time resolution = 5 ms). The IR-laser was triggered at time zero.

Superimposed electron density distributions of the original L_α-phase (straight line) and of the intermediate phase $L_{\alpha*}$ (dashed line) immediately after the laser flash



T-jumps: Phospholipid Phase Transition



G. Pabst, M. Rappolt, H. Amenitsch, S. Bernstorff & P. Laggner, Biophys. J., (2000)

Mesoporous Materials: Bulk MCM-41

In-situ study of the Formation of the MCM-41 Structures using liquid crystal templating mechanism
P. Ågren, J.Phys. Chem. B, (1999), 103, 5943

Aim:
Influence of the co-surfactant and its concentration on the phase behaviour of the TEOS synthesis.

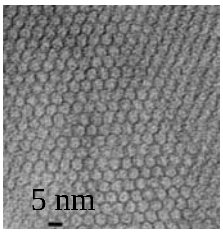
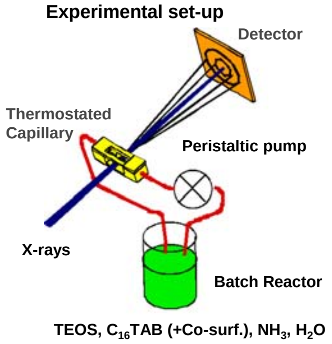


Fig. Representative electron transmission micrograph of a MCM41 structure depicting the mesoporous hexagonal nano-structure.



TEOS Tetraethylorthosilicate
C_{16}TAB Hexadecyltrimethylamonium bromide

Industrial applications: -adsorbents
-ion-exchangers
-catalysts
Hosts for technologically advanced materials

Mesoporous Materials: Bulk MCM-41

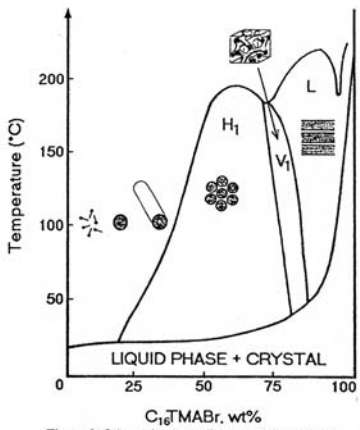
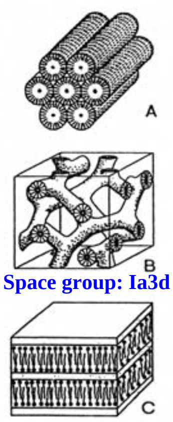


Figure 2. Schematic phase diagram of C_{16}TMABr in water [44].



Space group: Ia3d

Figure 3. Schematic representation of liquid-crystal structures, (A) hexagonal, (B) bicontinuous cubic, (C) lamellar.

MCM-41

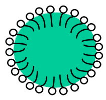
MCM-48

MCM-50

From: Sayari, Studies in Surface Science and Catalysis (1996), Vol 102, 1

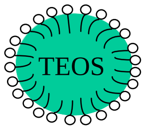
Model for synthesis of mesophases in the system: TEOS/CTAB MCM-41

1
CTAB (surfactant) + H_2O



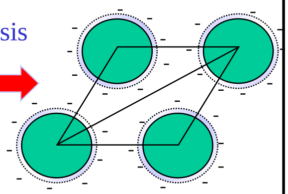
Spherical/elliptical Micells

2
Micelles + H_2O + TEOS (oil)



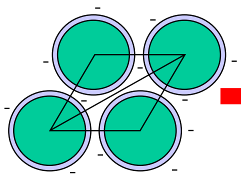
Microemulsion

3
Silanhydrolysis on the surface of the micelles

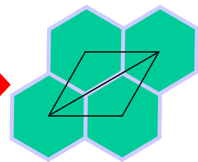


Formation of mesophases

4
condensation to poly-silicates between the aggregates of micelles



Inter-aggregat condenstation



Intra-aggregat condenstation

Mesoporous Materials: Bulk MCM-41

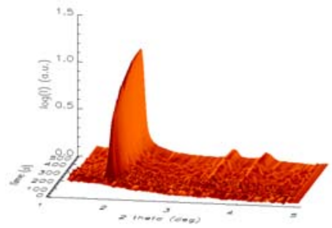
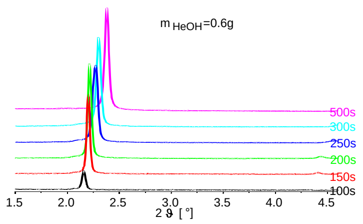
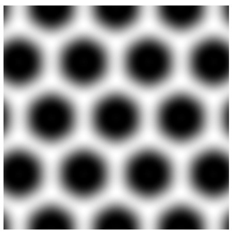


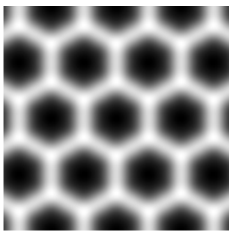
Fig. : Time-resolved diffraction pattern of the TEOS synthesis
Time resolution: 0.3 s/frame, Transition: micellar solution - ordered phases (standard synthesis: hexagonal D = 4.67 nm)



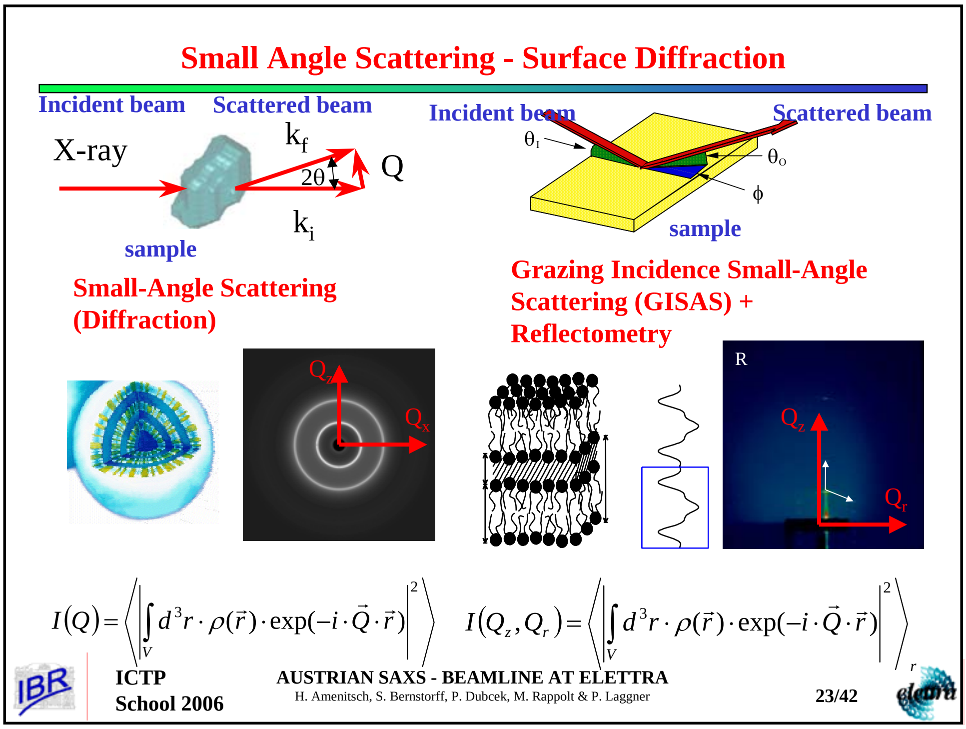
Calculated Electron Density



After 150s



Final Structure


Small Angle Scattering - Surface Diffraction
Incident beam
Scattered beam
X-ray
k_f
2θ
Q
k_i
sample
Small-Angle Scattering (Diffraction)
Incident beam
Scattered beam
θ_i
θ_o
ϕ
sample
Grazing Incidence Small-Angle Scattering (GISAS) + Reflectometry
Q_z
Q_x
R
Q_z
Q_r
$I(Q)=\left\langle\left|\int_V d^3r\cdot\rho(\vec{r})\cdot\exp(-i\cdot\vec{Q}\cdot\vec{r})\right|^2\right\rangle$
$I(Q_z,Q_r)=\left\langle\left|\int_V d^3r\cdot\rho(\vec{r})\cdot\exp(-i\cdot\vec{Q}\cdot\vec{r})\right|^2\right\rangle_r$
ICTP
School 2006
AUSTRIAN SAXS - BEAMLINE AT ELETTRA
H. Amenitsch, S. Bernstorff, P. Dubcek, M. Rappolt & P. Laggner
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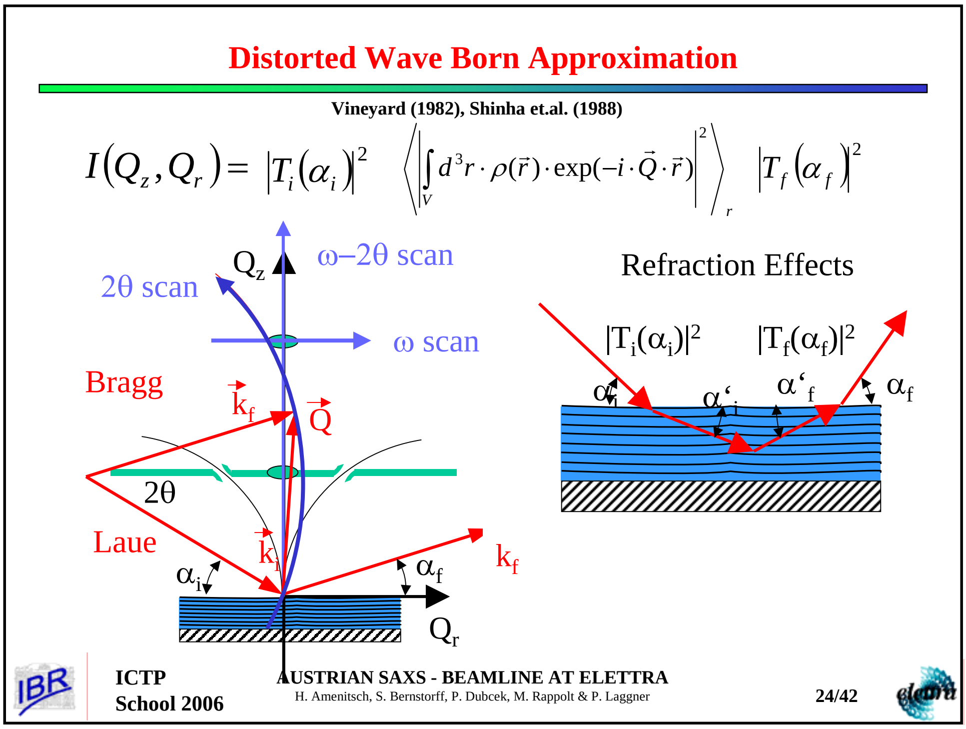
Distorted Wave Born Approximation
Vineyard (1982), Shinha et.al. (1988)
$I(Q_z,Q_r)=\left|T_i(\alpha_i)\right|^2\left\langle\left|\int_V d^3r\cdot\rho(\vec{r})\cdot\exp(-i\cdot\vec{Q}\cdot\vec{r})\right|^2\right\rangle_r\left|T_f(\alpha_f)\right|^2$
Q_z
$\omega-2\theta$ scan
2θ scan
ω scan
Bragg
$\vec{k}_f$
$\vec{Q}$
2θ
Laue
$\vec{k}_i$
α_i
α_f
k_f
Q_r
Refraction Effects
$|T_i(\alpha_i)|^2$
$|T_f(\alpha_f)|^2$
α_i
α'_i
α'_f
α_f
ICTP
School 2006
AUSTRIAN SAXS - BEAMLINE AT ELETTRA
H. Amenitsch, S. Bernstorff, P. Dubcek, M. Rappolt & P. Laggner
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Distorted Wave Born Approximation

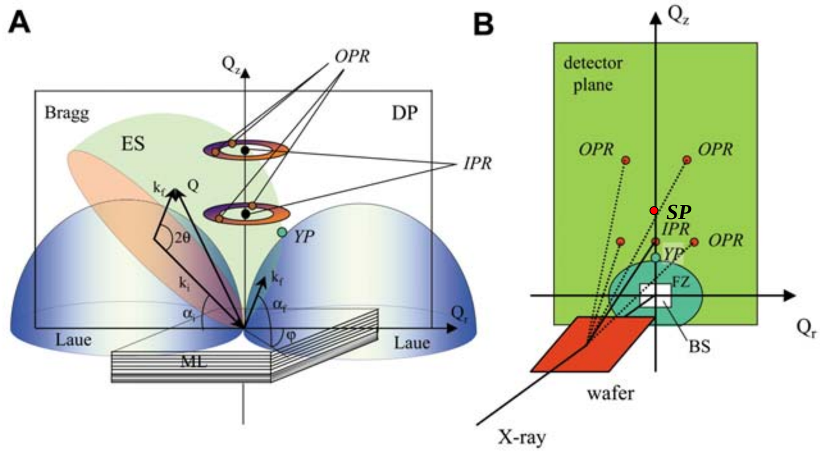
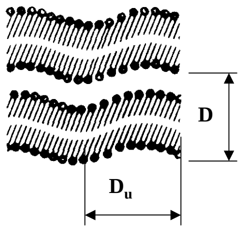
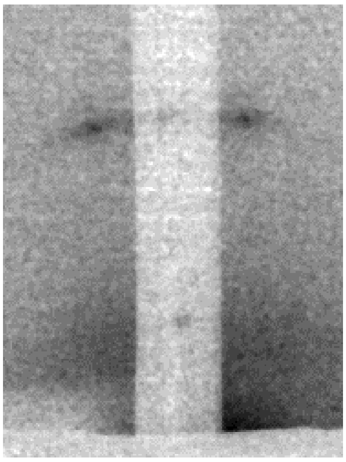


Fig. (A) the scattering geometry in reciprocal space. (B) Scattering geometry in real space. The abbreviations are: (ES) Ewald sphere, (DP) diffraction plane, (OPR) out-of plane reflections, (IPR) in-plane reflections, (ML) multi-layer, (FZ) forbidden zone, (BS) beam stop.

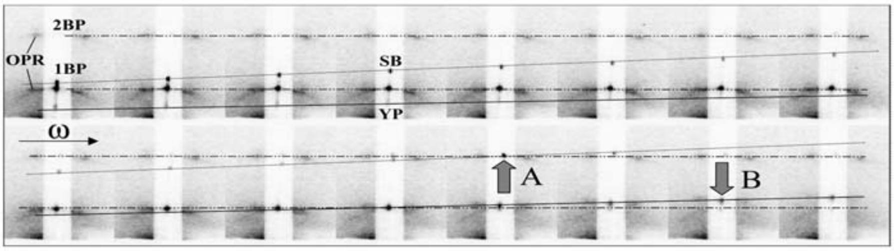
Experiment To Distorted Wave Born Approximation

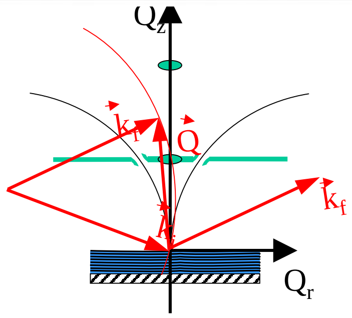
DOPC @ 39 °C
gel



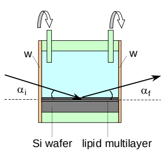


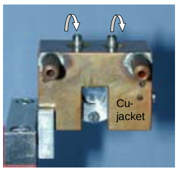
Experiment To Distorted Wave Born Approximation



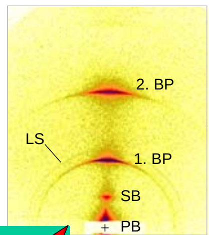


Surface Diffraction Lipids – Surface Chemistry

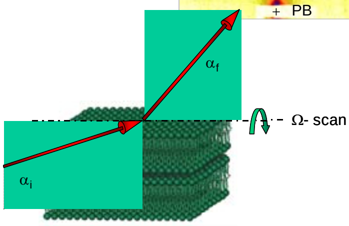




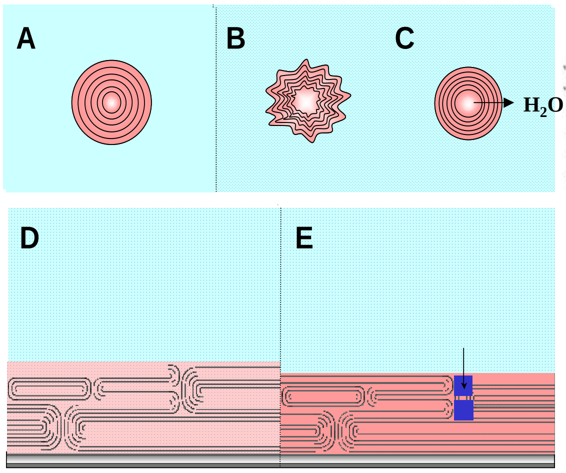
Sketch of the exp. set-up and 2D diffraction pattern of POPC and 0.5 M LiCl

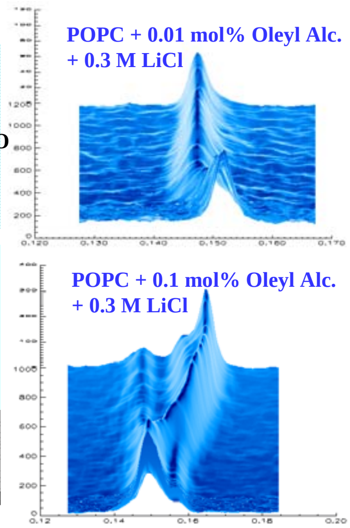


Sketch and photograph of the sample cell in transmission geometry for GISAXS.



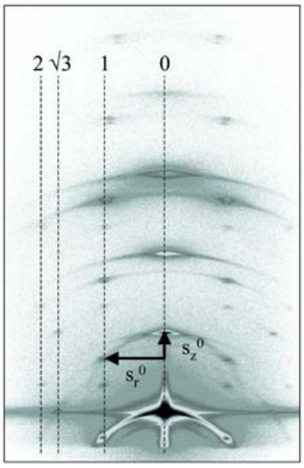
Surface Diffraction Lipids – Surface Chemistry

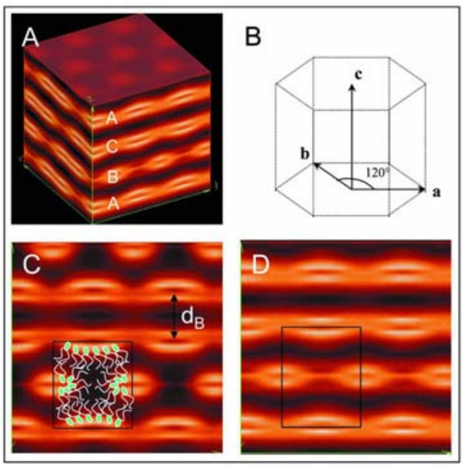




Amenitsch, H.; et.al. *Langmuir* **2004,** *20,* 4621-4628.

Surface Diffraction Lipids – Rhombohedral Phase





Diffraction Pattern DOPC @ 25°C, 35% rel. humidity

Rappolt,M, et.al., Advances Colloid and Interface Science, 111 (2004)

Electron Density Reconstruction: -C DPhPC (d_B= 44.3 Å) -D DOPC (d_B= 48.7 Å), but a= 67 Å / 68 Å

L. Yang, H.W. Huang, Biophys. J. 84 (2003)

Surface diffraction: Formation of aligned mesoporous thin films

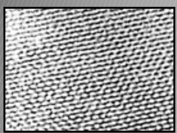
Sol-gel chemistry
+
surfactant mesophase

Self-assembly

Mesostructured hybrids

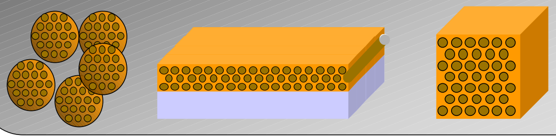
Treatment

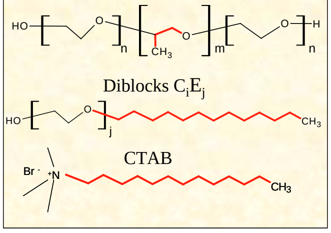
Mesoporous materials with organised porosity



C. J. Brinker et al. Adv. Mater., 1999, 11, 579.

Particles made by aerosols	Films and fibres made by liquid deposition	Monoliths made by controlled evaporation

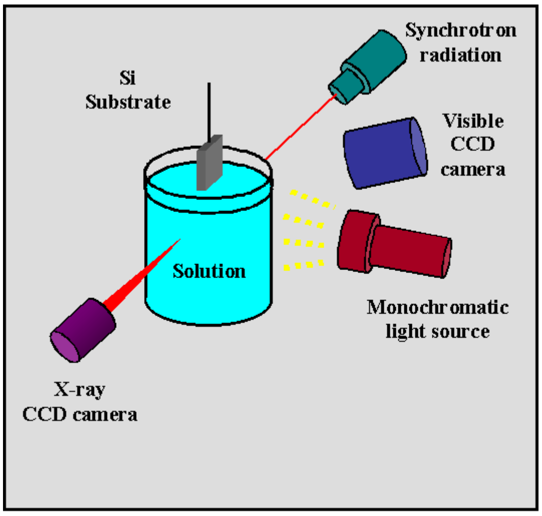




SiO_2 : $Si(OR)_4$
TiO_2 : $TiCl_4$ - $Ti(OR)_4$
ZrO_2 : $ZrCl_4$ - $Zr(OR)_4$
Al_2O_3 : $AlCl_3$
VO_{2-x} : $VOCl_3$
Y_2O_3 : YCl_3
Nb_2O_5 : $NbCl_5$
And binaries systems

The Self-Assembly of thin films as seen by In-Situ SAXS and interferometry

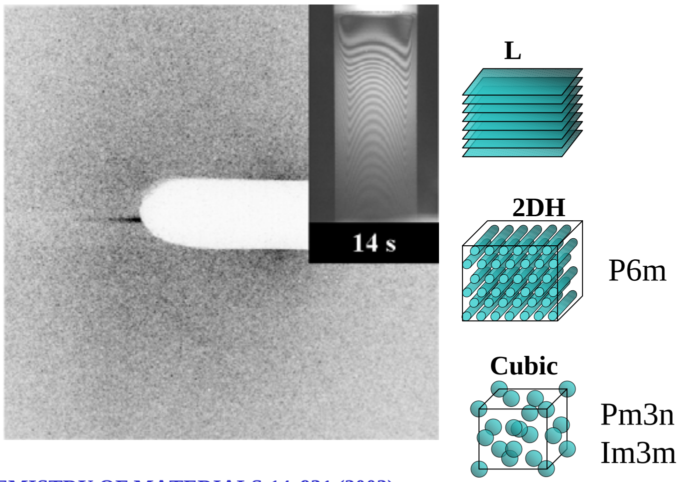
Film mesostructure



Film thickness profile

Surface diffraction: Formation of aligned mesoporous thin films

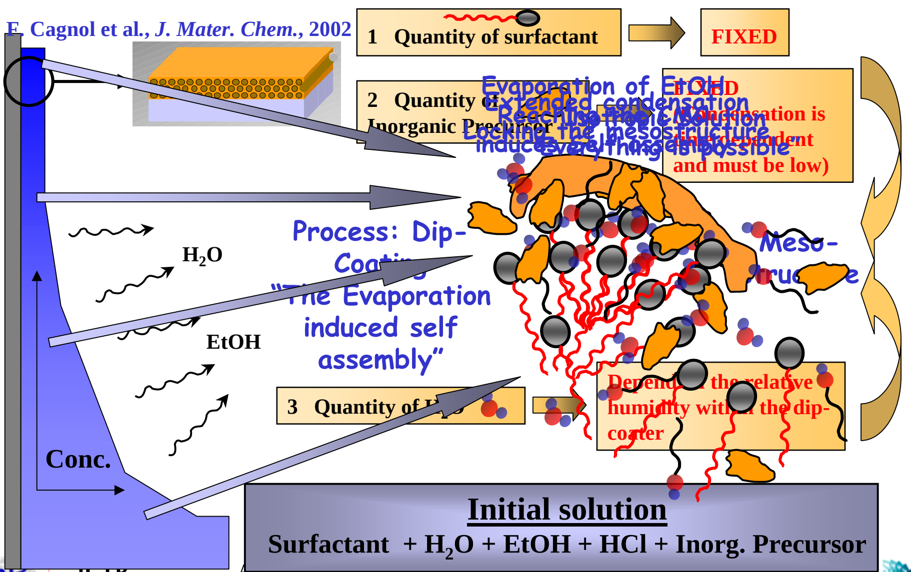
CTAB / Si = 0,18
H_2O / Si = 5
HCl / Si = 0.15
Ageing time
Relative Humidity



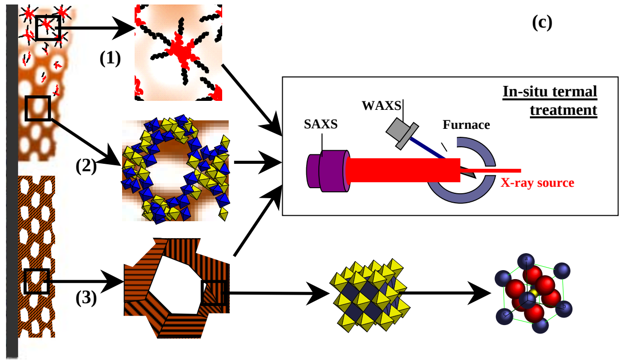
Grosso D, et.al., CHEMISTRY OF MATERIALS *14*, 931,(2002)

The Modulable Steady State

F. Cagnol et al., *J. Mater. Chem.*, 2002



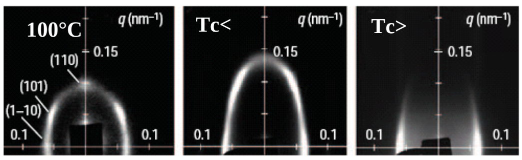
Formation of Nanocrystals



Surfactant: KLE3739

Precursors to form:
$Co_xTi_{1-x}O_{2-x}$ (fer.-semic.)
$SrTiO_2$ (photocatalyst)
$MgTa_2O_6$ (photocatalyst)

(1) Volatile species
(2) Template, porosity
(3) Crystallization and diffused sintering

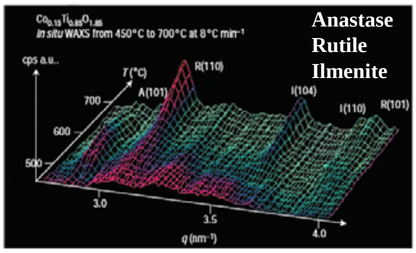


Grosso, D. et.al. *Nature Materials* 2004, *3*, 787-792.

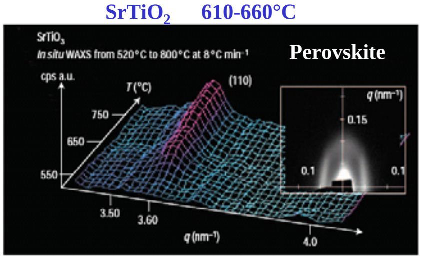
$Co_xTi_{1-x}O_{2-x}$

Formation of Nanocrystals

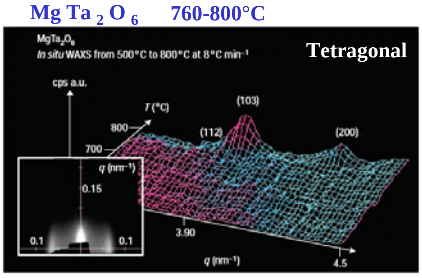
$Co_xTi_{1-x}O_{2-x}$ 500-570-650-660°C

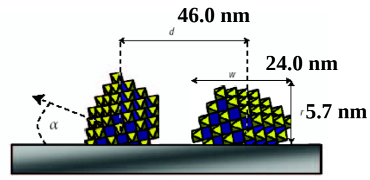


$SrTiO_2$ 610-660°C



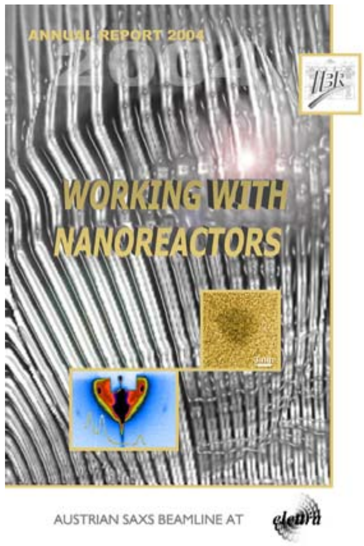
$MgTa_2O_6$ 760-800°C





Grosso, D. et.al. *Nature Materials* 2004, *3*, 787-792.

Further Reading



Annual Reports SAXS Beamline:
-Time resolved studies
-Surface diffraction
-GISAXS

Conclusion

Time-Resolved Measurements:
- How to Trigger the Reactions
- Biological Samples
  Muscle, Proteins, Phospholipids
- Material Science
  Nanoparticles
  Mesoporous Materials

Grazing Incidence Small Angle Scattering (GISAXS/GISAD):
- Theory
- Surface Diffraction Lipids
- Mesoporous Materials
- Nanoparticles/Nanocrystals

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