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Single crystal diffraction at extreme pressure

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Pictures: C. Argoud and E. Bruas

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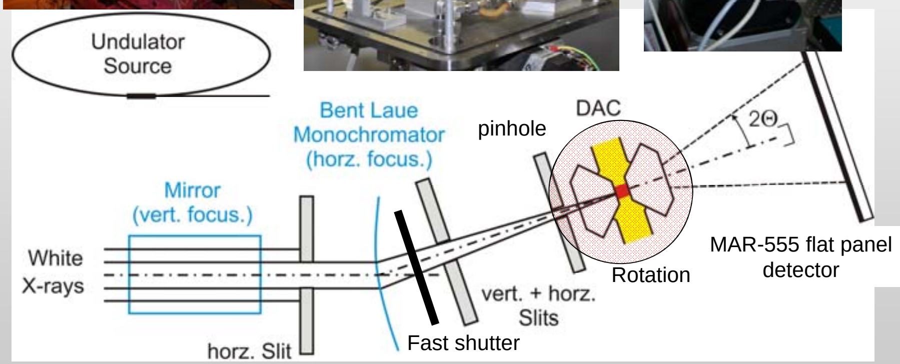
Storage Ring with a circumference of 844.4 meters

Energy	GeV	6.03
Maximum Current	mA	200
Horizontal Emittance	nm	4
Vertical Emittance (*minimum achieved)	nm	0.025 (0.010*)
Coupling (*minimum achieved)	%	0.6 (0.25*)
Revolution frequency	kHz	355
Number of bunches		1 to 992
Time between bunches	ns	2816 to 2.82

Two beamlines for high pressure diffraction experiments: ID27 and ID09A

The ID09A setup

U20 in vacuum undulator



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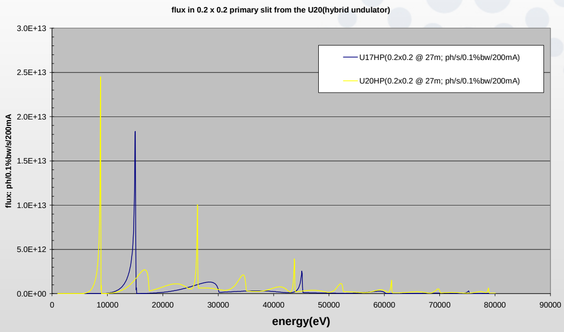
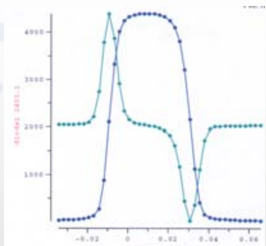
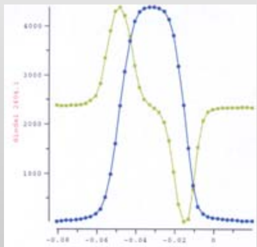
beam through 30 µm pin-hole





cleanh



cleanv

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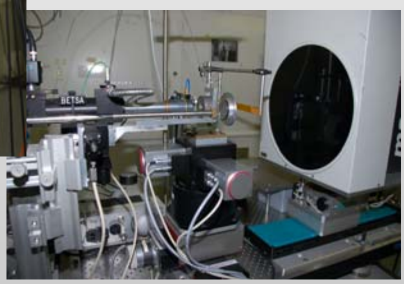
MAR555 detector

MAR555

MAR345



Large area (430 x 350 mm) amorphous Se flat panel detector, Pixelsize 139 x 139 µm, fast readout (~ 1.2 sec).

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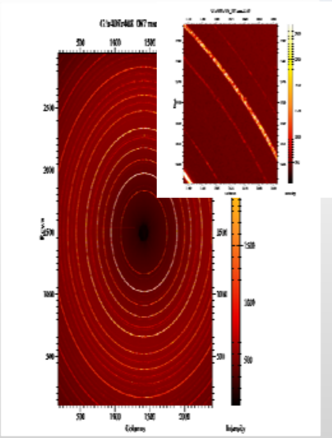
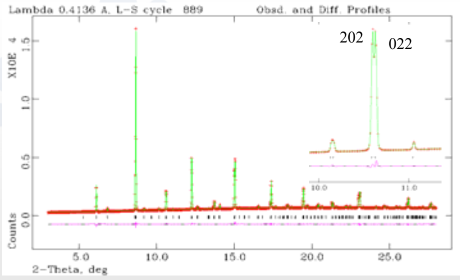
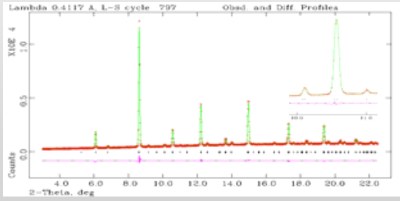
LaFeO$_3$ powder in He at 8.4 GPa







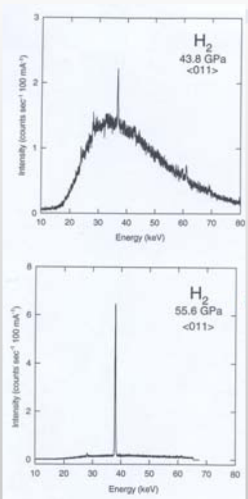
- Resolution: doubles the angular resolution (0.025º compared to 0.05º)
- Dynamic range: 18 bit compared to 16 bit
- Time: quasi real-time for powder diffraction, a few minutes for single crystal data set
- Stability and accuracy: no moving parts, no distortions

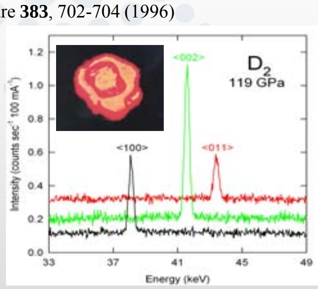
Energy dispersive single crystal diffraction

Loubeyre P. et al.

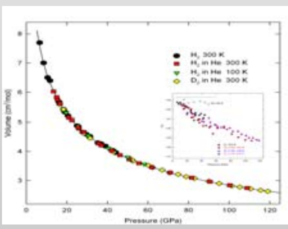
X-ray diffraction and equation of state of hydrogen at megabar pressures

Nature **383**, 702-704 (1996)





D$_2$ single crystal with He pressure medium.



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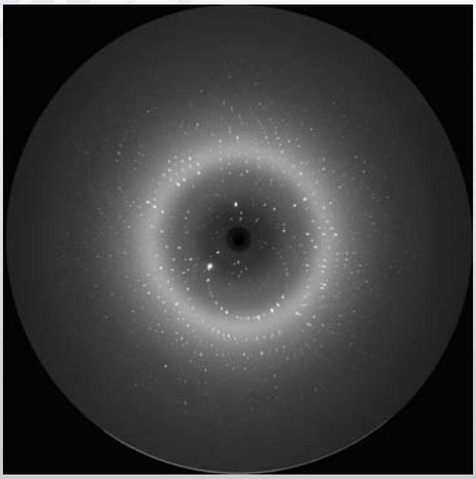
Bragg's law: d = λ/2sin(θ)

Laue diffraction:
Wavelength (energy) and angle variable, collect images at various angles.

Energy dispersive diffraction:
Wavelength (energy) variable, angle fixed, orient the sample.

Angle dispersive diffraction:
Wavelength (energy) fixed, angle variable, collect images while sample is rotating.

Laue diffraction image of a myoglobin crystal 100 ps after flash photolysis, M. Wulff et al. (ID09B)



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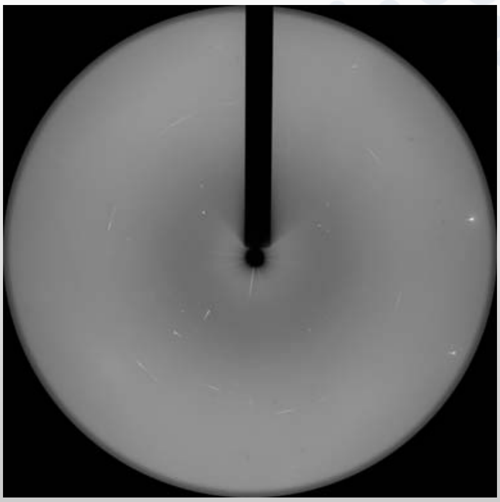
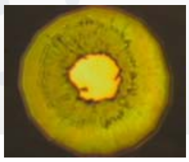
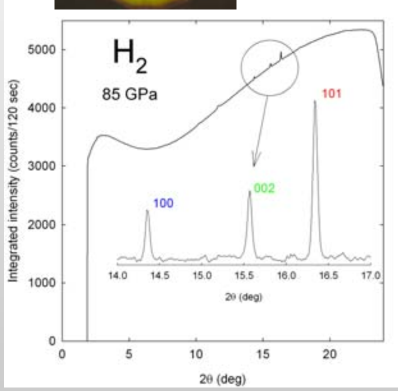
Angle dispersive diffraction

single crystal, large mosaic spread, optimum orientation, all reflections can be observed with a ±4° rotation





no He as pressure transmitting medium



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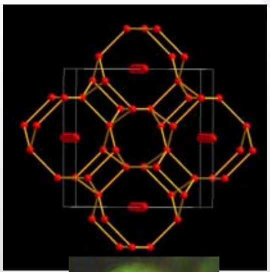
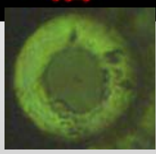
Single crystals grown in a diamond anvil cell

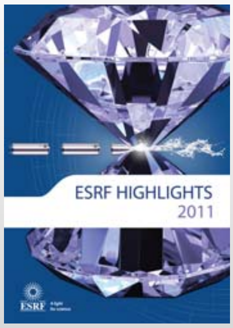
Form liquid: molecular solids like H_2, H_2O, N_2, O_2, CO_2, …
By chance: Na, Li, …





"tI20" – phase of Na at 126 GPa
see also: **Lundegaard L.F. et al.**
Single-crystal studies of incommensurate Na to 1.5 Mbar, Phys. Rev. B **79**, 064105 (2009).

New high pressure phases of Li
Guillaume C.L. et al.
Cold melting and solid structures of dense lithium, Nature Physics **7**, 211-214 (2011)



Single crystals loaded in a diamond anvil cell

Since recently most published experiments were limited to relatively low pressures
Screening, orientation, opening, rotation range, pressure medium, seize, data treatment

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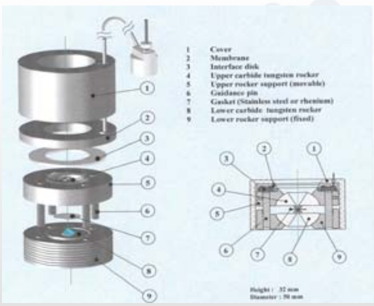
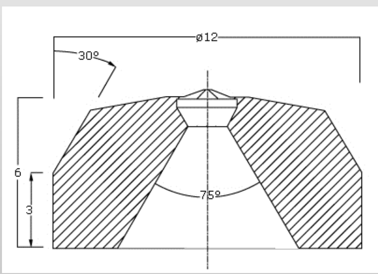
Rotation range



Membrane driven LeToullec type diamond anvil cell,
modified for Boehler-Almax anvils.



Large opening angle,
±32º rotation range (3.1 mm dia.), completeness ~ 30%
Pressures (with He):
30 GPa with 600 µm culet,
85 GPa with 300 µm culet
(with Re gasket).

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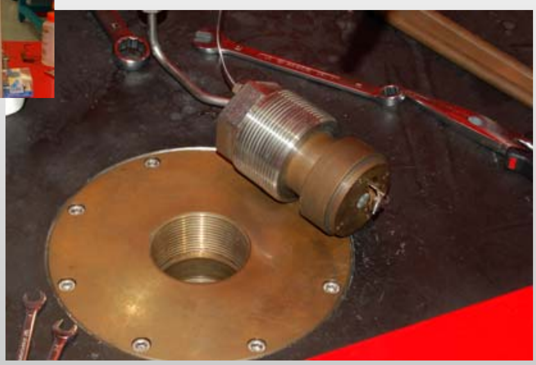
Gas loading

For loading He, Ne, …
Quasi hydrostatic pressure conditions at extreme pressures.



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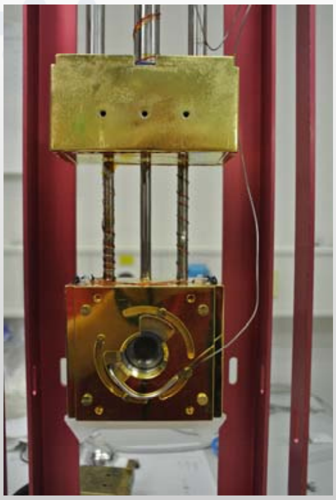
Low temperatures



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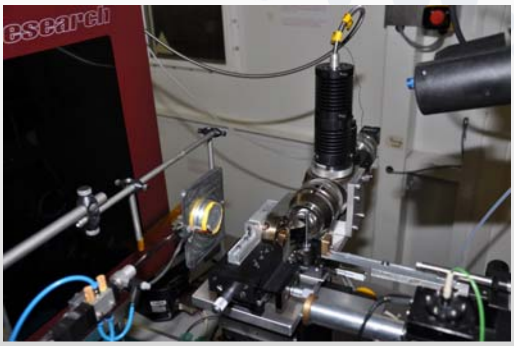
Very high temperatures



Laser heating set up for single crystals.

Dubrovinsky L. et al.
Single-crystal X-ray diffraction at megabar pressures and temperatures of thousands of degrees
High Pressure Research **30,** 620-633 (2010)

Having reached pressures well above 100 GPa, we can study earth's mineralogy till the core mantle boundary.

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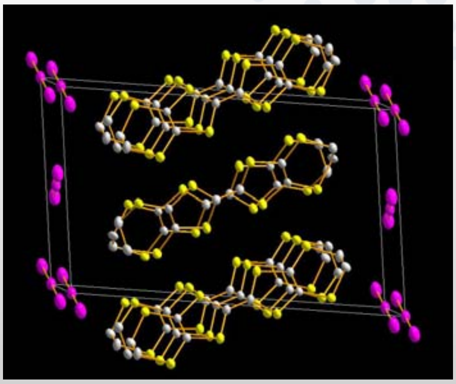
Complex structures: α-(bis(ethylenedithio)tetrathiafulvalene)$_2$I$_3$ (ET$_2$I$_3$)

PhD-Thesis **S. Brun**



Triclinic (P-1):
a = 9.1797(1) Å, b = 10.7970(1) Å,
c = 17.4095(2) Å,
α = 96.952(4)°, β = 97.930(4)°
and γ = 90.828(1)°
V = 1695.59(5) Å^3, Z = 2

Organic conductor, MI-transition at 135 K due to charge ordering (T. Kakiuchi et al., 2007), other modifications become superconducting at low T.

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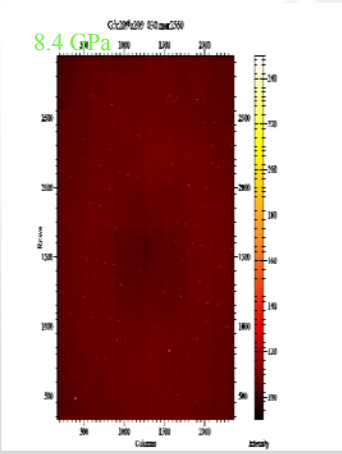

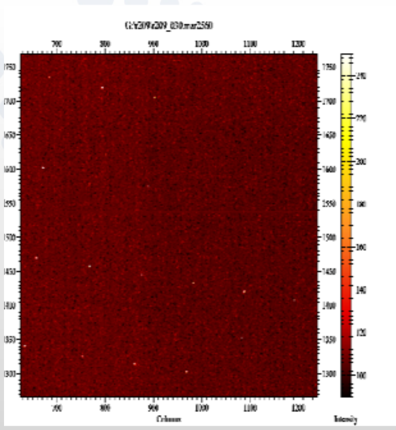

Crystal grown by H. Müller (ESRF Chemistry lab)
8.4 GPa, ± 3° rotation
λ= 0.413 nm, d = 340 mm
Datasets: -32° to 32°, 0.5° steps, 1 sec exposure
Indexing and integration: CrysAlis (Oxford Diffraction), refinement Jana or Crystals

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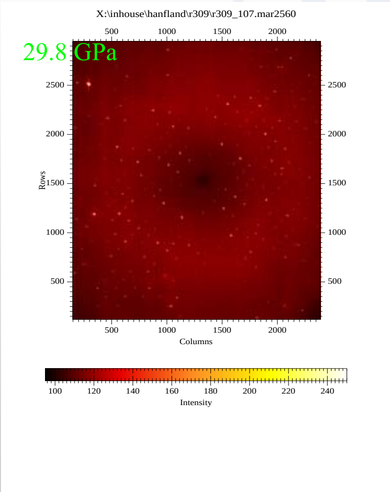
Phase transition at 135 kbar



The structure is triclinic (space group P-1), lattice parameters are a = 9.563 Å, b = 13.315 Å, c = 16.831 Å, α = 107.25°, β = 99.05° and γ = 90.00°, the unit cell volume is V = 2018.8 $Å^3$, Z =4. The transition is reversible.

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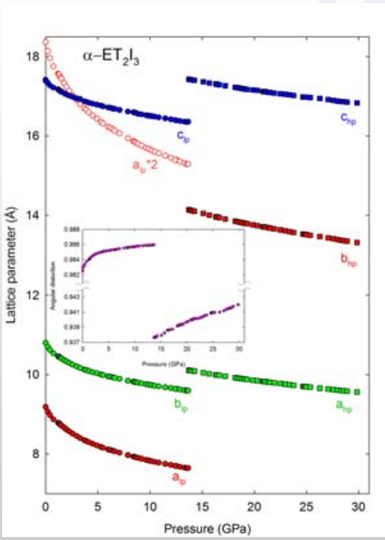
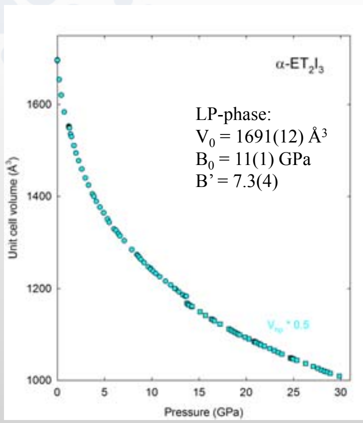
External changes





Strongly anisotropic: B_{alp} = 21(2) GPa, B_{blp} = 29(2) GPa, B_{clp} = 100(20) GPa at transition: $a_{hp} \approx b_{lp}$, $c_{hp} \approx c_{lp}$ and $b_{hp} \approx 2 * a_{lp}$

Angular distortion = $(1-\cos(\alpha)^2-\cos(\beta)^2-\cos(\gamma)^2+2\cos(\alpha)\cos(\beta)\cos(\gamma))^{1/2}$

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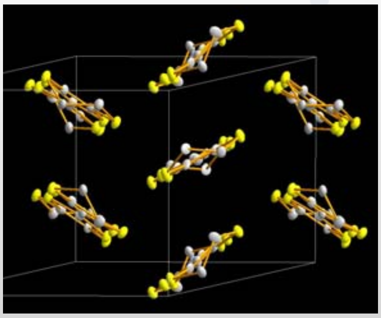
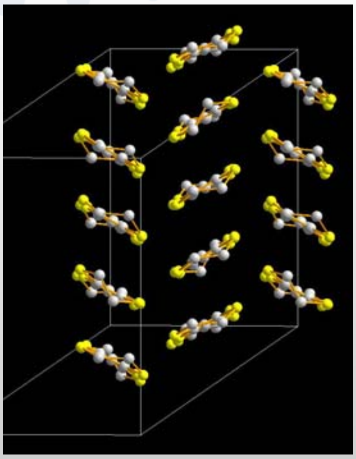
Structures

HP-phase = 16.6 GPa

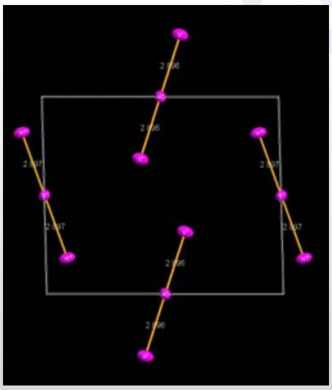
LP-phase at 9.6 GPa



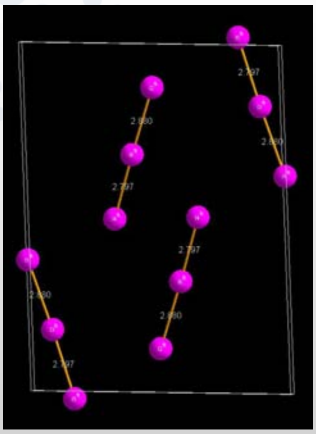


Stratural models with Sir2008 and superflip

The Iodines



LP-phase,
symmetric I_3-molecules



HP-phase,
the I_3-molecules are asymmetric
and no longer linear (~175°)

Summary:

- Single crystal data well in to the Mbar pressure range at variable temperature from a few K to 600 K using cryostat and external resistive heaters

- Data-sets suitable for:
  indexing
  accurate refinement of crystal structure
  structure solution for example by ab-initio or charge flipping methods