POWDER DIFFRACTION

Synchrotrons

Kenny Ståhl

DTU Chemistry

CONTENTS

- Why synchrotrons
- Resolution
- High angular resolution
- Energy resolution
- Time resolution
- High pressure

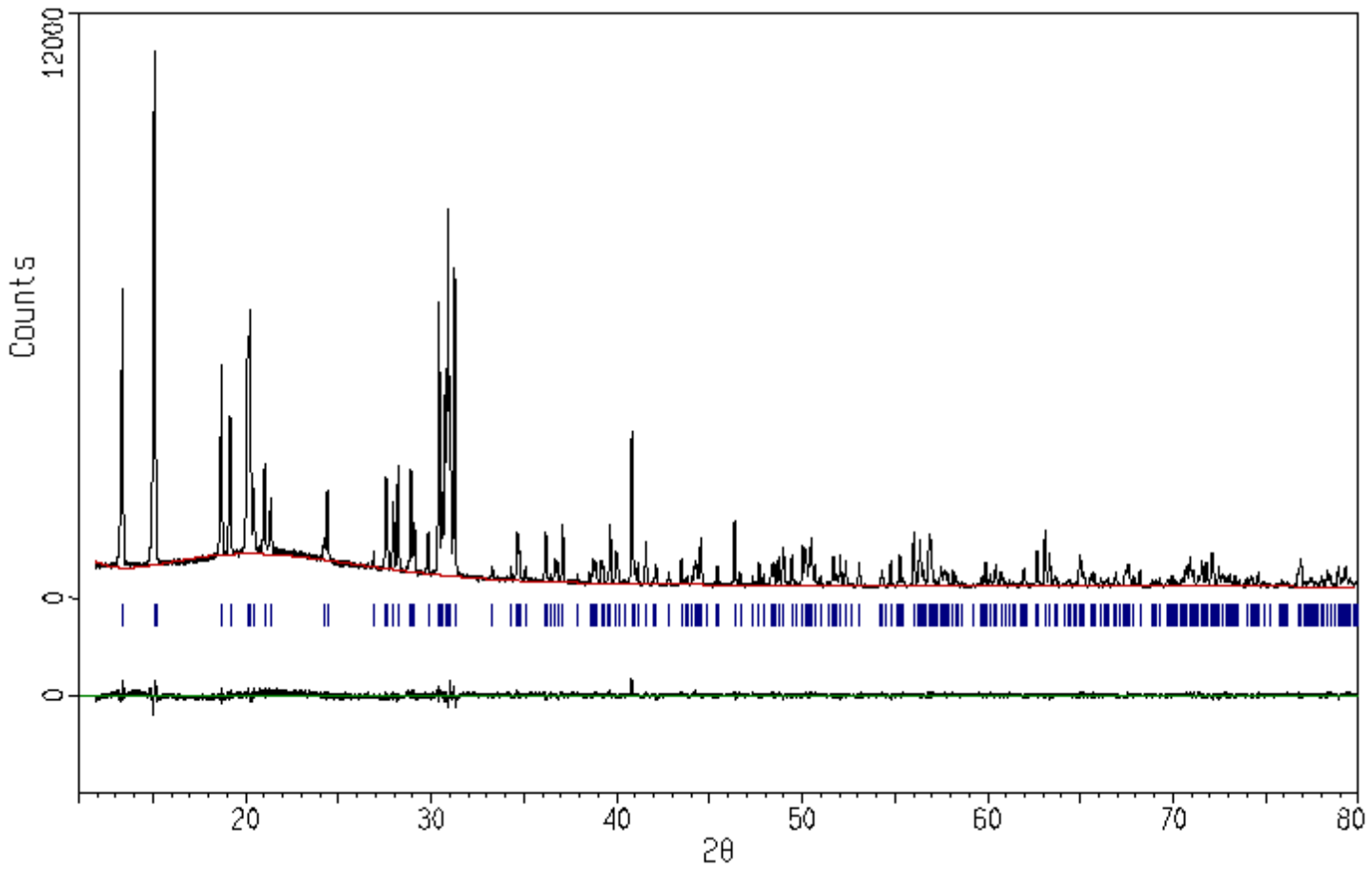
MATERIAL SCIENCES – WHY SYNCHROTRONS?

•High intensity	Good statistics Short exposure - In situ measurements Smaller samples
•High angular resolution	Phase identification, structure refinements, structure solutions
•Variable wavelength	Anomalous dispersion contrast, short wavelengths for environmental cells, avoid fluorescence
•High brilliance	Local probing

RESOLUTION

•Angular resolution	Peak resolution
	$\sin\theta/\lambda$-resolution
•Time resolution	Beam intensity (detector systems)
•Energy resolution	Peak resolution vs. time resolution
•Intensity resolution	Dynamic range
•Spatial resolution	Beam size
	Room for experiments

HIGH DATA QUALITY IN SECONDS

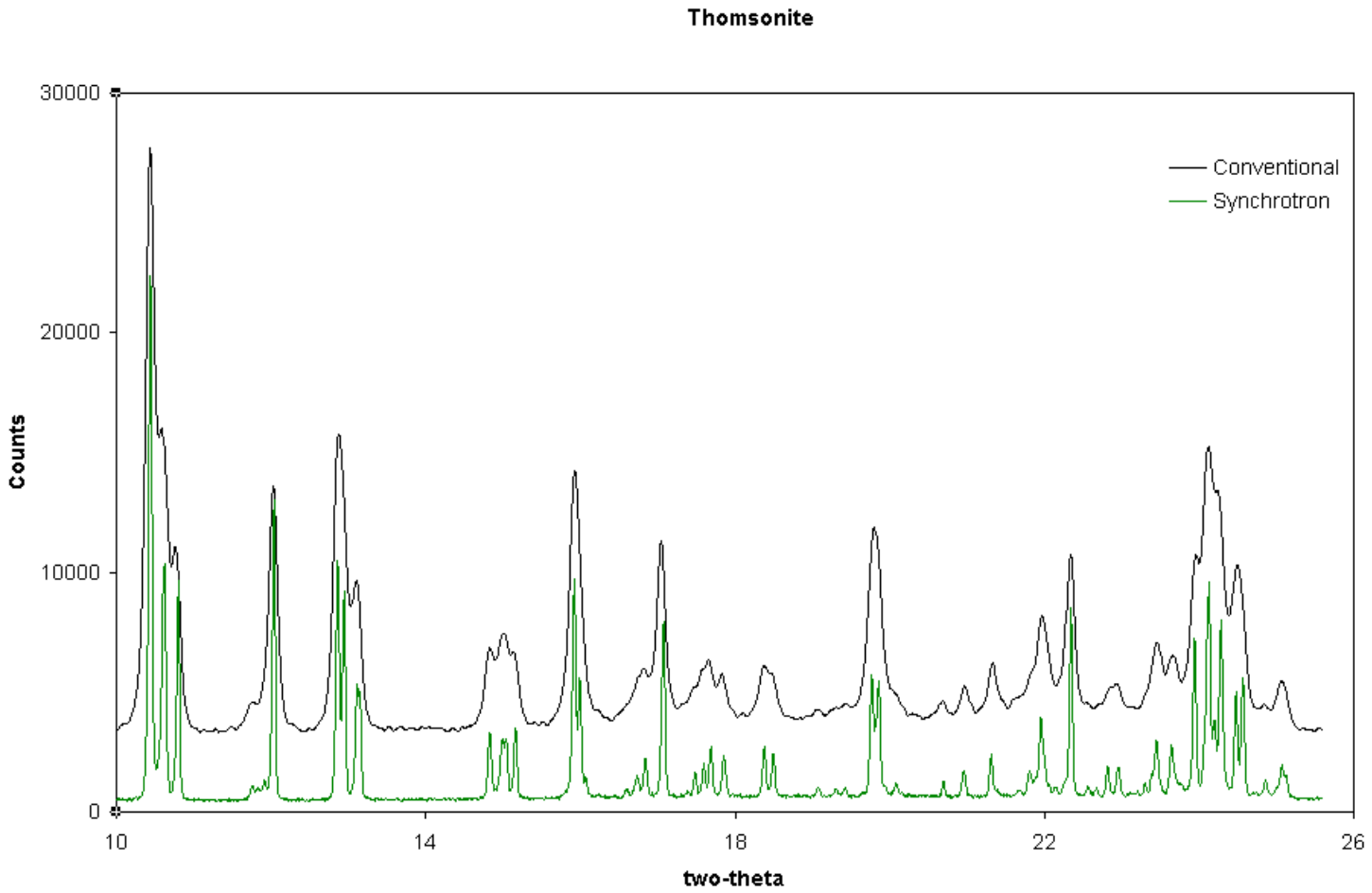


Rietveld refinements on scolecite:

Fd: a = 18.5073(1), b = 18.9780(1), c = 6.52472(4) Å, β = 90.6226(4)°.

19 non-H atoms, 82 parameters, 636 Bragg reflections

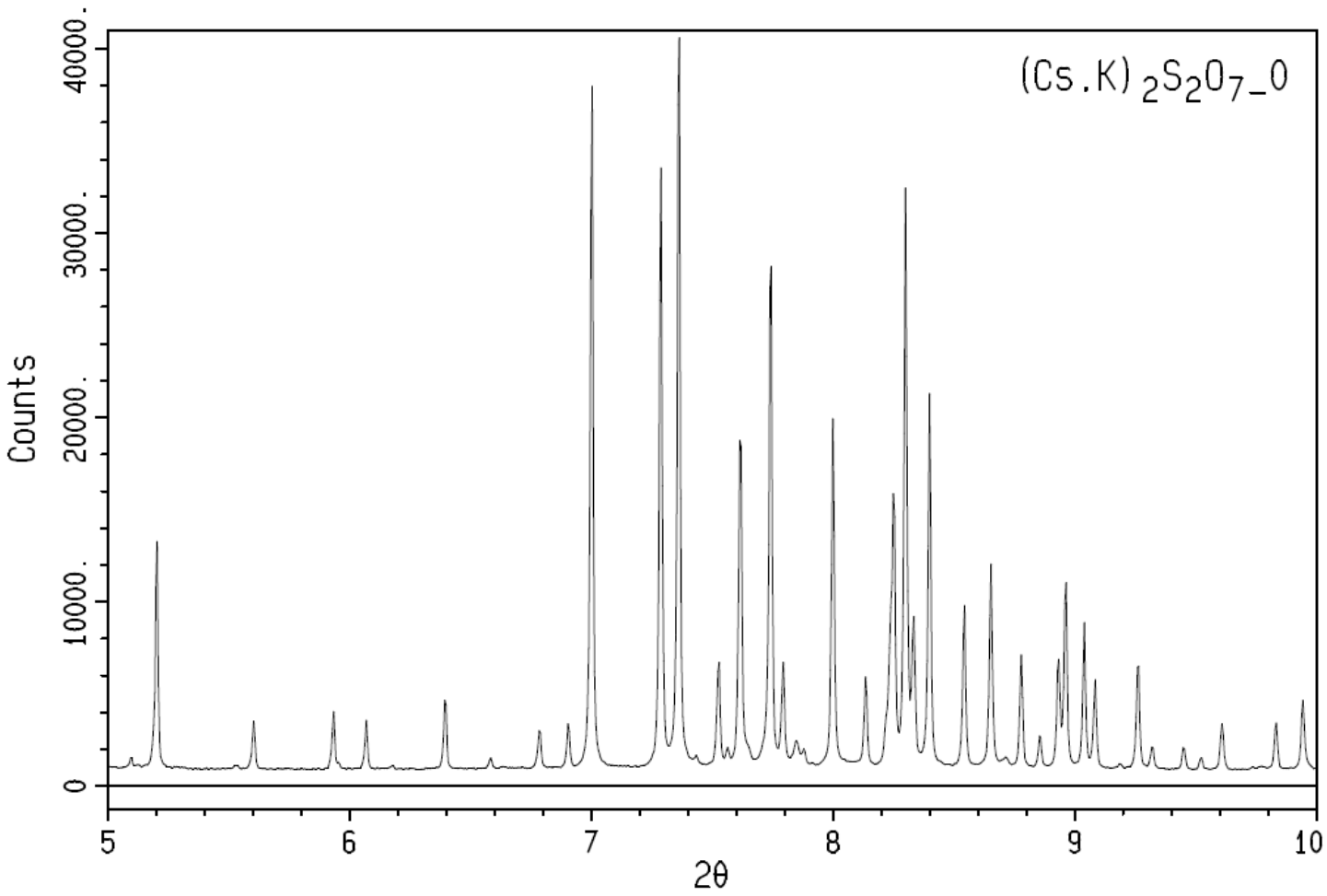
HIGH ANGULAR RESOLUTION



Pn; a=13.1979(3); b=12.7609(3); c=12.9860(3) Å; ∠=90.570(3)°

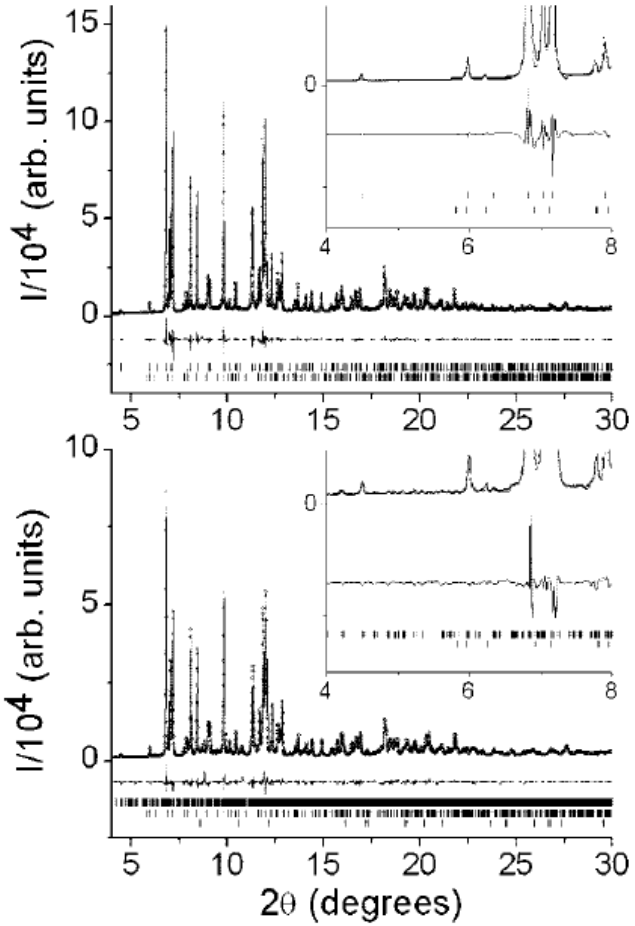
FWHM = 0.04°

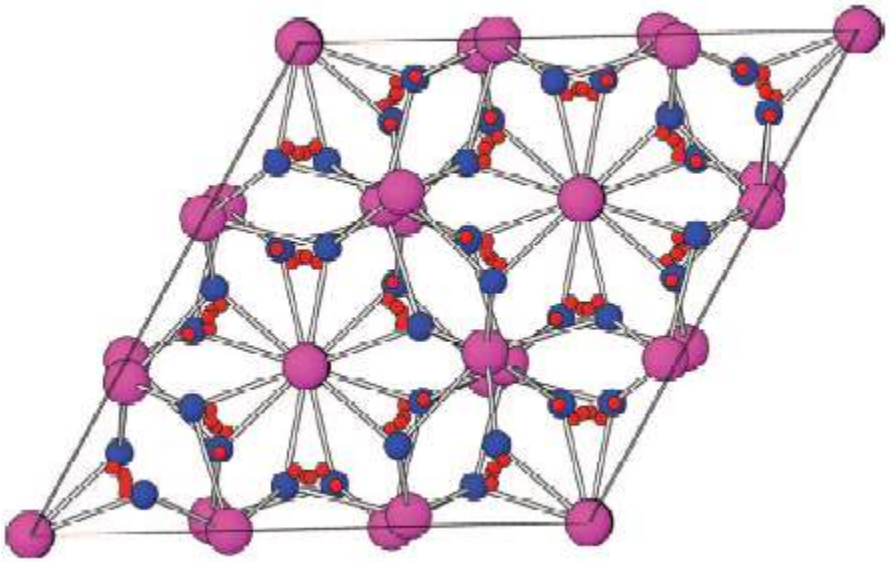
HIGH ANGULAR RESOLUTION



FWHM < 0.01° (ESRF < 0.003°)

THERMOELECTRIC MATERIALS, $Hg_{0.04}Zn_{3.96}Sb_3$



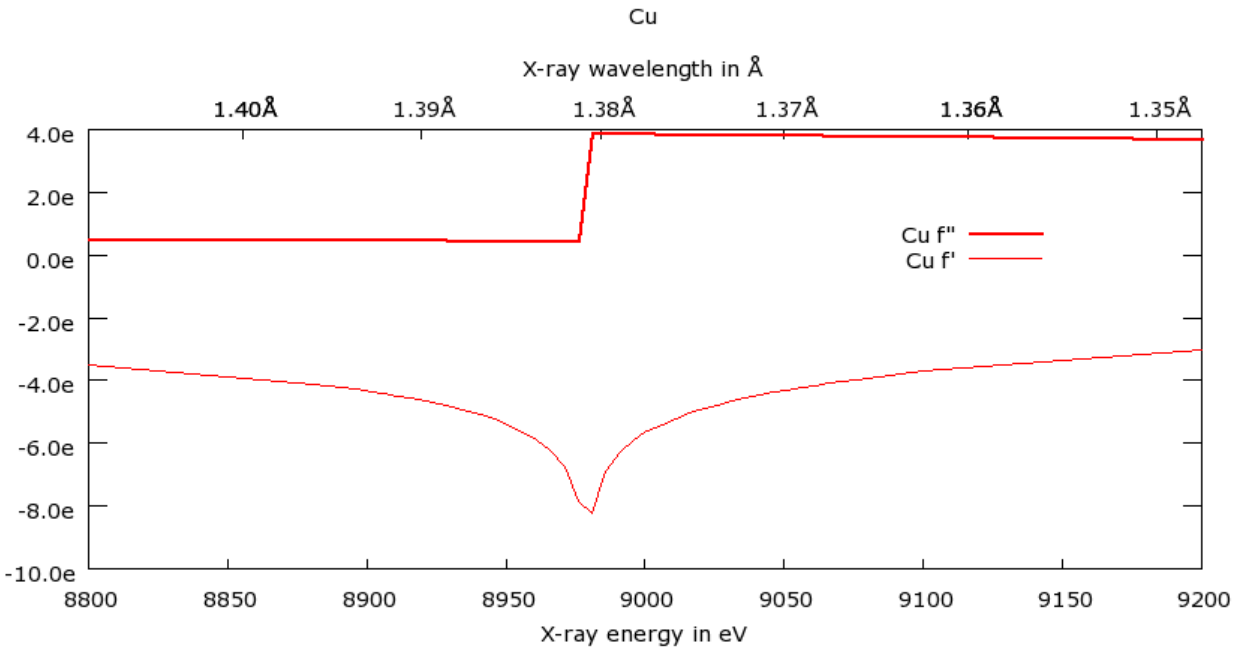


Pedersen et al. Chem. Mater. 2007, 19, 6304-6311.

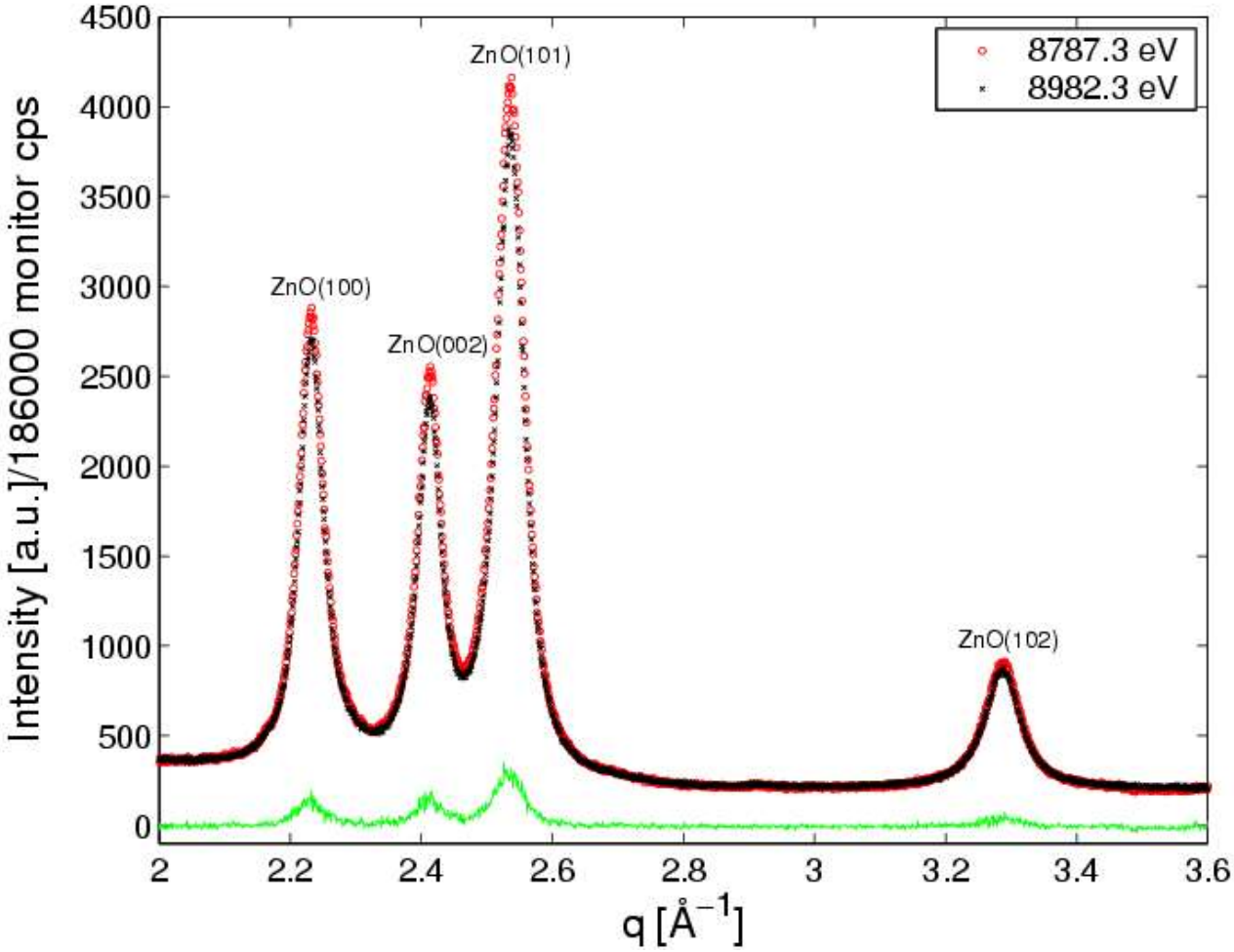
ANOMALOUS DISPERSION CONTRAST

$$f(\omega) = \omega^2 / (\omega^2 - \omega_s^2 - ik\omega)$$

$$f_\lambda(h,j) = f(h,j) + f'_\lambda(j) + if''_\lambda(j)$$

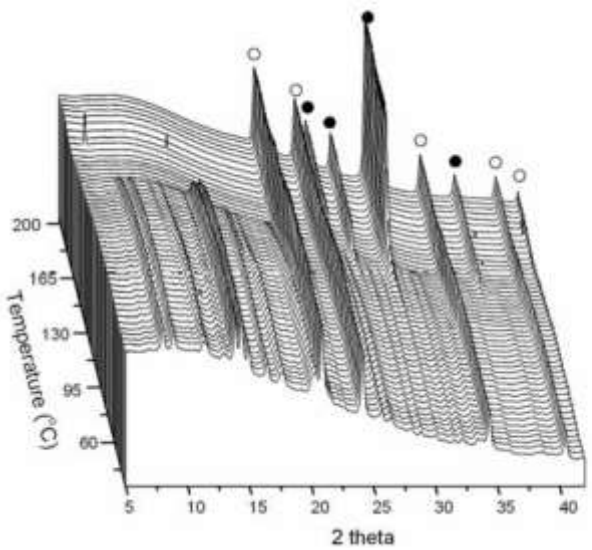


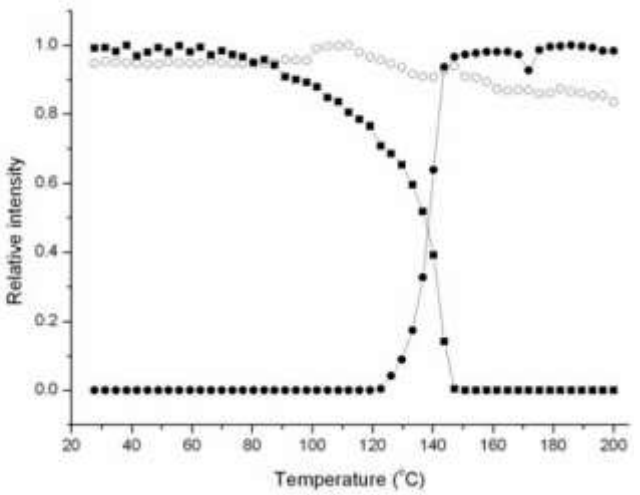
CuO/ZnO CATALYST FOR METHANOL SYNTHESIS

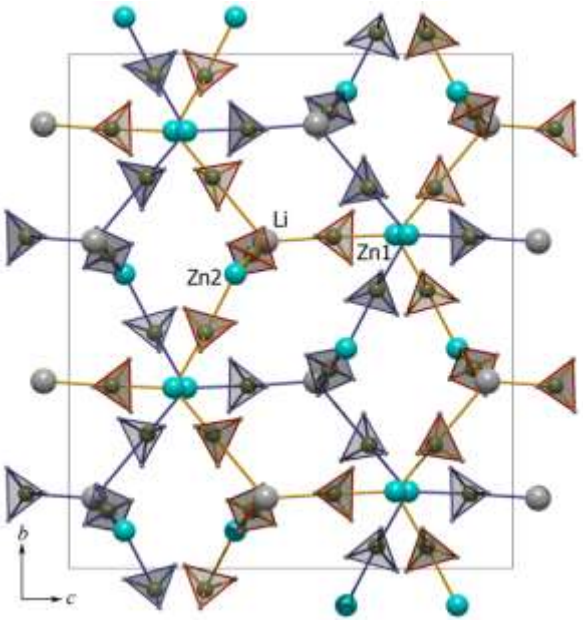


Andreasen et al. J. Appl. Cryst. 2006, 39, 209-221.

$LiZn_2(BH_4)_5$ NETWORK STRUCTURE







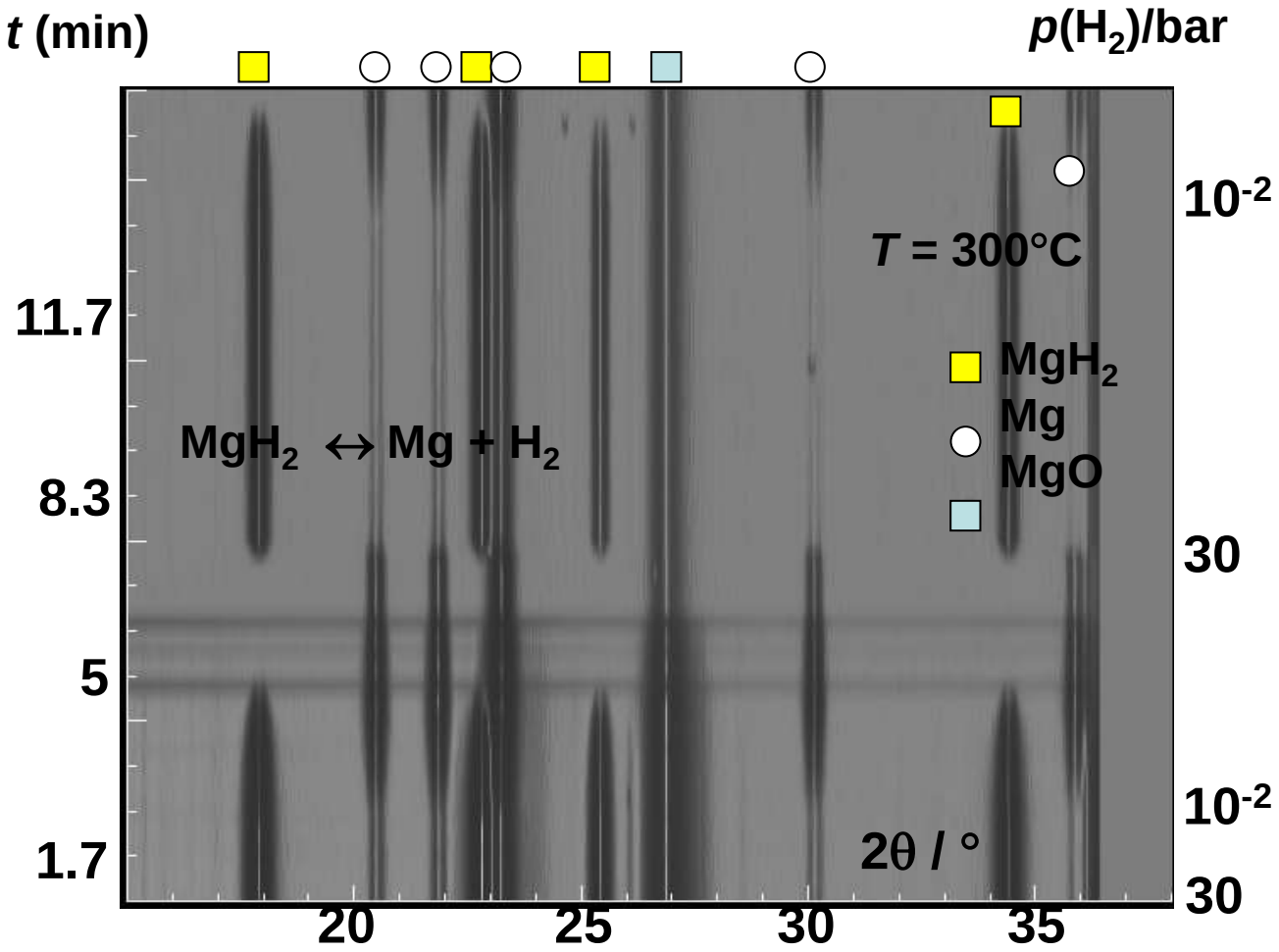
$$LiZn_2(BH_4)_5 \rightarrow 2Zn(BH_4)_2 + LiBH_4$$

$$Zn(BH_4)_2 \rightarrow Zn + B_2H_6 + H_2$$

$$2LiBH_4 + Li_2ZnCl_4 \rightarrow Zn + B_2H_6 + 2LiCl$$

Jensen et al. Angew. Chem. 2009, 48, 6659.

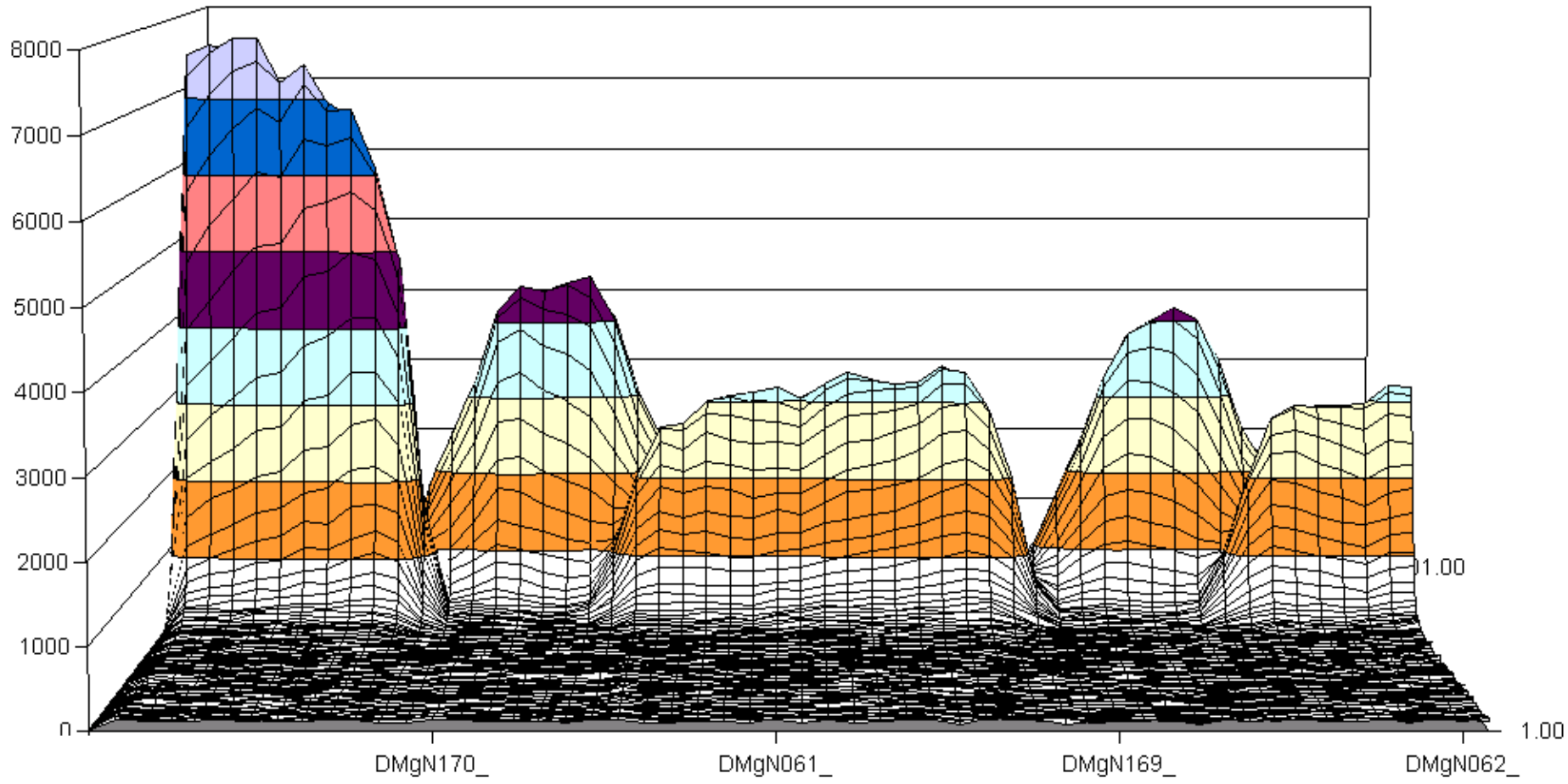
VERY QUICK H-CYCLING



MgH_2 + 4 mol% Nb_2O_5

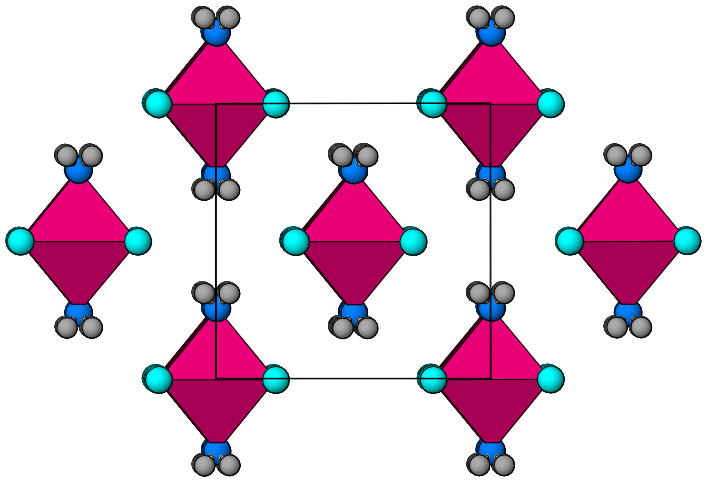
Kollin & Jensen To be published.

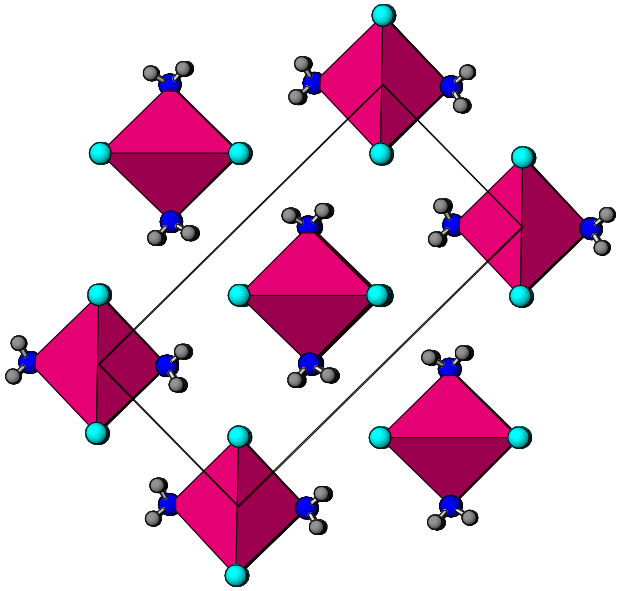
$$Mg(NH_3)_6Cl_2 \leftrightarrow Mg(NH_3)_2Cl_2 + 4NH_3$$



Jacobsen et al. Chem. Phys. Lett. 2007, 441, 255-260.

$Mg(NH_3)_2Cl_2$





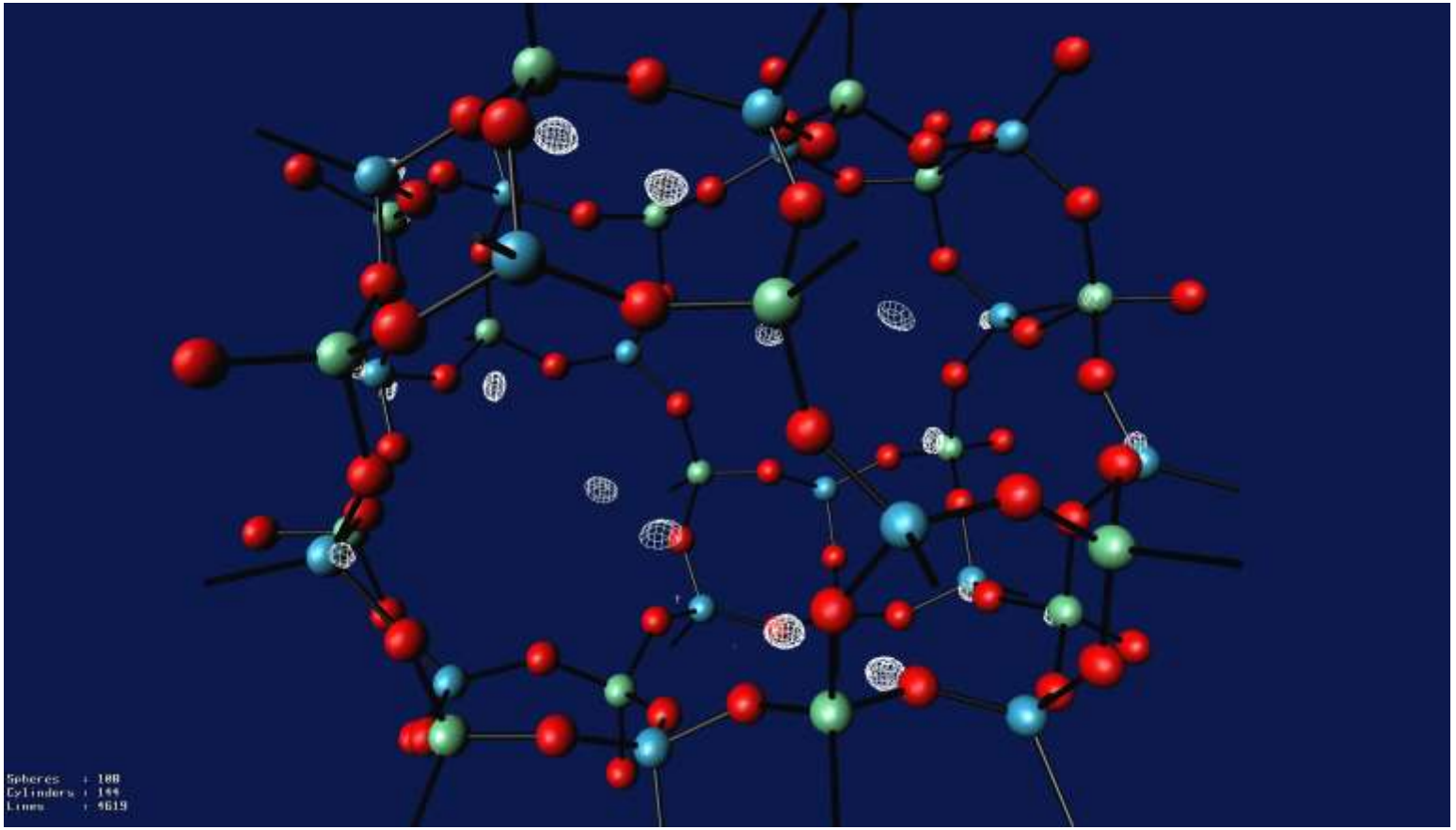
Cmmm $\rho = 1.68$ g/cm^3

Pbam $\rho = 1.82$ g/cm^3

Sørensen et al. To be published.

SAPO-34 METHANOL-TO-OLEFIN CONVERSION

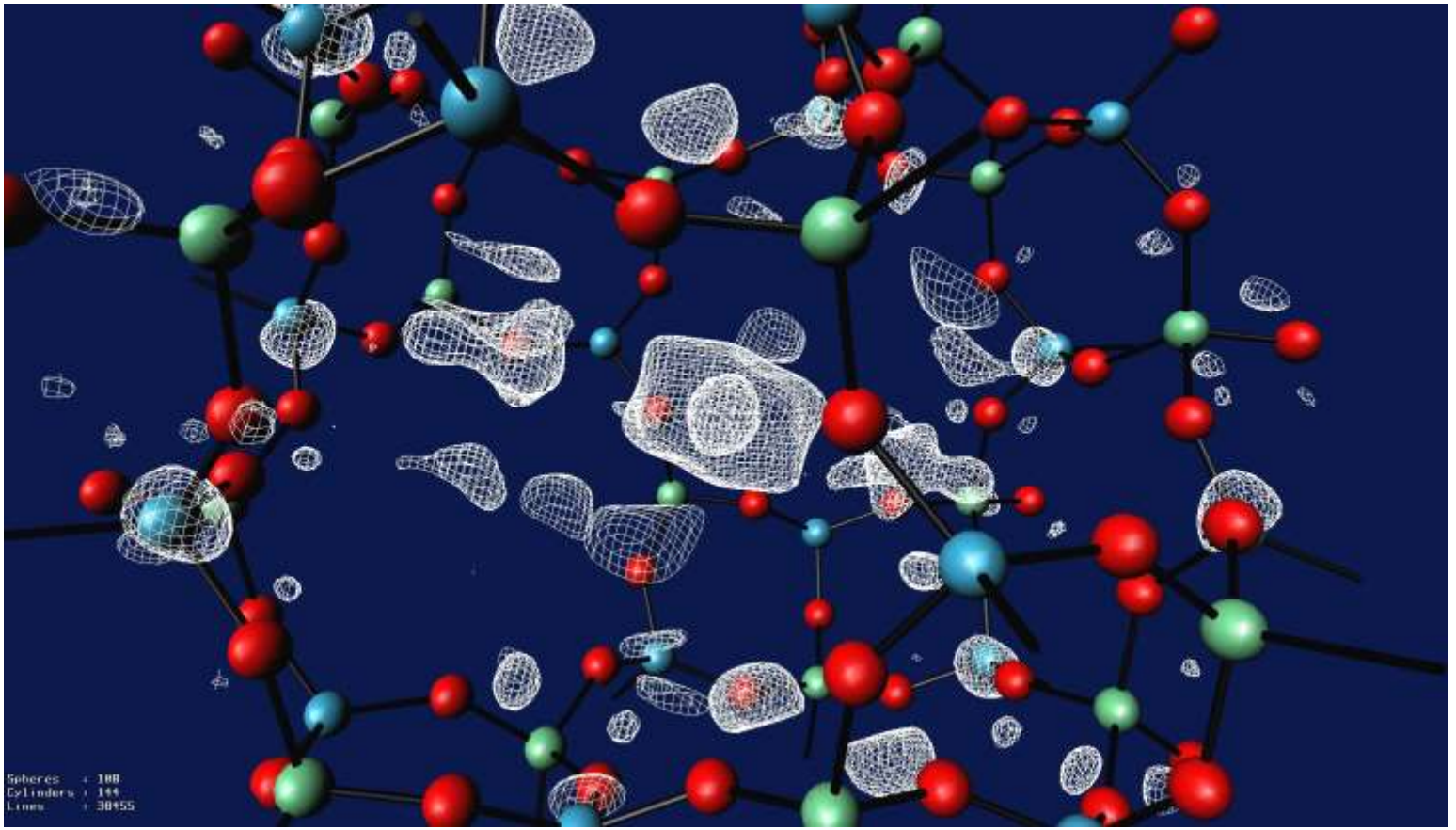
t = 0 min



Wragg et al. J. Catal. 2009, 268, 290-296.

SAPO-34 METHANOL-TO-OLEFIN CONVERSION

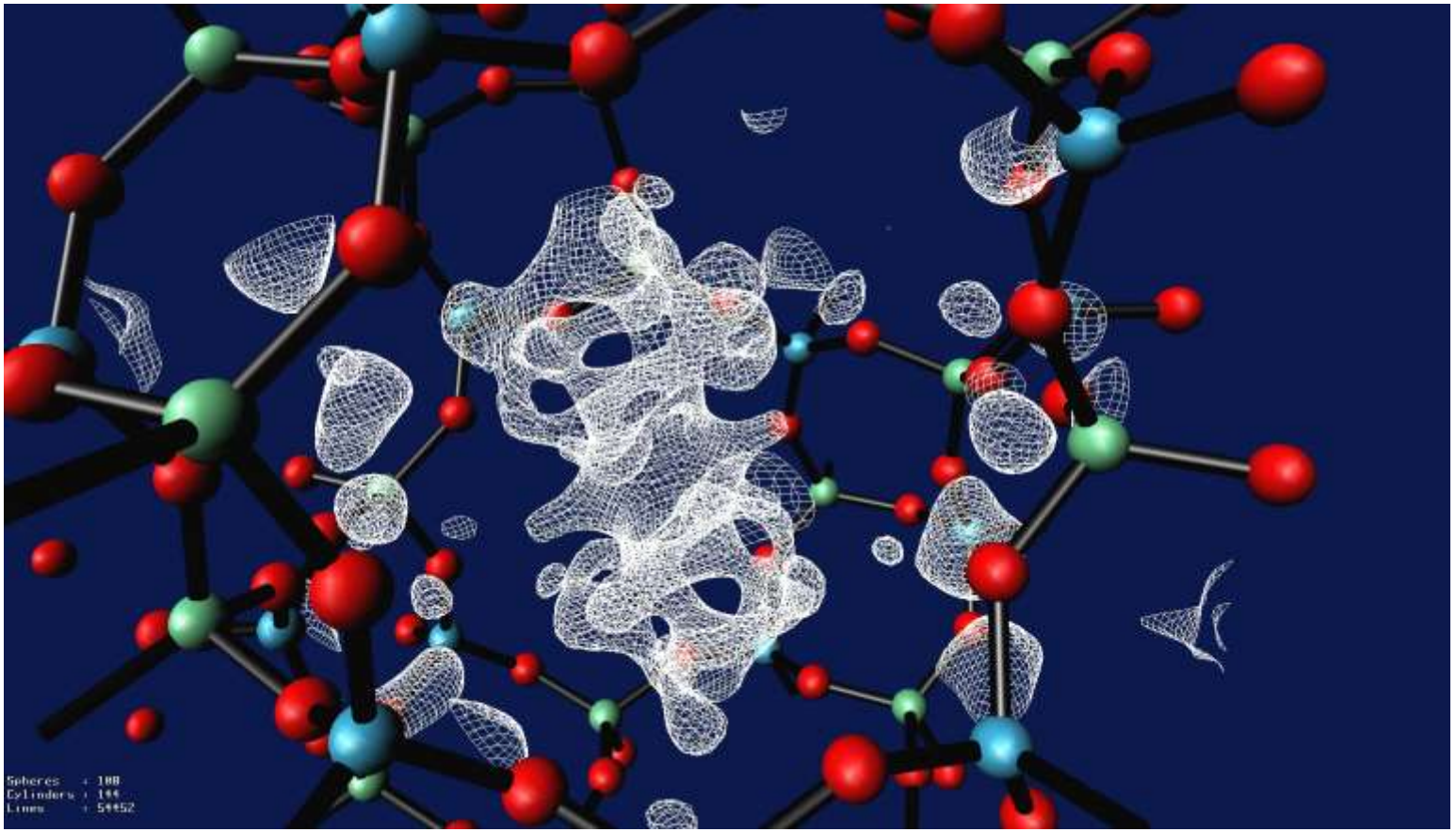
t = 3 min



Wragg et al. J. Catal. 2009, 268, 290-296.

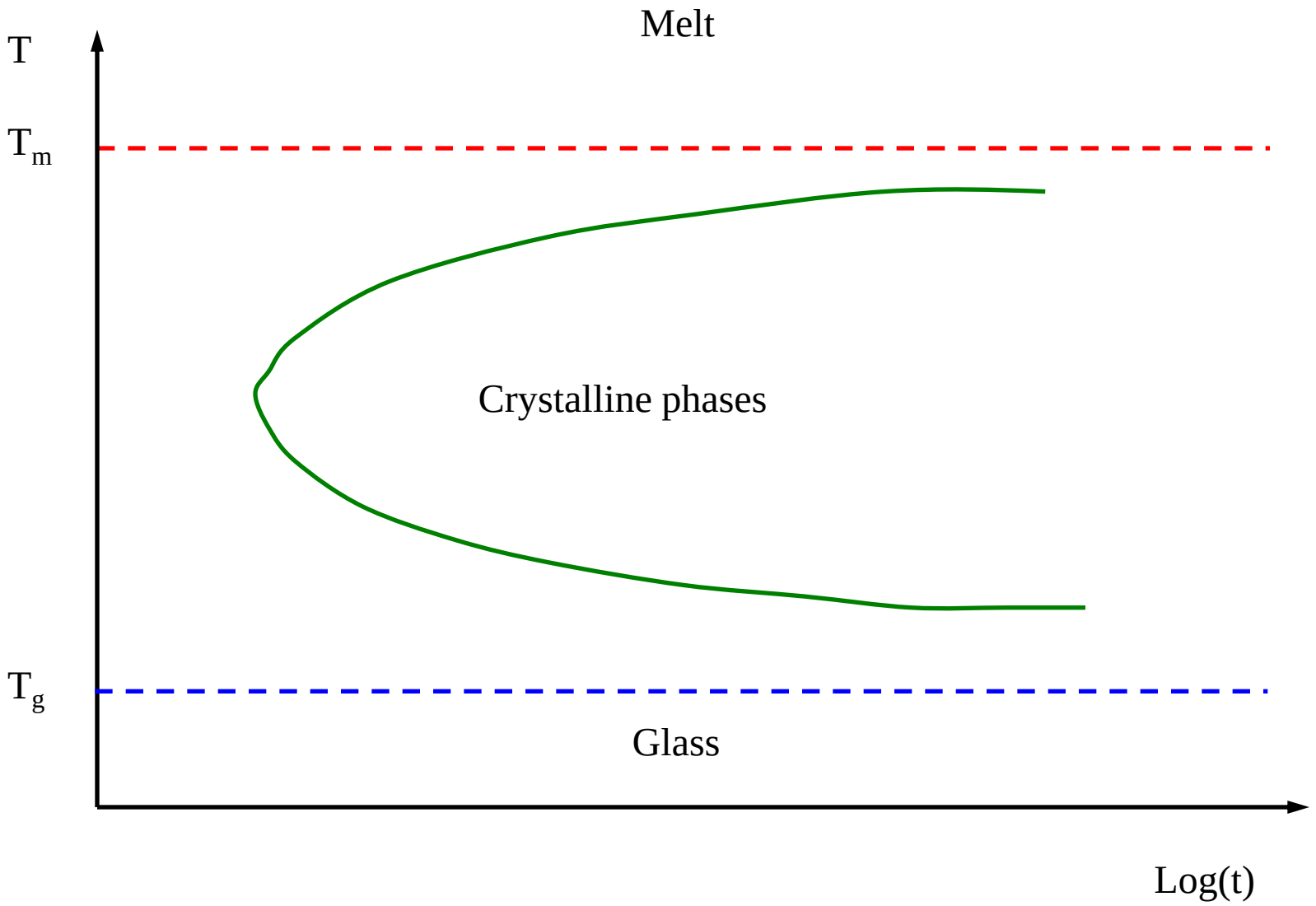
SAPO-34 METHANOL-TO-OLEFIN CONVERSION

t = 180 min

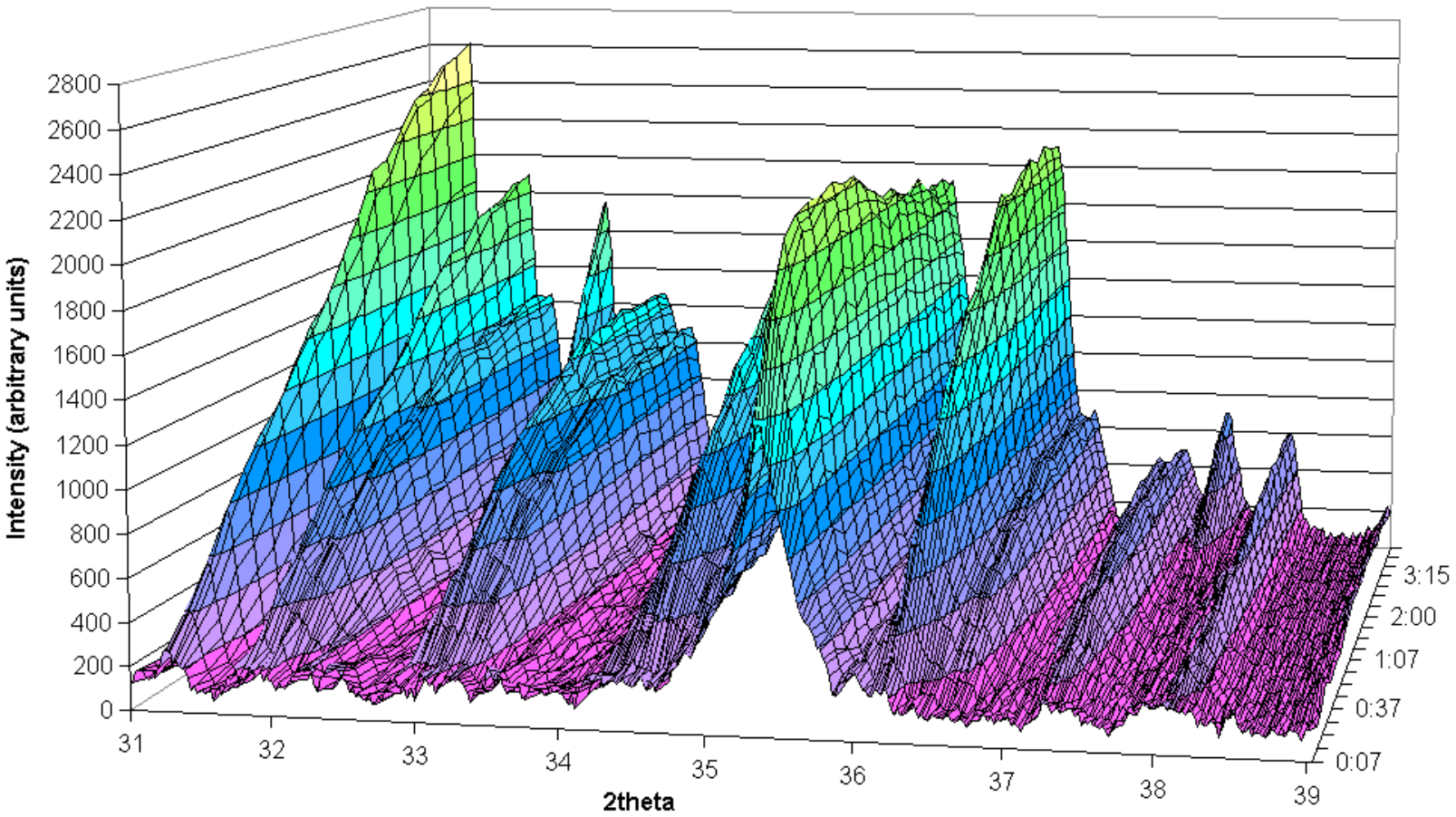


Wragg et al. J. Catal. 2009, 268, 290-296.

CRYSTALLIZATION

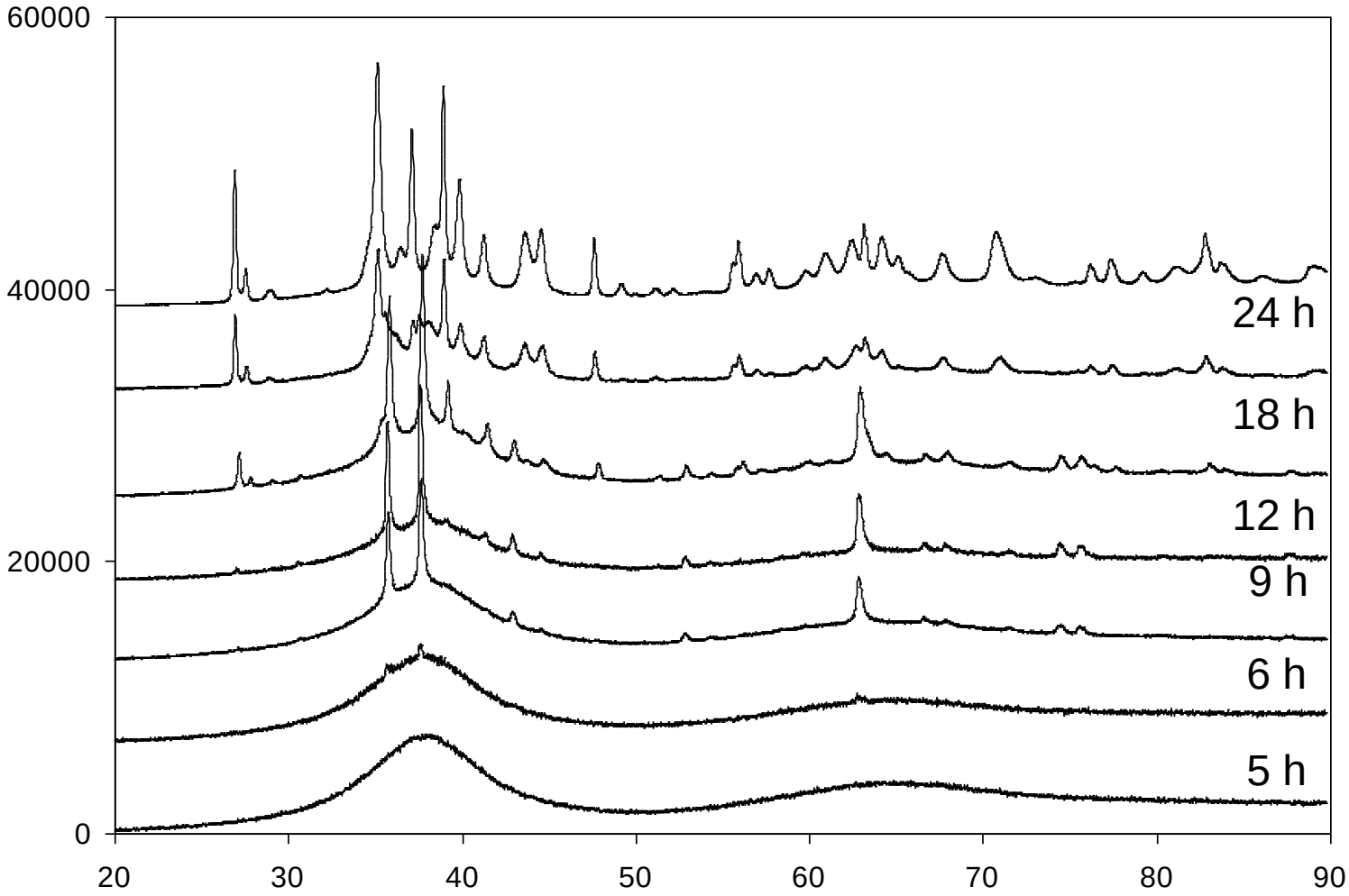


MINERAL WOOL



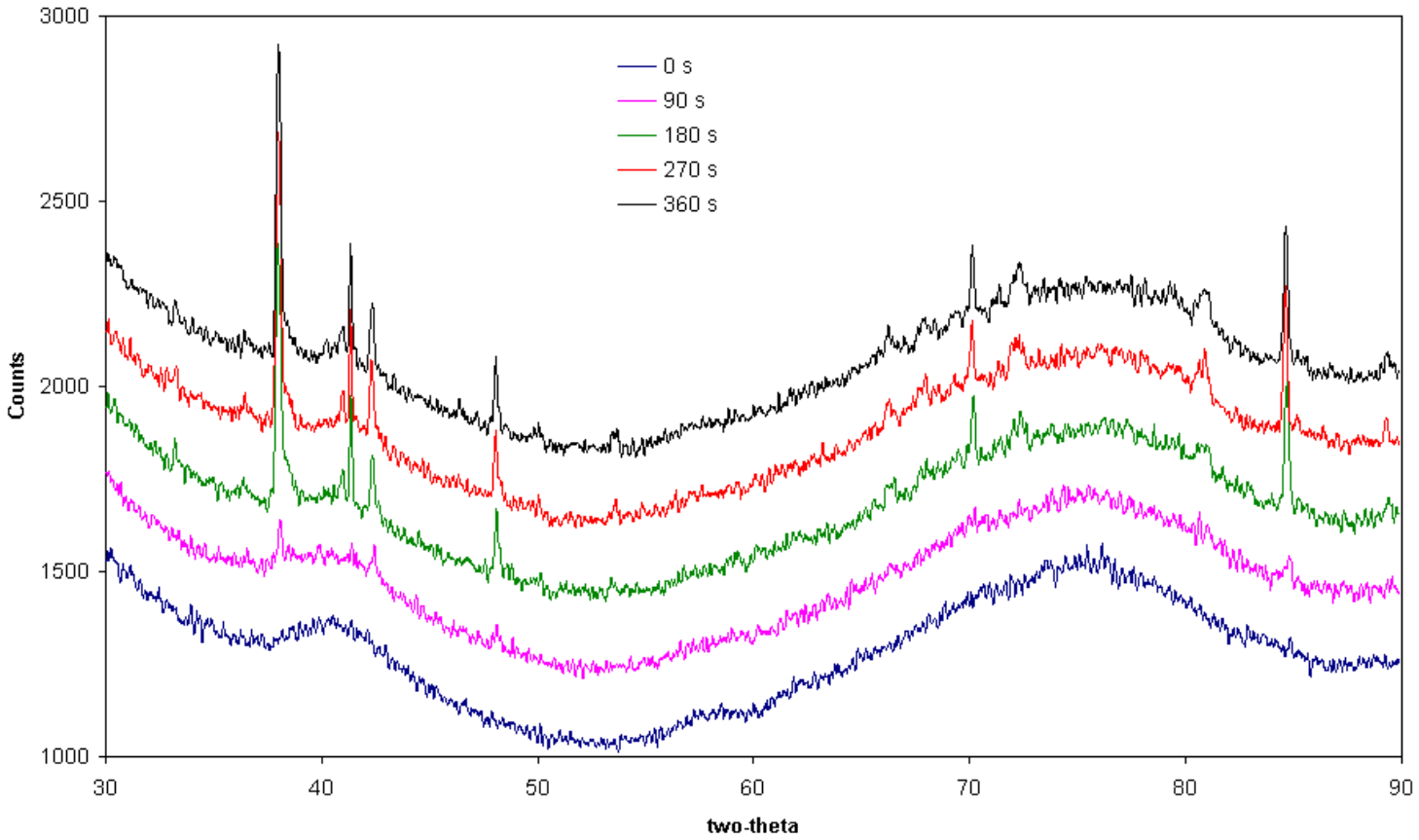
Nielsen et al. Mat. Science For. 558-559 (2007) 1255-1260.

BULK METALLIC GLASSES



$Zr_{46.8}Ti_{8.2}Cu_{7.5}Ni_{10}Be_{27.5}$ 643 K

BULK METALLIC GLASSES

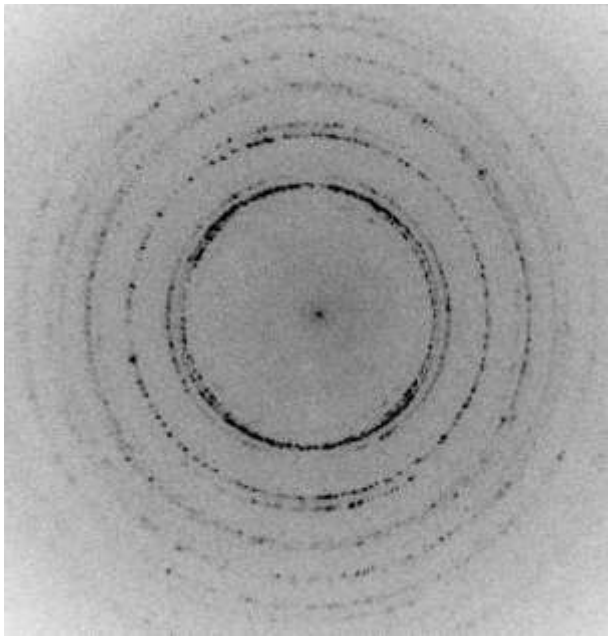


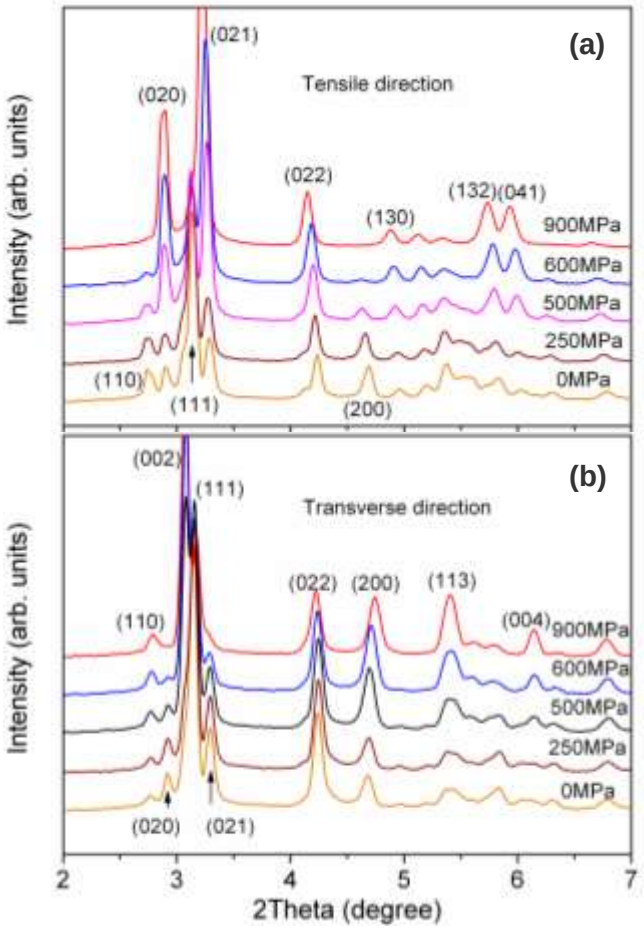
Pd-based

Jiang et al. To be published

SUPER-ELASTIC MATERIALS

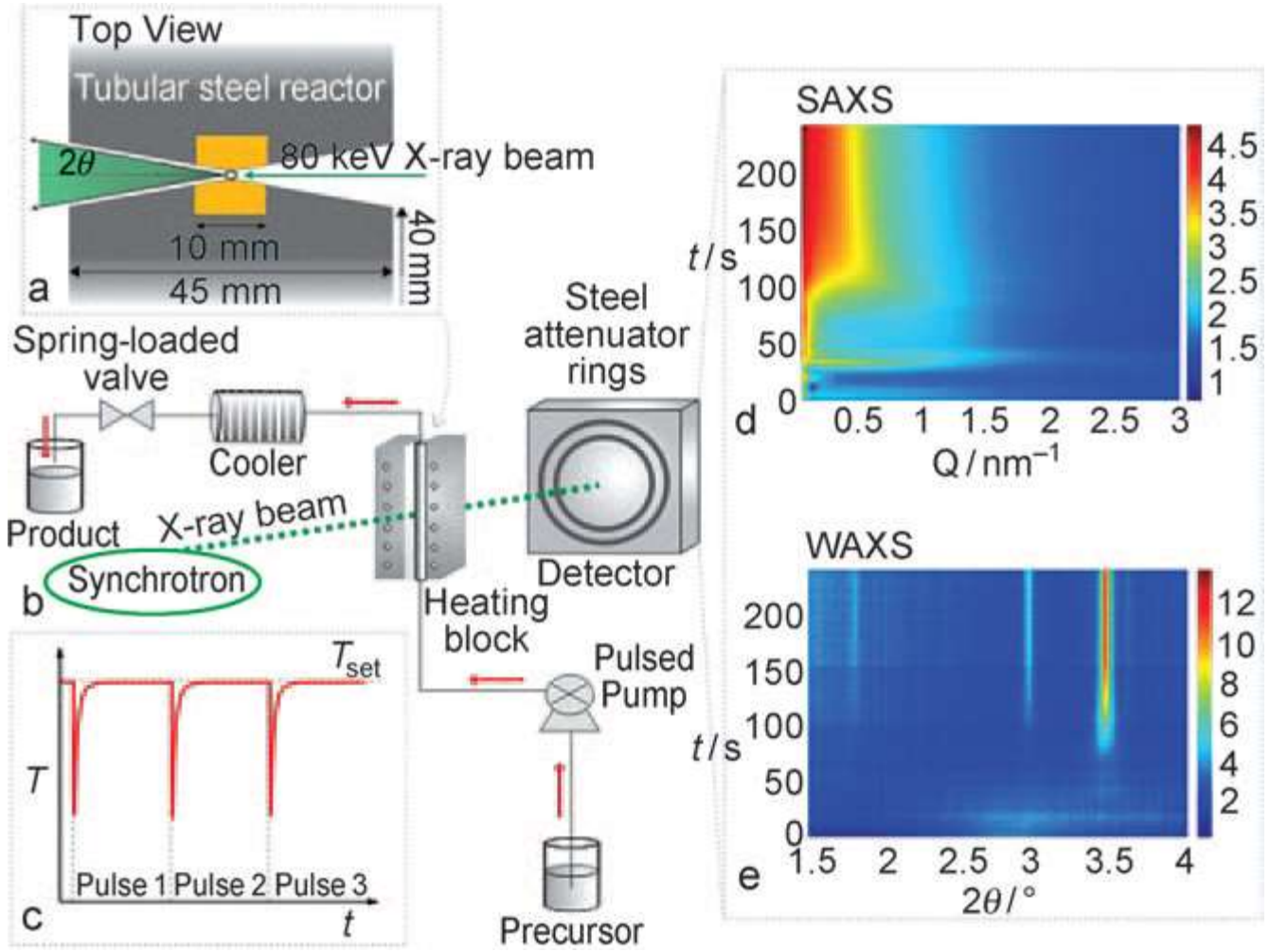
Ti-11%Zr-14%Nb-10%Sn





Wang et al. Mat. Sci. Eng. A, 527 (2010) 6596-6600.

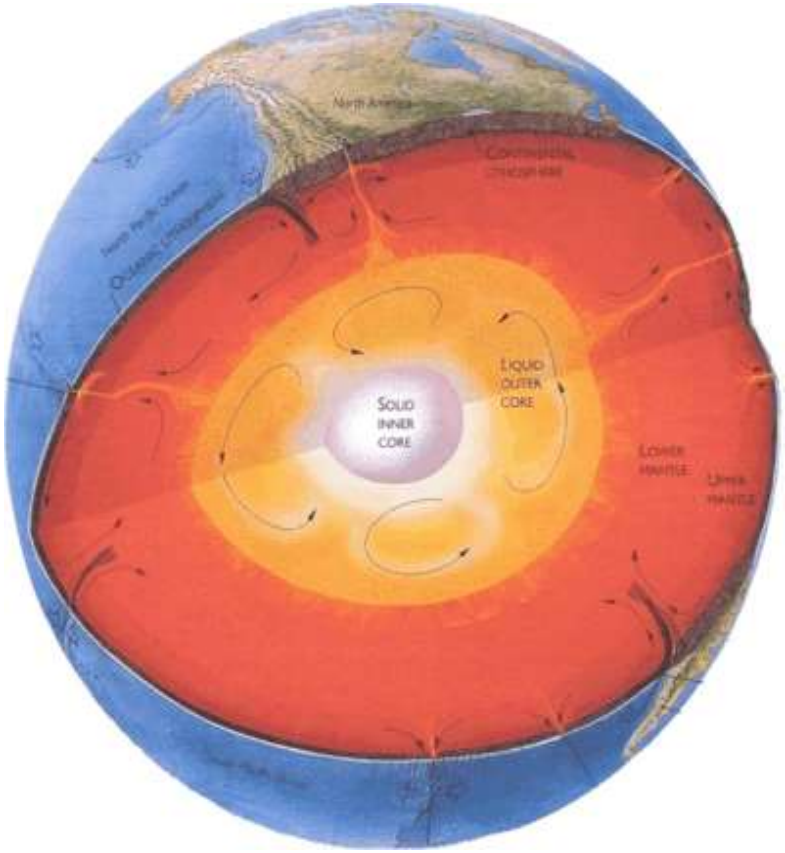
MAGNETITE NANOPARTICLES IN SUPERCRITICAL WATER



Bremholm et al. Angew. Chem. 2009, 121, 4882-4885

HIGH PRESSURE CRYSTALLOGRAPHY

1 atm = 1 bar = 100 kPa, 10 kbar = 1 GPa 100 GPa = 1 Megabar



LVP: 0 – ~100 GPa
DAC: 0- ~550 GPa

10^{-8} **Atmosphere at 300 miles**

10^{-6} **Radiation P at Sun**

10^{-4} **Sound at threshold of pain**

10^{-2} **Water vapor at triple point**

1 **Sea level pressure**

10^{2} **Deepest ocean**

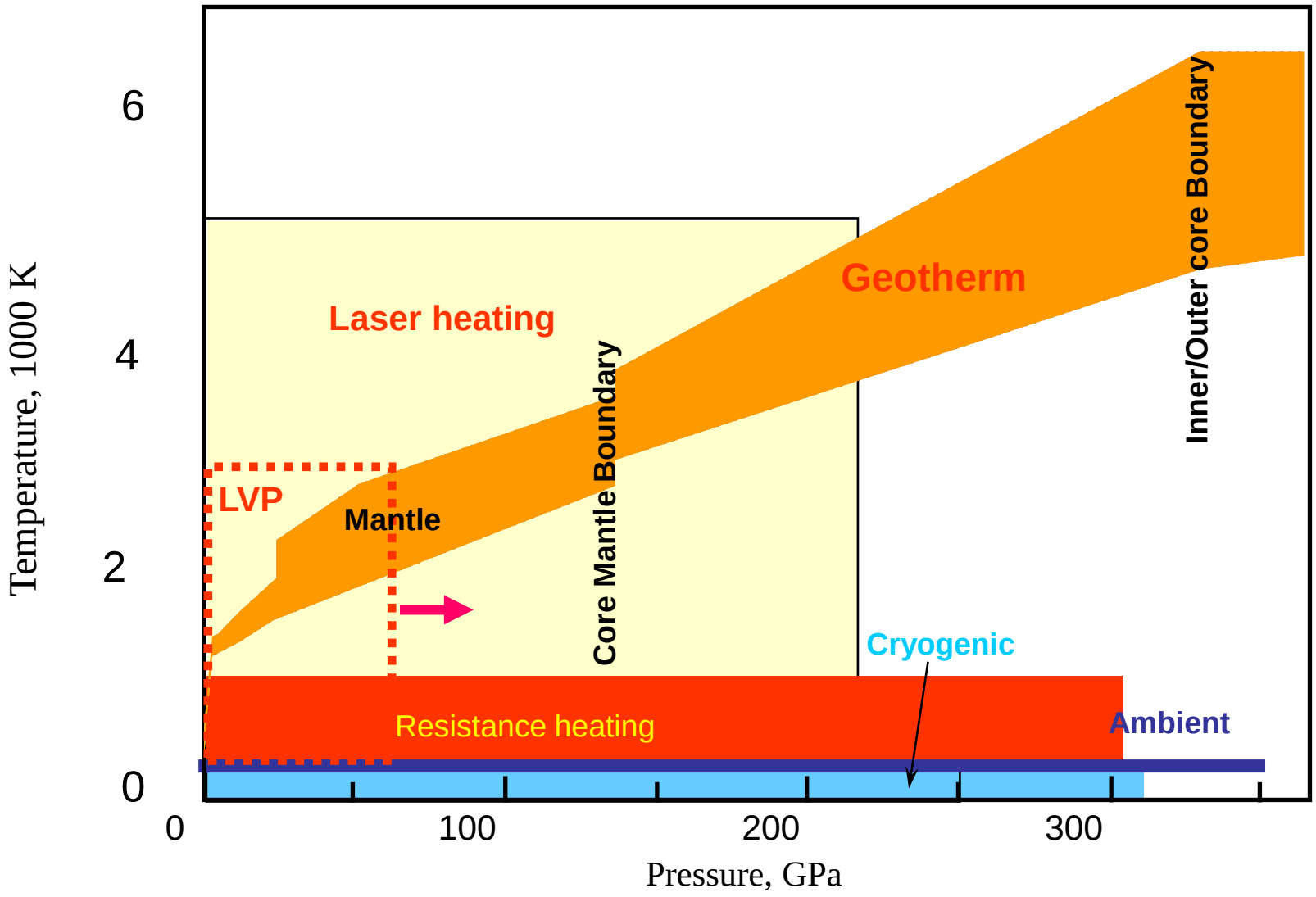
10^{4}

10^{6} **Center of the Earth (~350 GPa)**

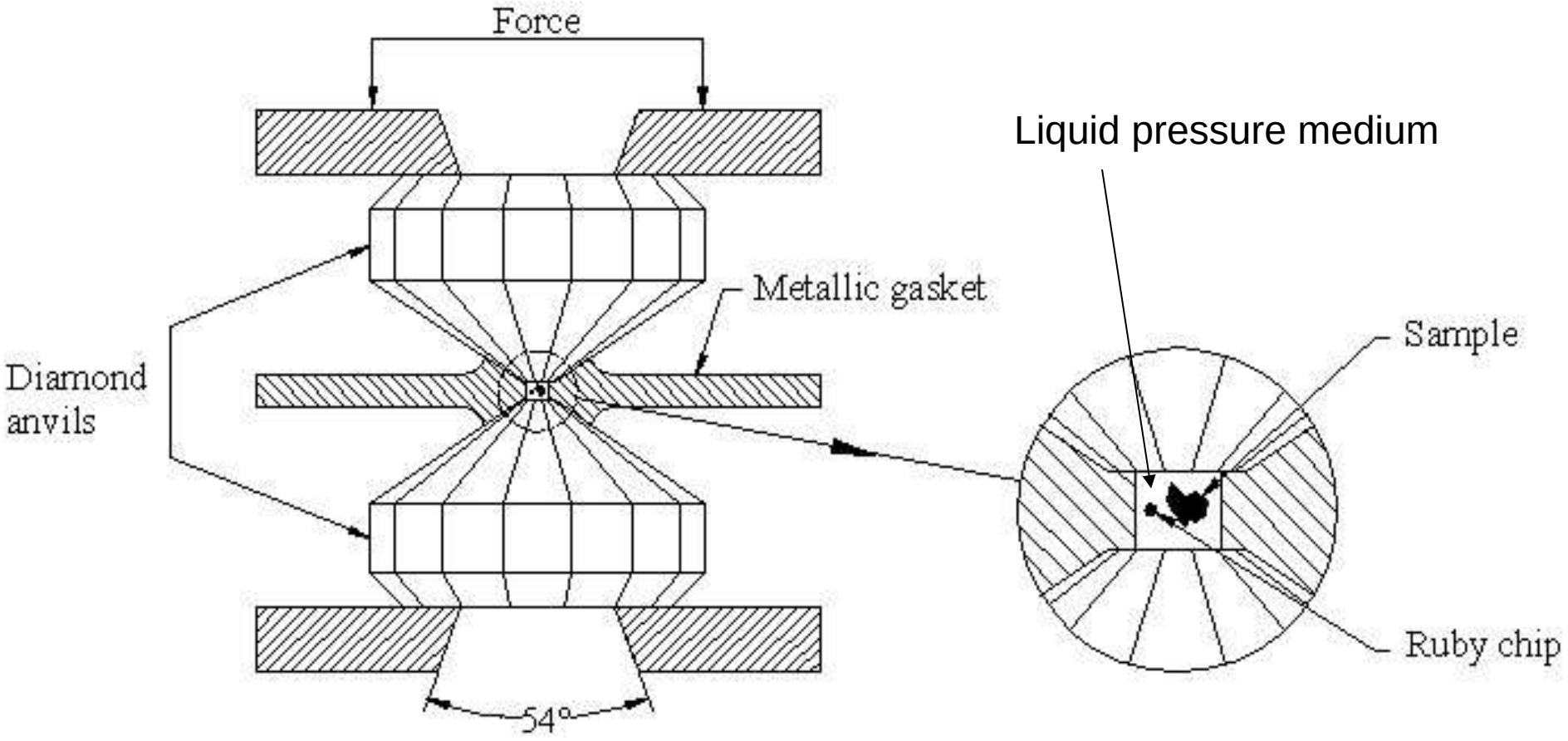
10^{8} **Metallic hydrogen**

Pressure, bars

HIGH PRESSURE CRYSTALLOGRAPHY

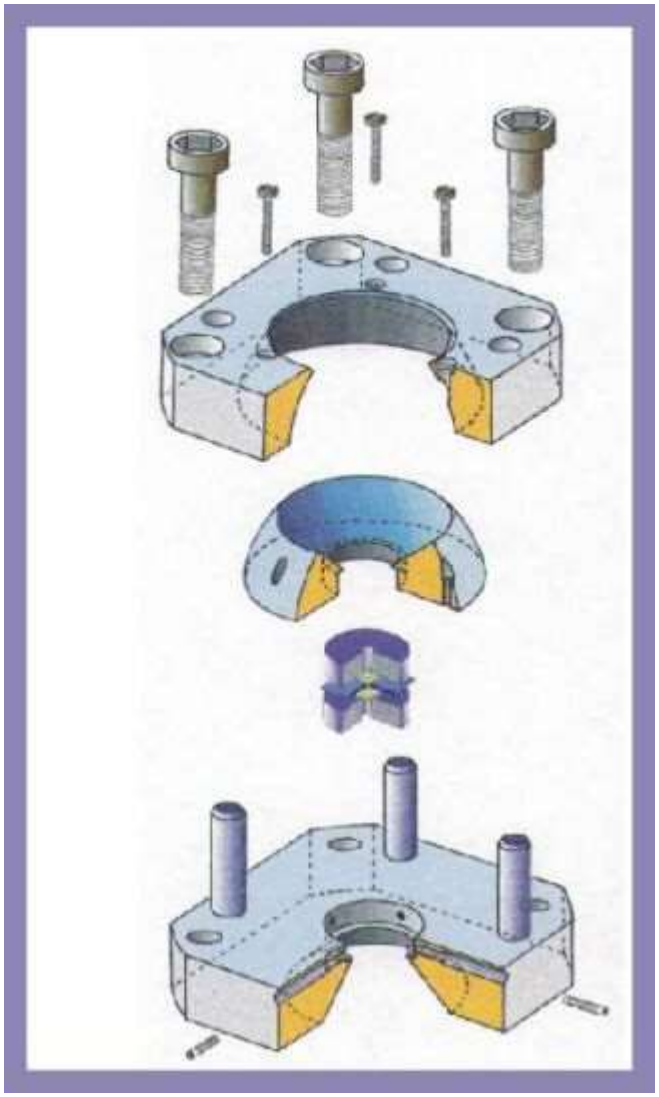


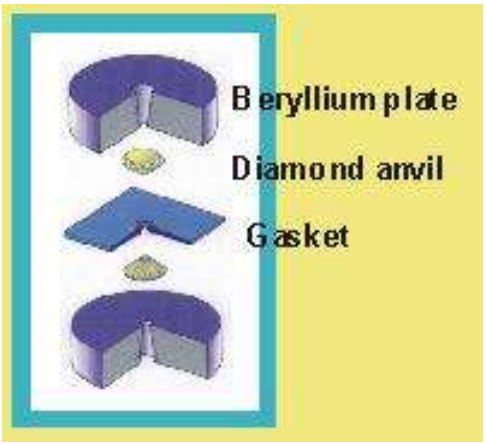
DAC – DIAMOND ANVIL CELL



Principle of the HP DAC (useful apertures now increased to about 90°)

DAC – DIAMOND ANVIL CELL





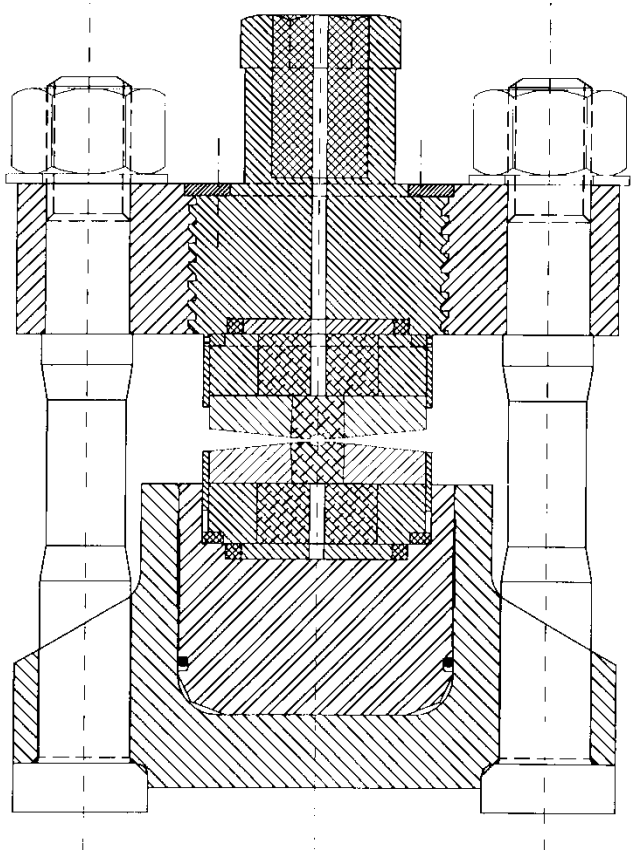
PRESSURE MEASUREMENT

- Ruby is an optical pressure marker
- Ruby at zero pressure wavelength = 694.041nm

$$P = 380.8\left[\left(\frac{\lambda}{\lambda_0}\right)^5 - 1\right] GPa$$

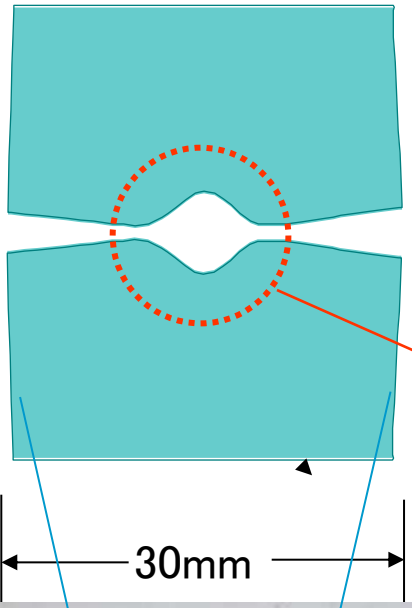
HK Mao, J Xu, and PM Bell, J. Geophys. Res. 91, 4673 (1986)

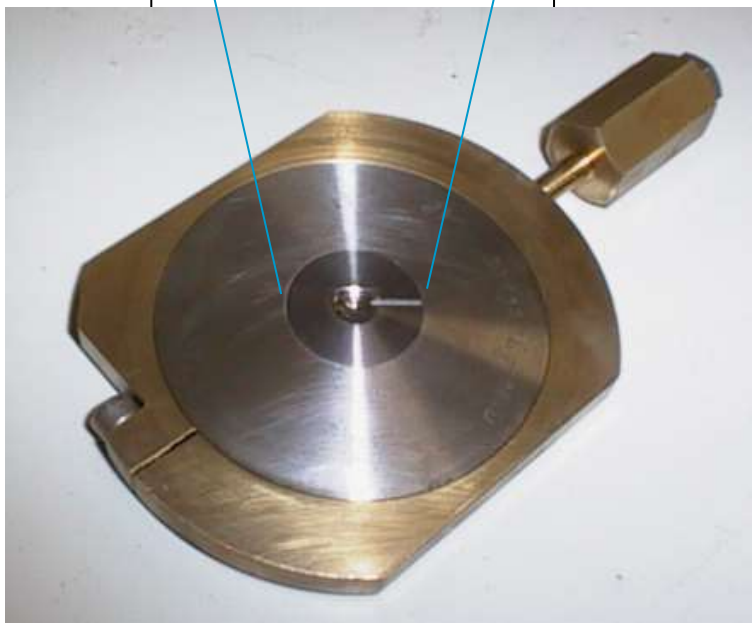
PARIS EDINBURG CELL



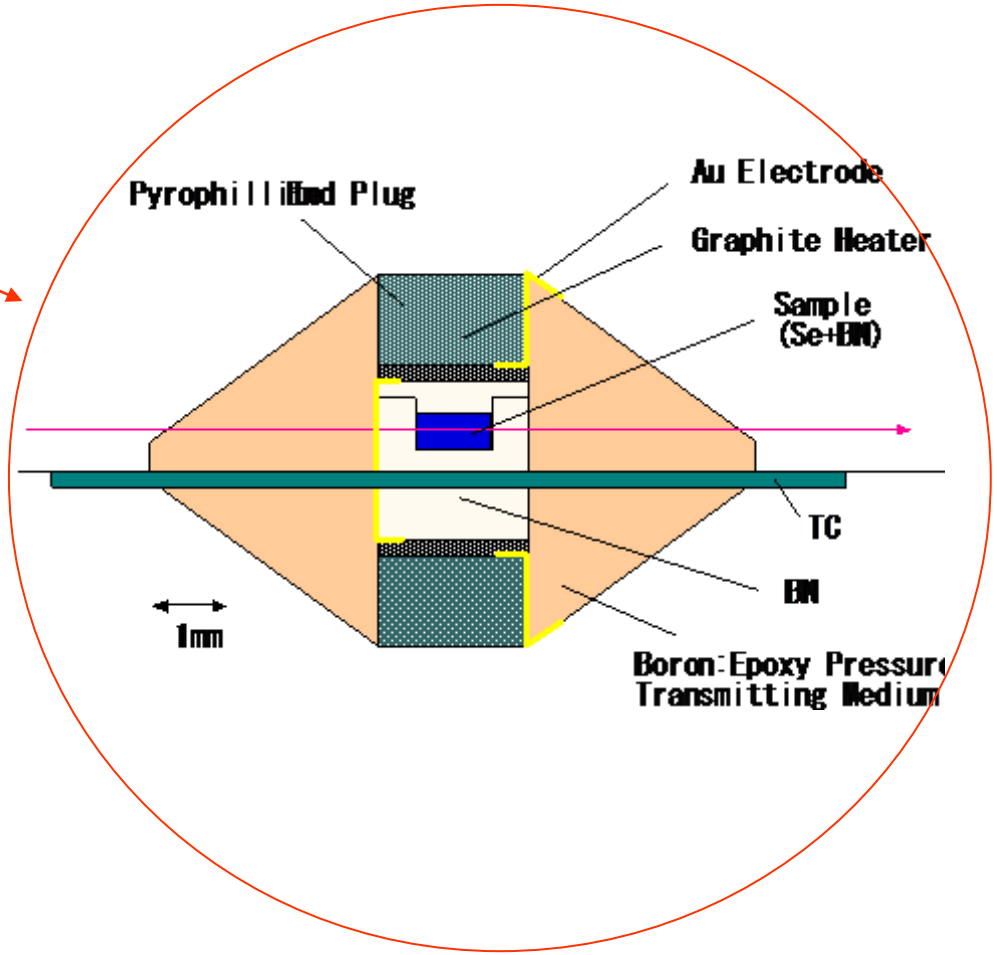
Compact: 160mm×160mm×210mm
Lightweight: 30 kg

PARIS EDINBURG CELL

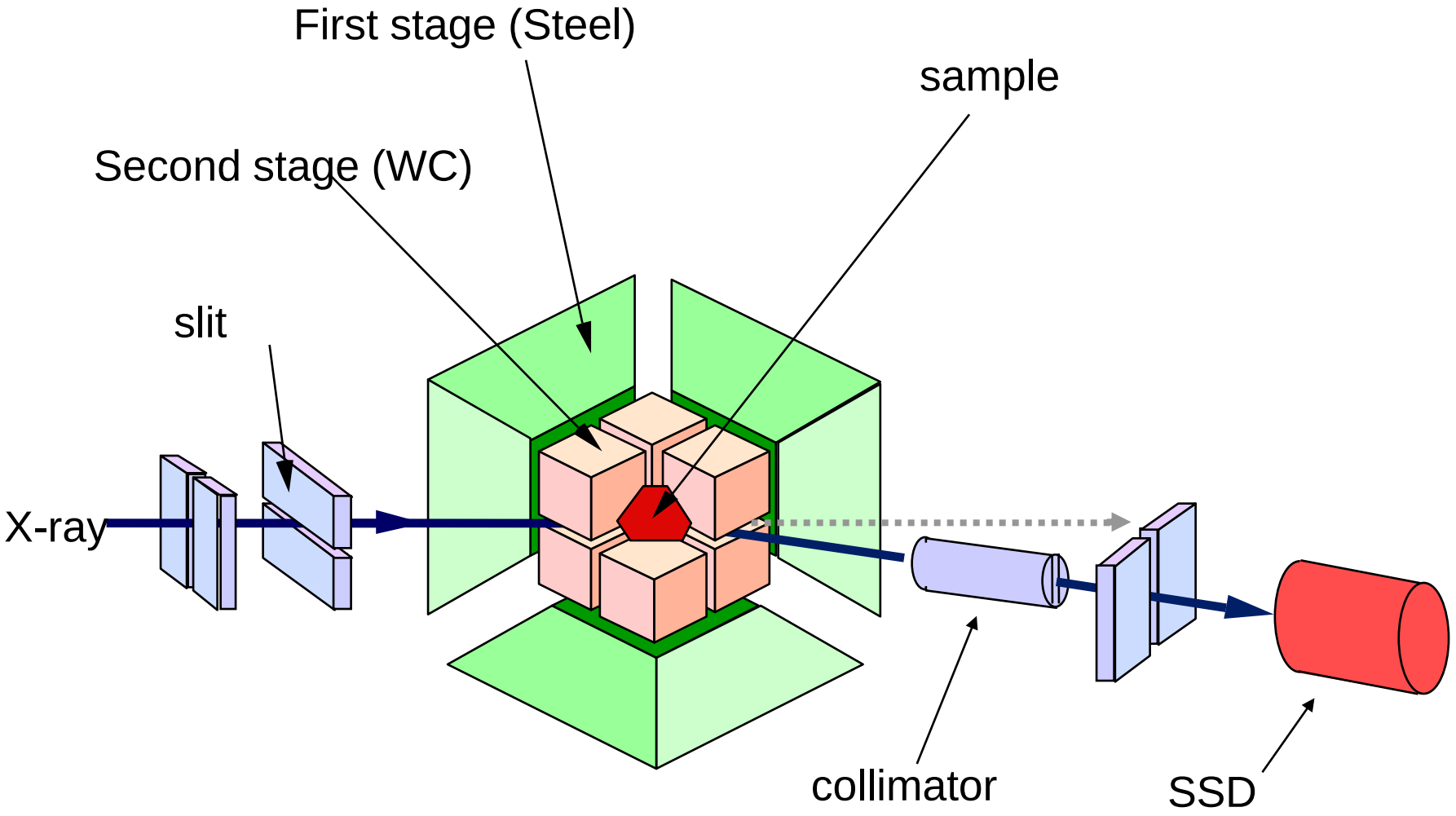




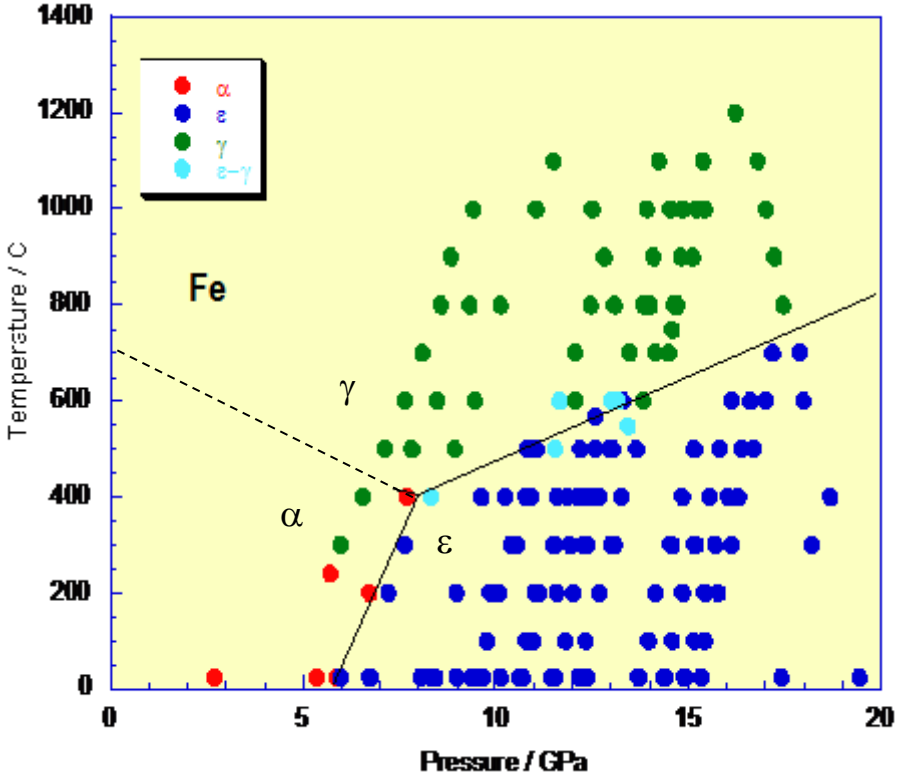
Cell assembly for P-E cell

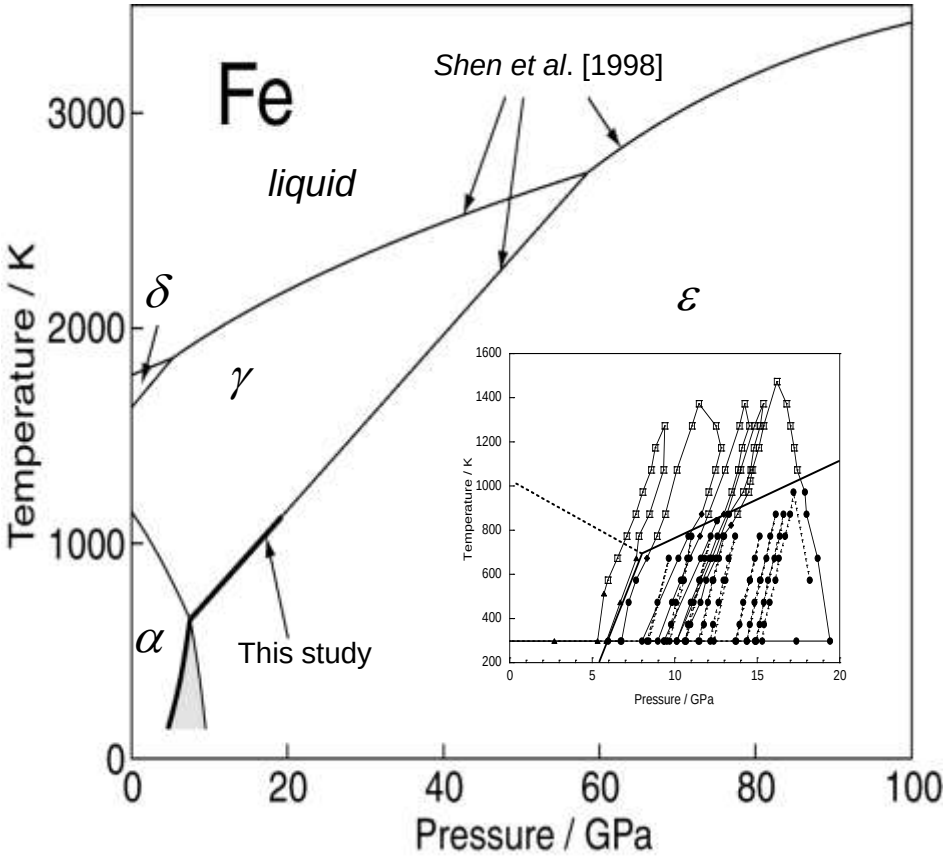


DOUBLE ANVIL CELL

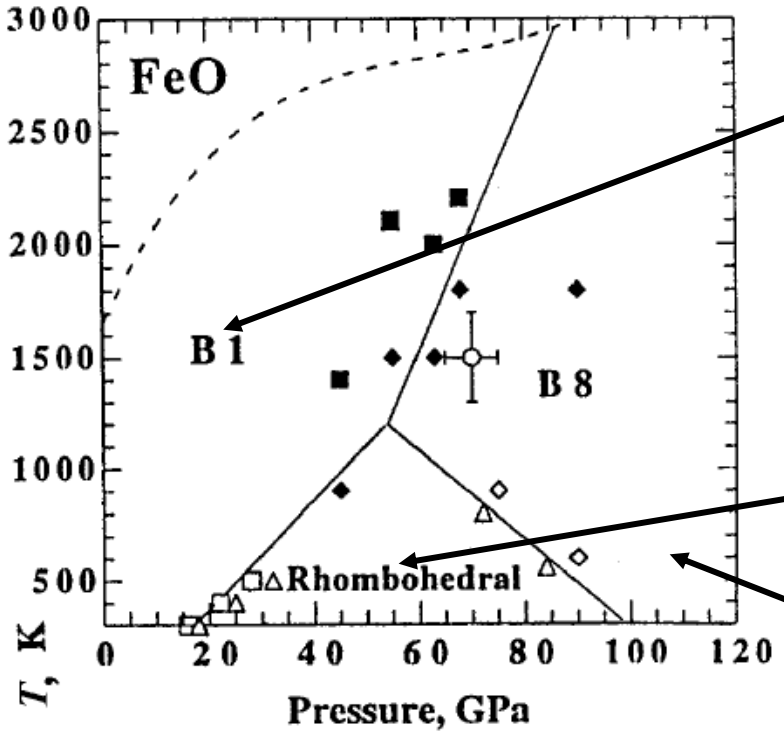


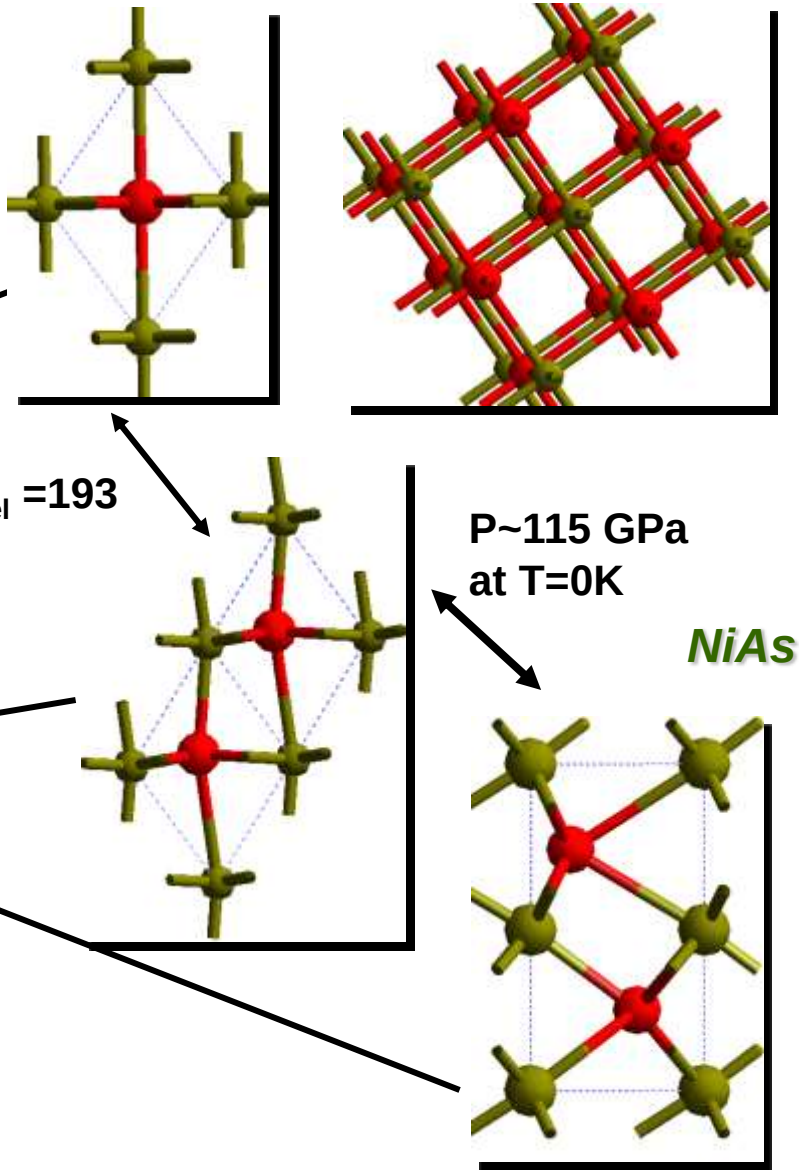
IRON


α
ε
γ
ε–γ
Fe
γ
α
ε
Temperature / C
Pressure / GPa
0
200
400
600
800
1000
1200
1400
0
5
10
15
20


Fe
Shen et al. [1998]
liquid
δ
γ
ε
α
This study
Temperature / K
Pressure / GPa
0
1000
2000
3000
0
20
40
60
80
100
Temperature / K
Pressure / GPa
200
400
600
800
1000
1200
1400
1600
0
5
10
15
20

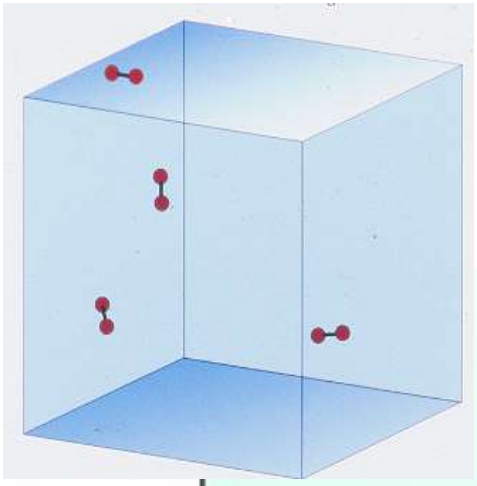
IRON OXIDE



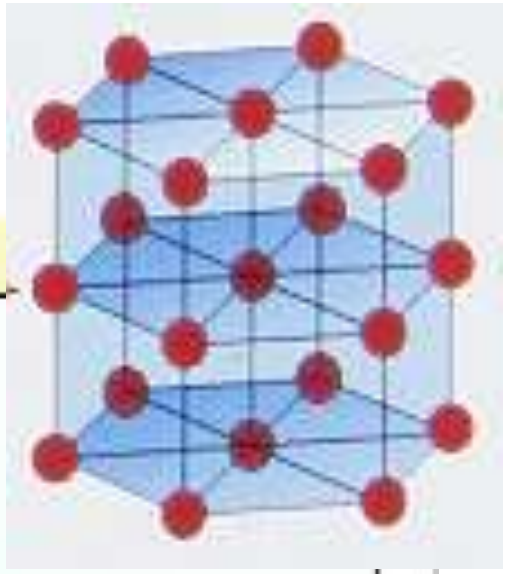


Fei & Mao, Science (1994)

HYDROGEN



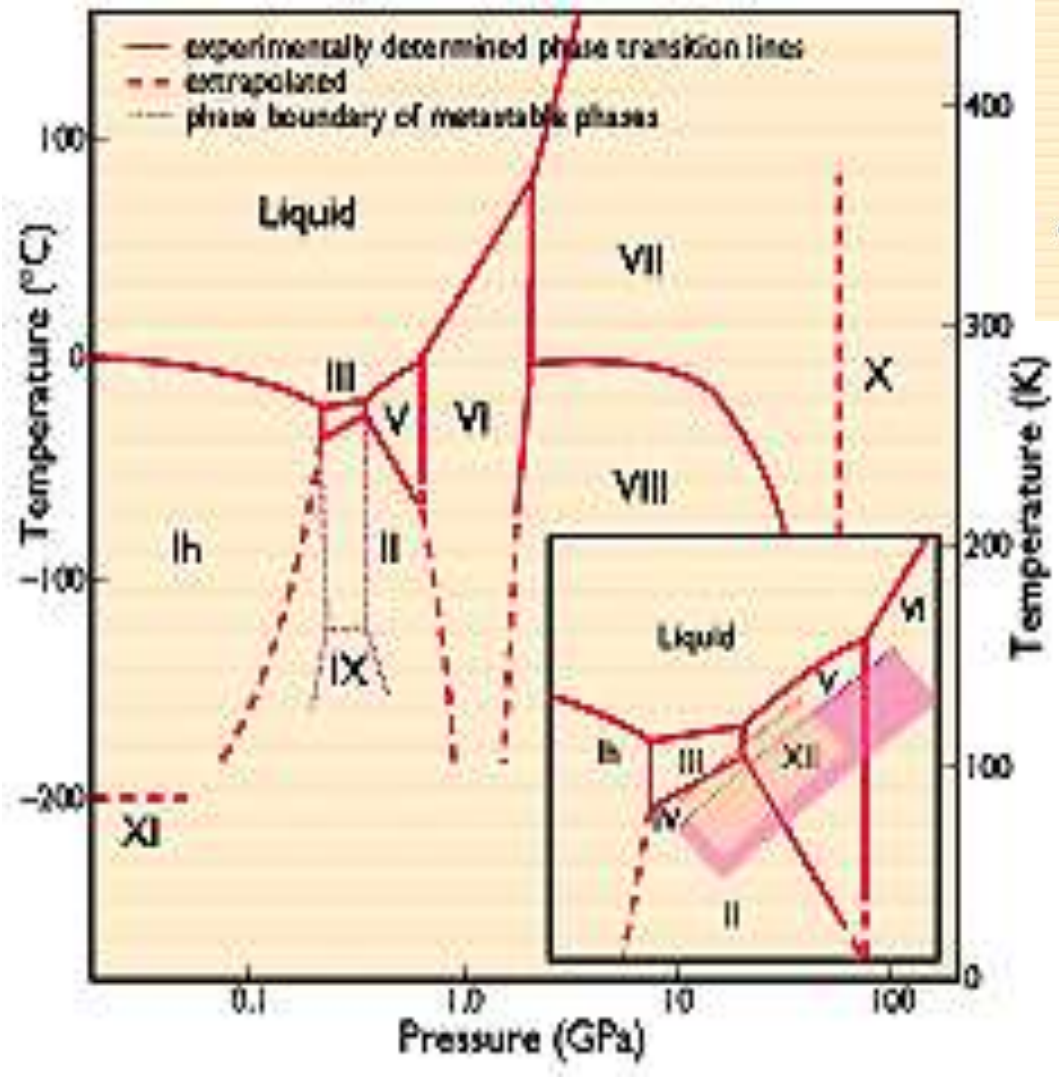
H_2

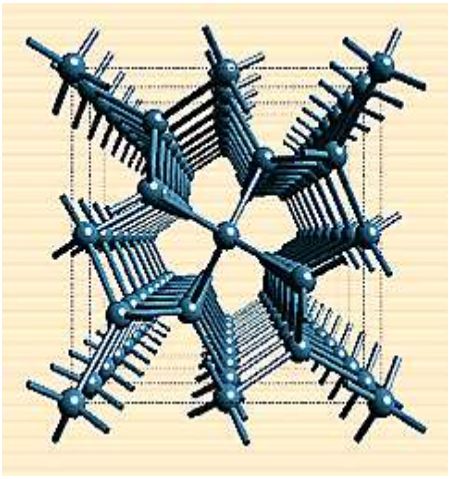


shocked metal
Weir et al.
Temperature (K)
2000
1500
1000
500
0
molecular fluid
nonmolecular fluid
Gregoryanz et al.
Scandolo,
Militzer et al.,
Ashcroft
molecular solid
metal
I
II
III
0
50
100
150
200
250
300
350
Pressure (GPa)

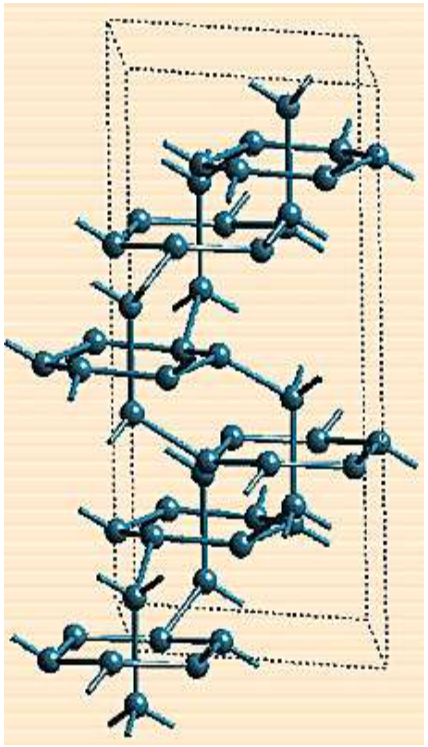
WATER

11 confirmed H2O crystalline phases



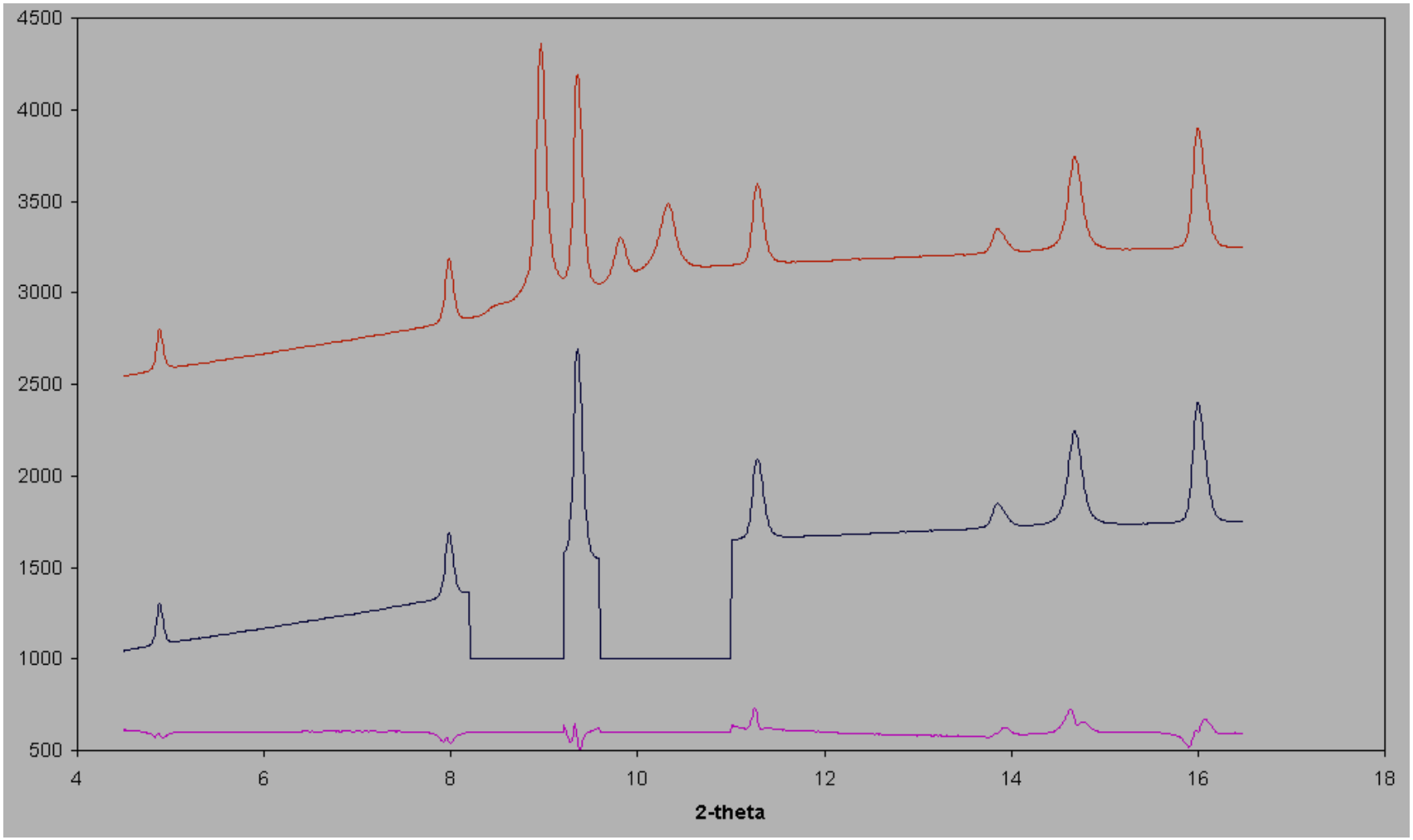


Tetragonal
ice XII
Spacegroup: I42
lattice constants:
a = 8.304 Å
c = 4.024 Å.

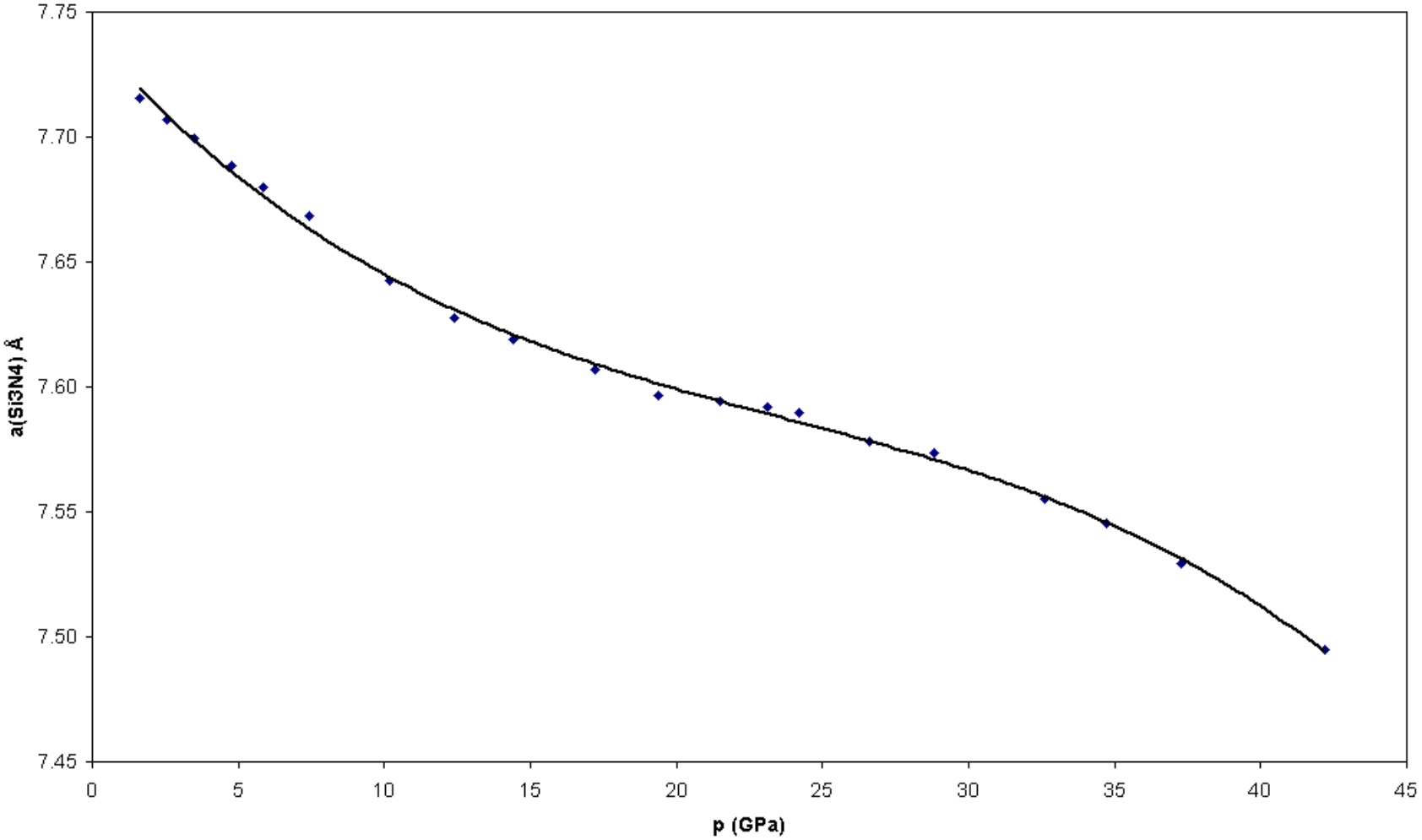


Rhombohedral
ice IV

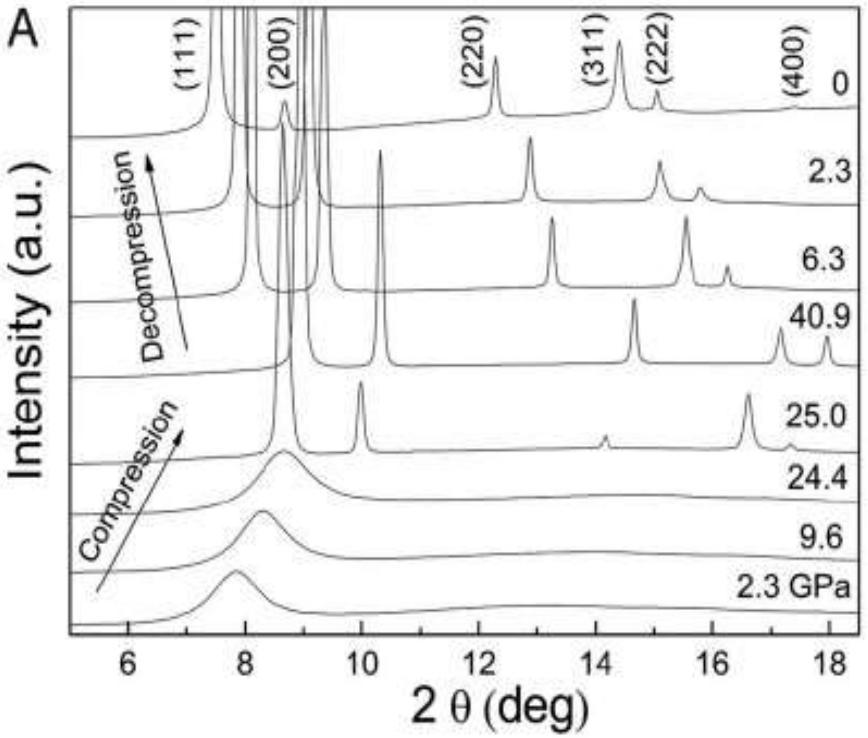
HIGH PRESSURE c-Si_3N_4

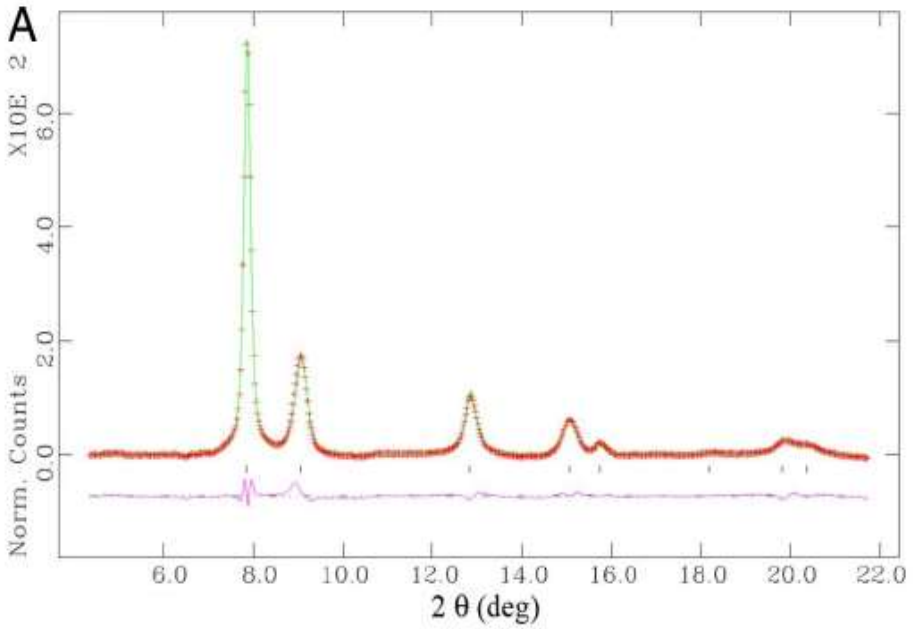


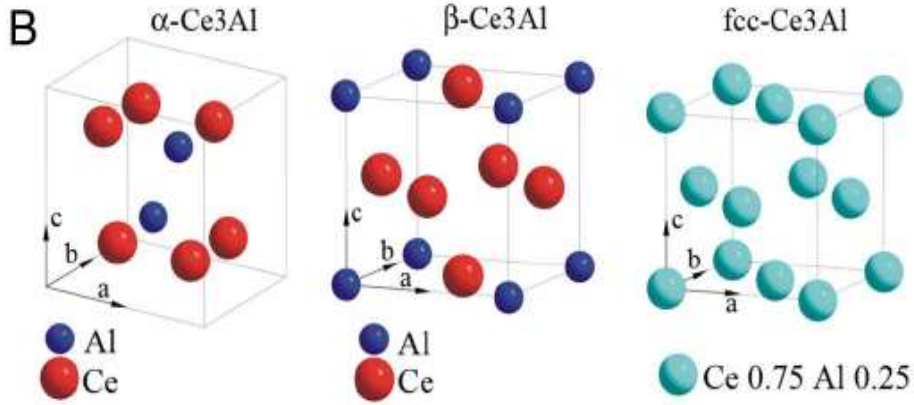
HIGH-PRESSURE c-Si_3N_4



SUBSTITUTIONAL ALLOY OF Ce AND Al

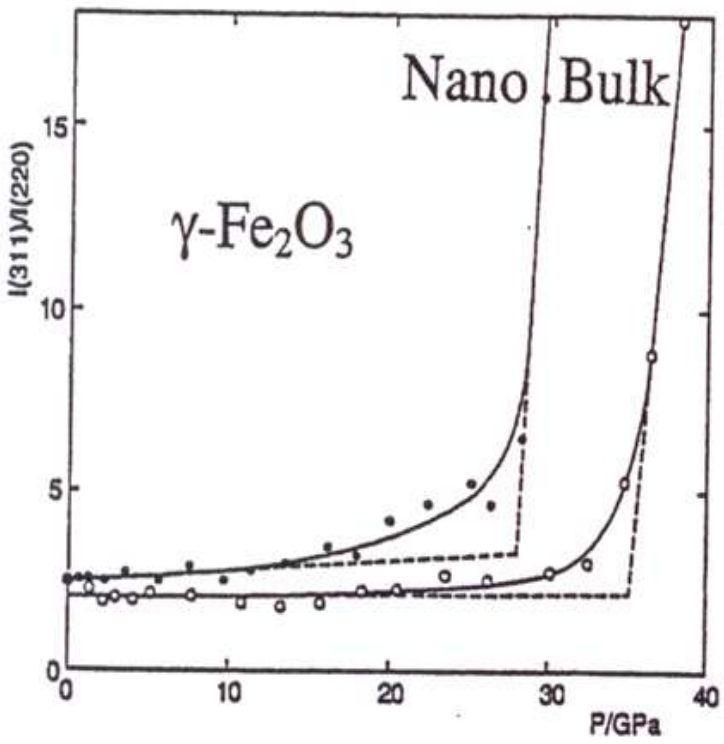


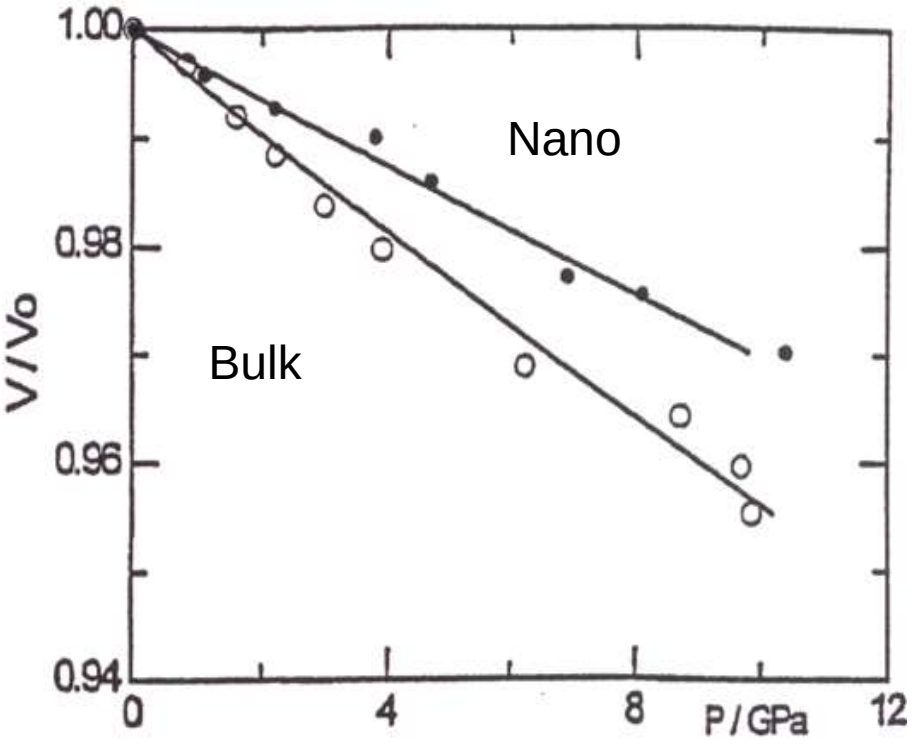




Q.S. Zeng, J.Z. Jiang et al., PNAS 106, 2515 (2009)

BULK VS. NANO-SIZE

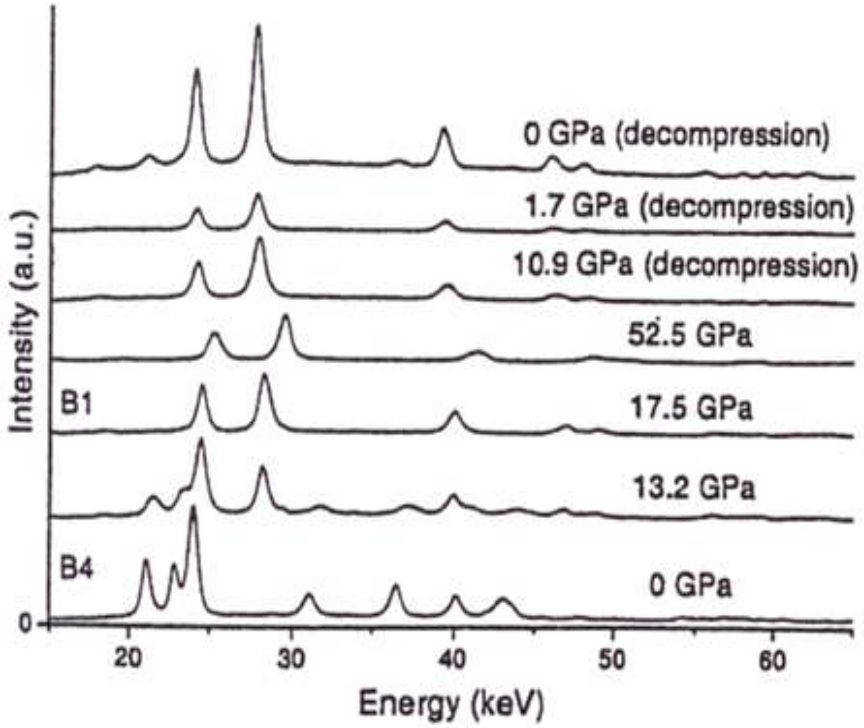


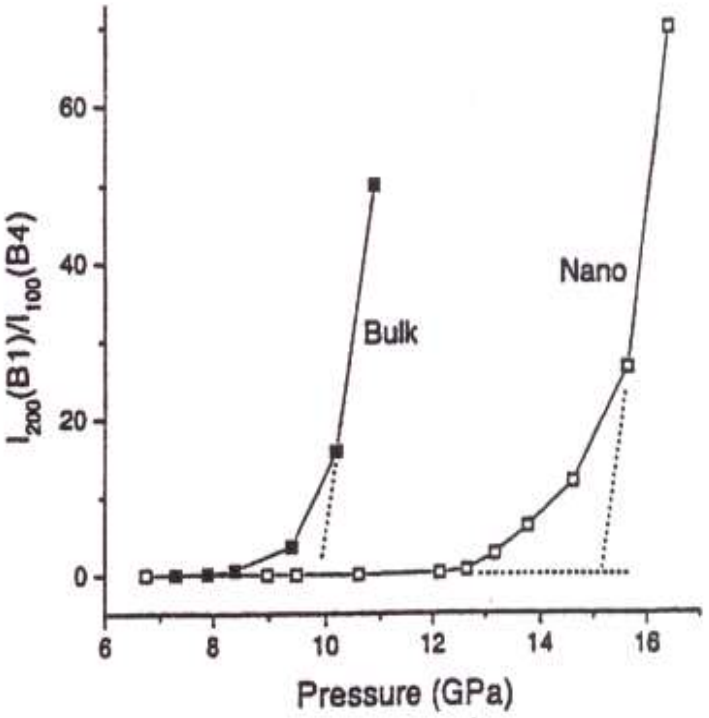


J.Z. Jiang et al., Europhys. Lett. **44**, (1998) 620.

BULK VS. NANO-SIZE

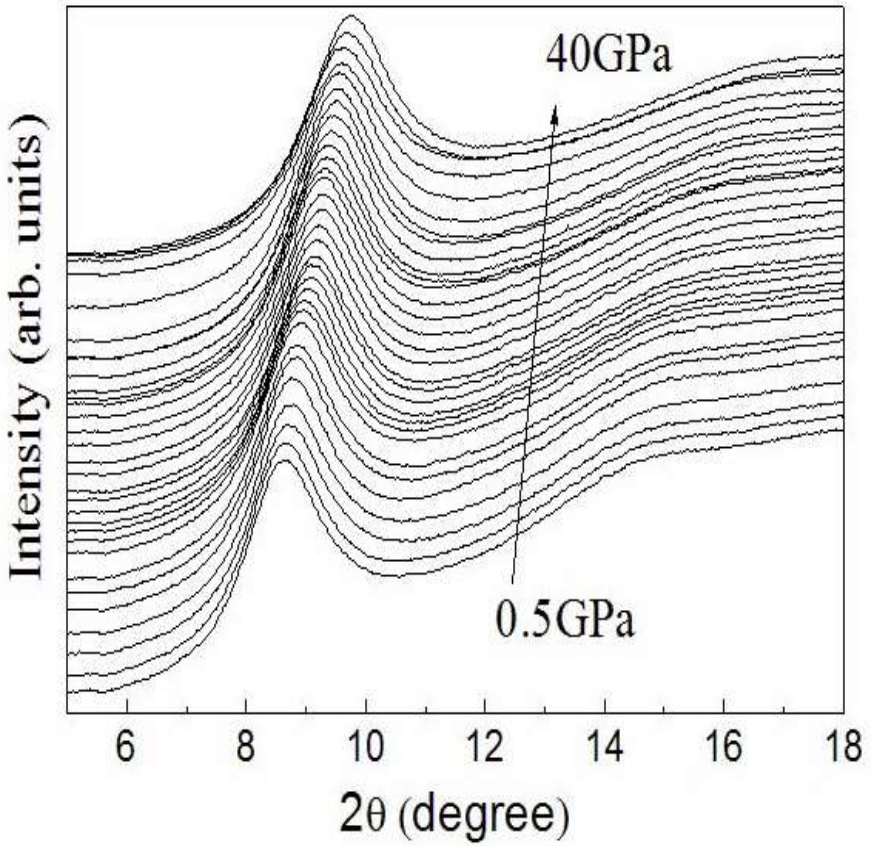
10nm ZnO

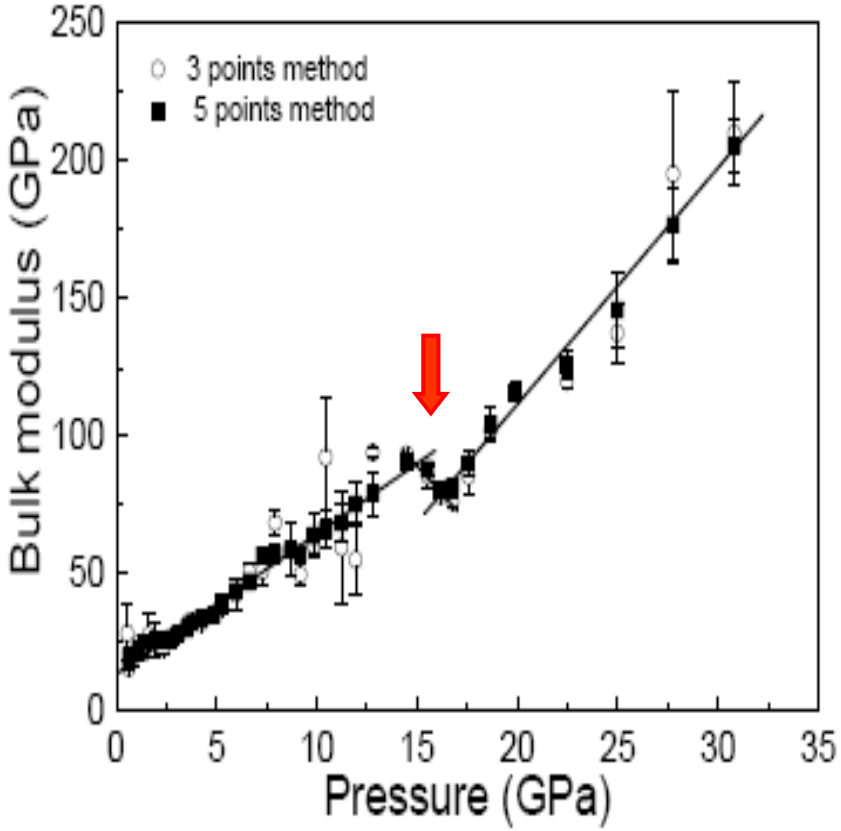




J.Z. Jiang et al., Europhys. Lett. **50**, (2000) 48.

AMORPHOUS - AMORPHOUS TRANSITION





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