Elettra
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Studies of matter at extreme conditions

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“Ambient conditions”

As far as we know, human beings and other biological organisms exist in the universe only on or near the surface of the Earth, where the physical conditions permit the existence of self-replicating long-chain molecules

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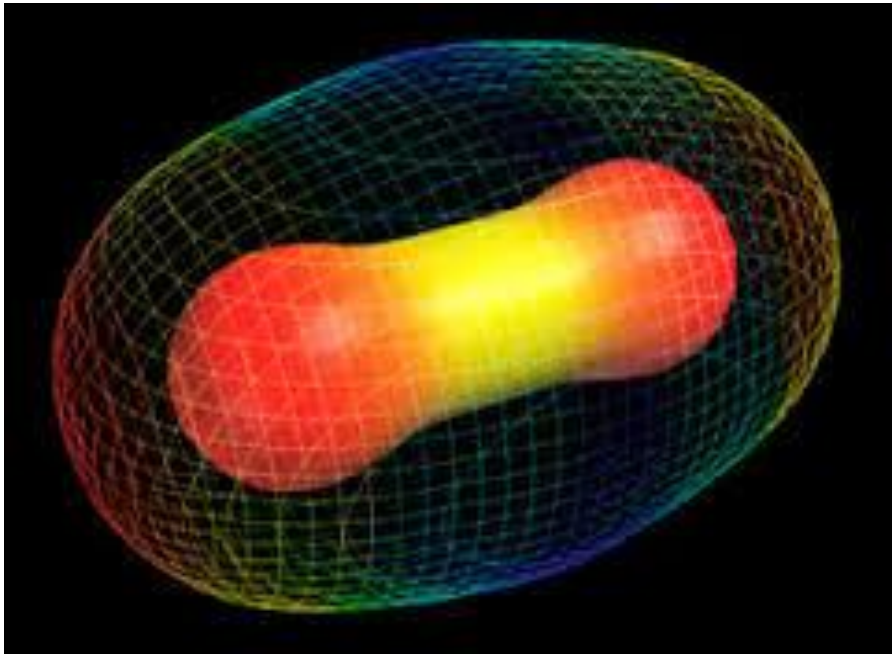
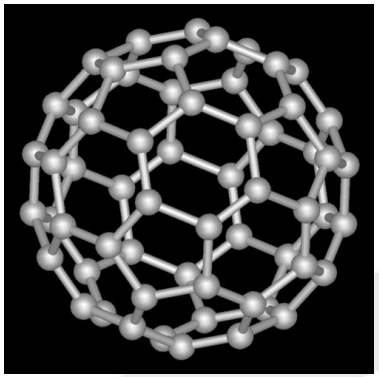
Chemical bonds

Binding takes place when the individual atoms are close enough together that the outer valence electrons of each atom can experience the potential well of the neighboring atom's nucleus as comparable to the potential well of its own atom's nucleus



Chemical bonds: values

- Electron binding energy: few eV
- Binding energy of typical covalent carbon–carbon molecular bond: 4 eV
- In graphite, potential energy of adjacent planes of carbon atoms: 0.05 eV per carbon atom
  - This energy *E* corresponds to a temperature $T = E/k \approx 600$ K



“Ambient conditions”

- The surface of the Earth, at an average temperature of 300 K and an average pressure of 1 atm = 0.1 MPa, is at ideal conditions for the existence of stable large molecular structures

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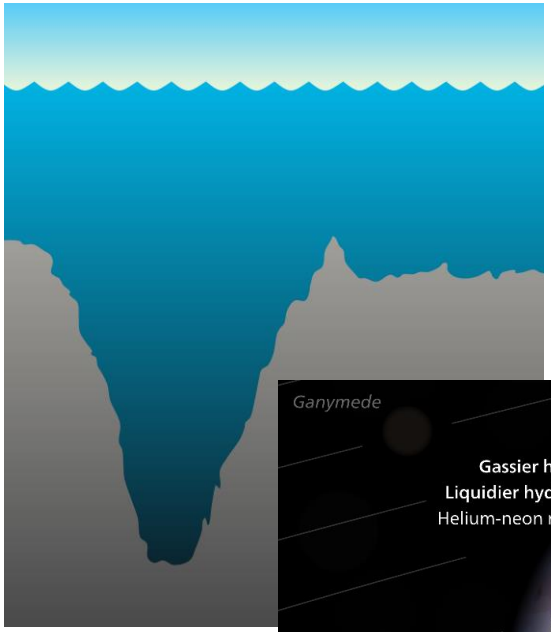
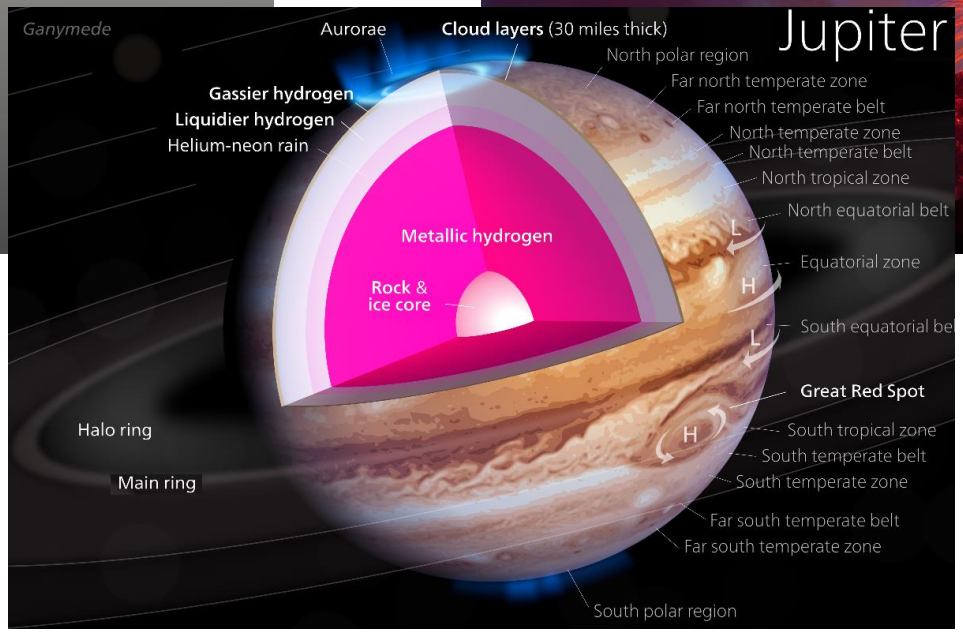
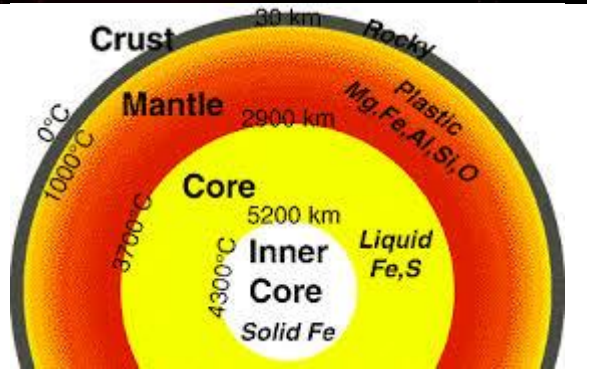
“Extreme conditions”







At much higher temperatures or pressures, matter will likely be in an entirely different physical state, and will behave differently

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Physical and chemical transformation

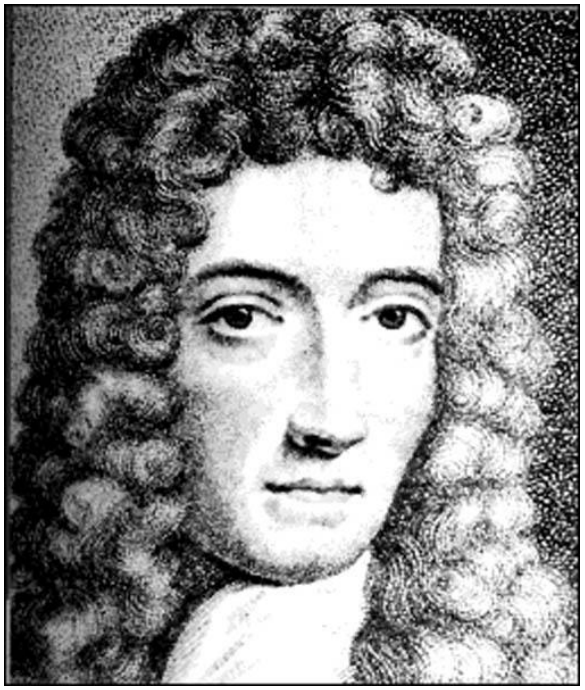
- All physical (and chemical) transformations are controlled by:
  - Temperature
  - Pressure
  - Chemical potential
- Acting on these external or internal parameters it is possible to affect the equilibrium composition of the systems and the kinetics of the transformation

Physical and chemical transformations

- Chemical events occur as bonds are broken and other are formed, with the nuclei circumventing energetic barriers
- Temperature accelerates the motion in crossing these barriers
- Pressure changes the structure of the barriers height: so while they are decreased in some cases, they are increased in others.

The thermodynamic variable Pressure

- Of the common thermodynamic variables pressure and temperature, it is temperature that has played by far the most prominent role in probing condensed matter and in our fundamental understanding of it

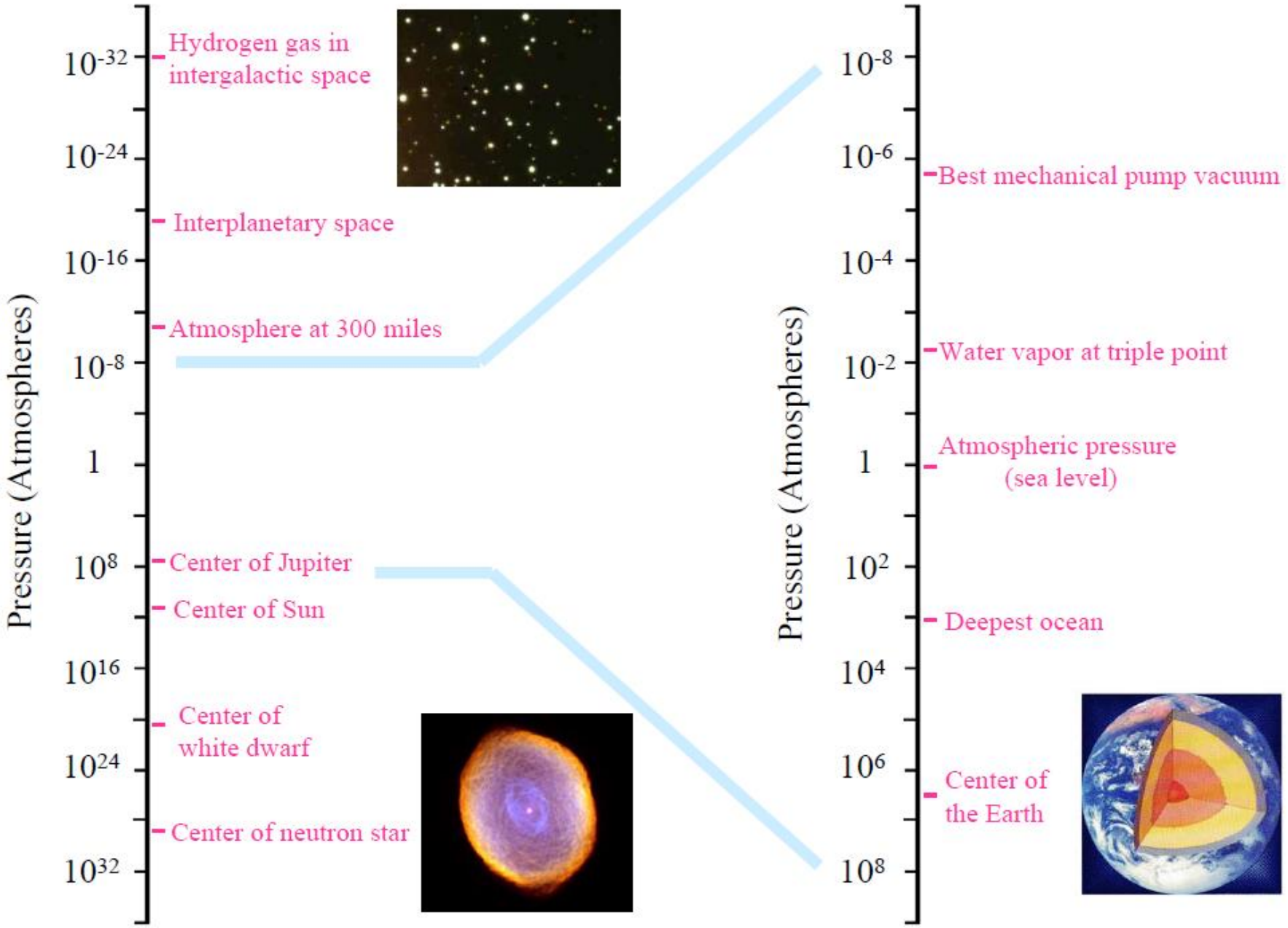


Robert Boyle (1622-1691)

Touching
the Spring of the Air, and its effects

"the pressure of the air might have an interest in more phenomena than men have hitherto thought"

Pressures in the universe



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Outline

- Introduction
- Effects of pressure
  - Insulator to metal transitions
  - Metal to insulator transitions
  - Effects on magnetism
  - Structural phase transitions
- High pressure and Earth's science
- Tools and methods
- Examples of high pressure studies using XAS
  - Polyamorphism in glassy GeO_2
  - Melting of iron at megabar pressures
  - Revealing Earth's interior
- Bibliography

Pressure and G

At 1 Megabar

$$G = E + pV - TS \sim 10 \text{ eV}$$

Gibbs free energy

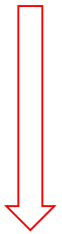
New bonds creates, existing bonds deformed

Pressure and volume reduction

At 2 Megabar

Typical volume reduction of a factor 1.5 – 5

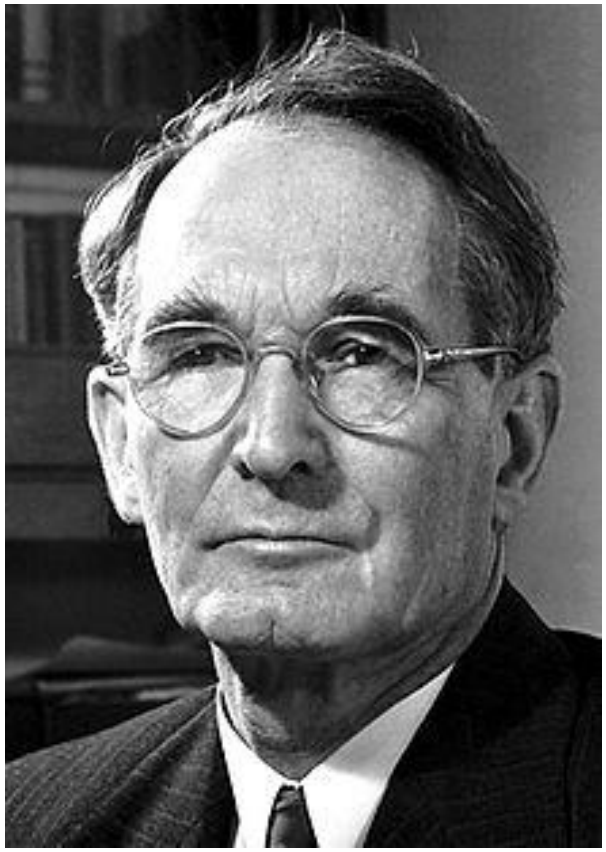
(the atoms are driven close together)



Shrinking of the distance along one direction

(if isotropic) of factor 1.1 -1.7

Pressure and electronic structure



Percy W. Bridgman (1882-1961)

Nobel laureate in physics (1946)

"This compression offers a route to "breaking down" the electronic structure of the atoms themselves and to the possibility of entirely different bulk properties"

Insulator-to-metal transitions

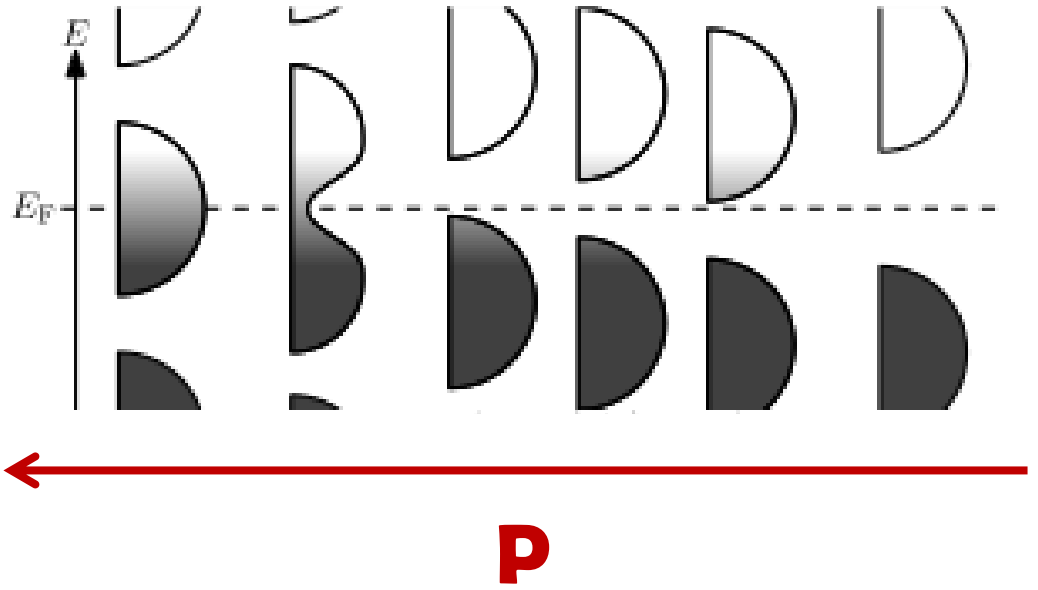
- Through application of pressure, we can bring about one of the most basic of all changes, the crossing of the “great divide” from insulators to metals

- As early as 1935, Bernal (cited by Wigner and Huntington) noted what we might call a rough rule: All materials become metallic under sufficiently high pressure

Insulator-to-metal transitions

- Compressions leads to greater overlap and, thus, to greater interactions among filled and unfilled MOs

- Pressure-induced insulator-to-metal transitions have been documented in a long list of materials and over a broad range of pressures



Insulator-to-metal: example 1

Silicon

J. Phys. Chem. Solids Pergamon Press 1962, Vol. 23, pp. 451–456. Printed in Great Britain.

PRESSURE INDUCED PHASE TRANSITIONS IN SILICON, GERMANIUM AND SOME III–V COMPOUNDS*

S. MINOMURA and H. G. DRICKAMER

Department of Chemistry and Chemical Engineering
University of Illinois, Urbana, Illinois

(*Received* 25 *September* 1961)

Abstract—Pressure induced phase transitions to a conducting state have been found for silicon (195–200 kbars), germanium (120–125 kbars), GaAs (245–250 kbars, 275–280 kbars), GaSb (80–100 kbars), InAs (100 kbars), InP (125–130 kbars) and AlSb (115–125 kbars). No transition occurred in GaP to 550 kbars. Although it cannot be definitely proven, it is the author's feeling that, with the exception of GaAs, all transitions are solid–solid transitions, apparently to a metallic state. For GaAs, it is postulated that the first transition involves melting to a metallic liquid, while the second transition constitutes the freezing of the liquid.

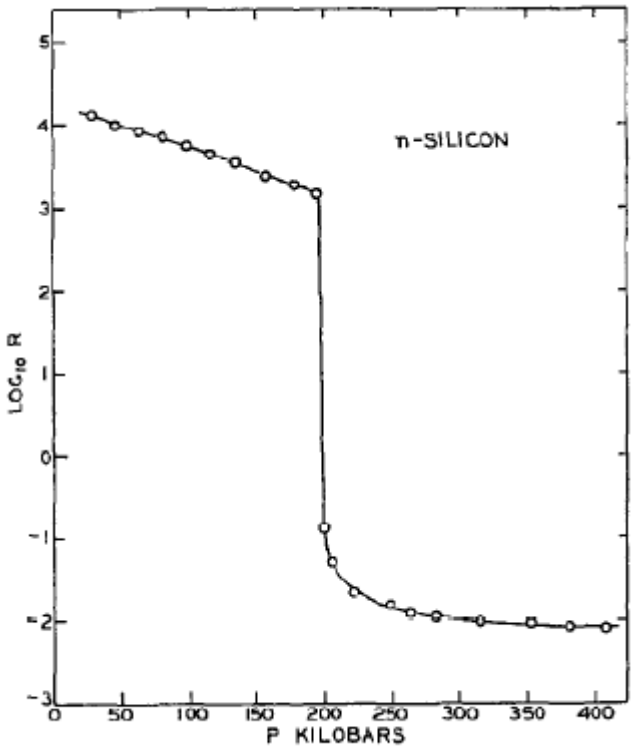
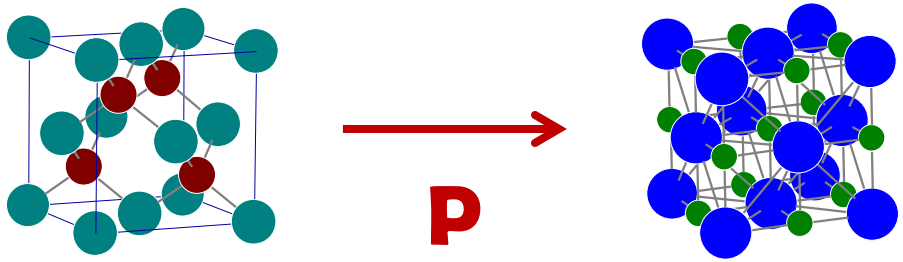


FIG. 1. Resistance vs. pressure—*n*-Silicon.



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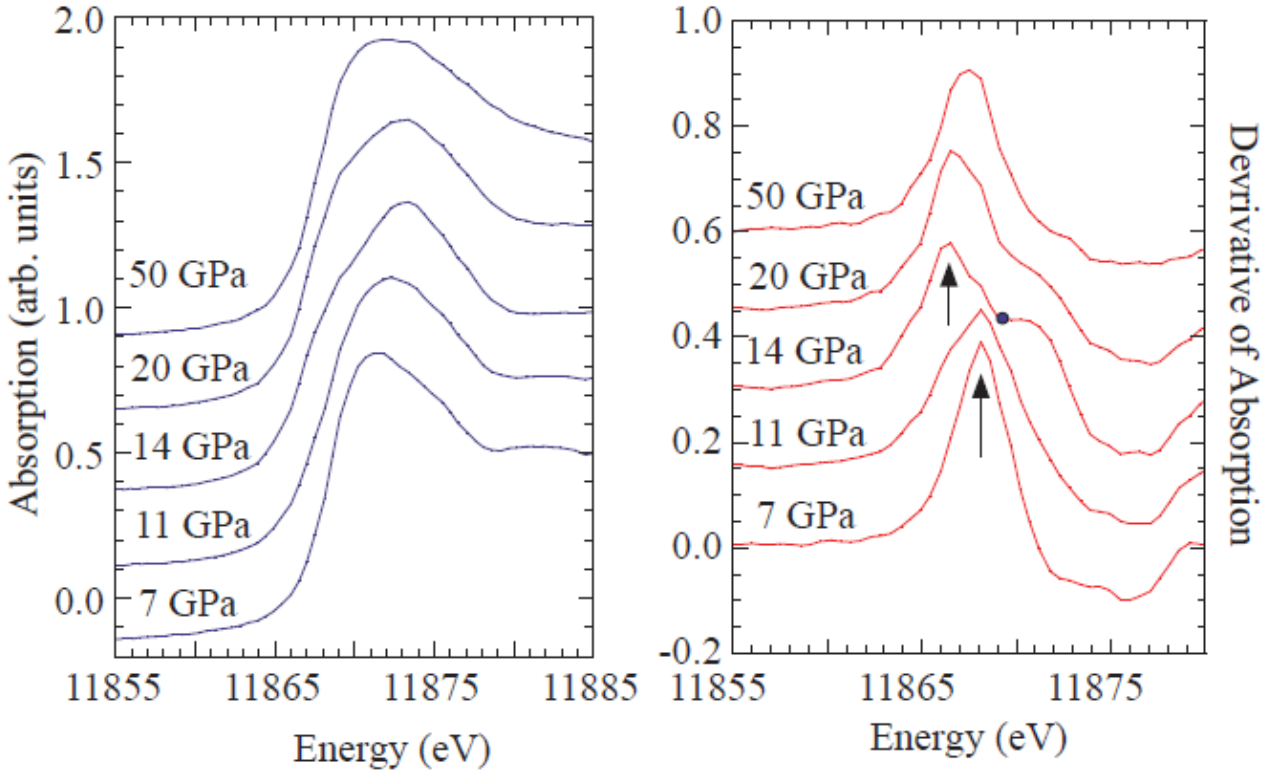
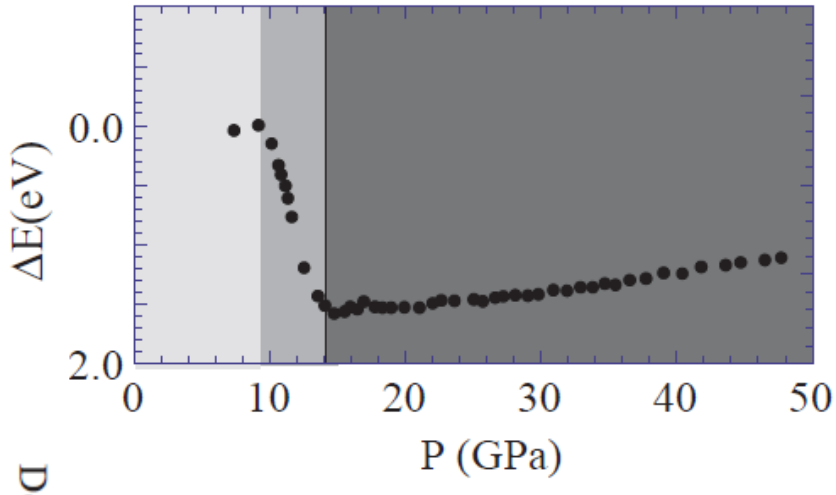
Insulator-to-metal: example 2

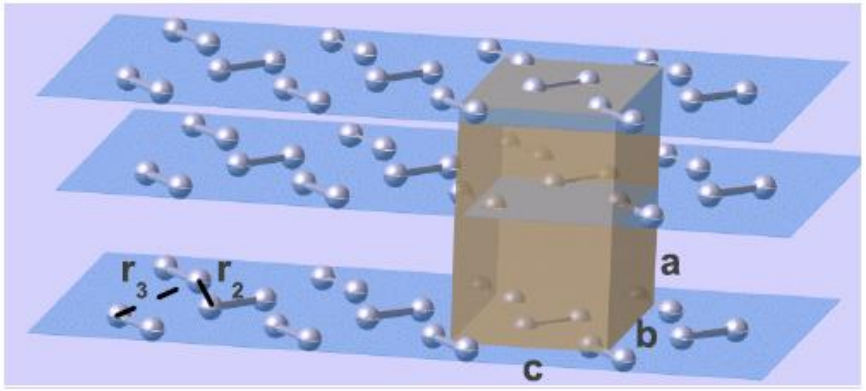
III-V compounds: InAs

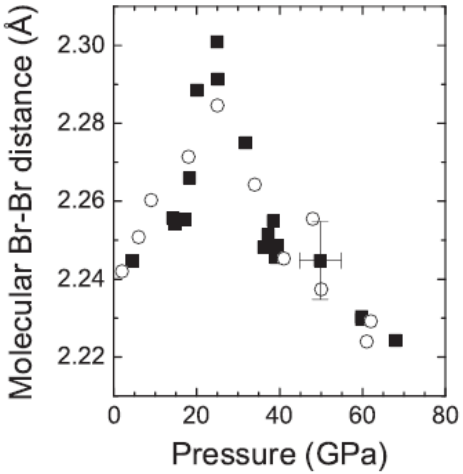


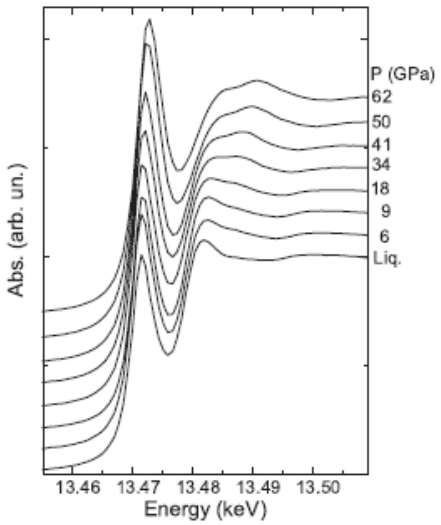


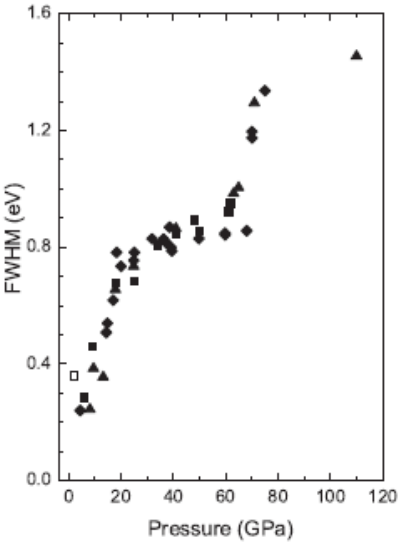
Insulator-to-metal: example 3

Diatomic molecular solids: the halogens (Br_2)







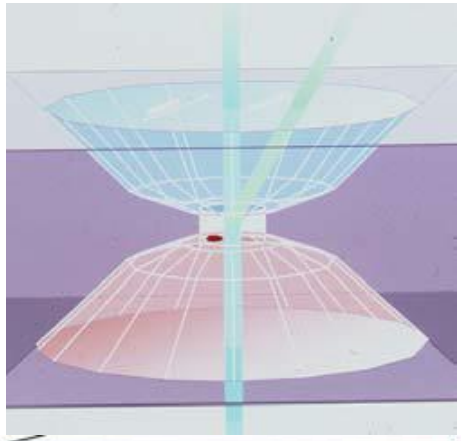


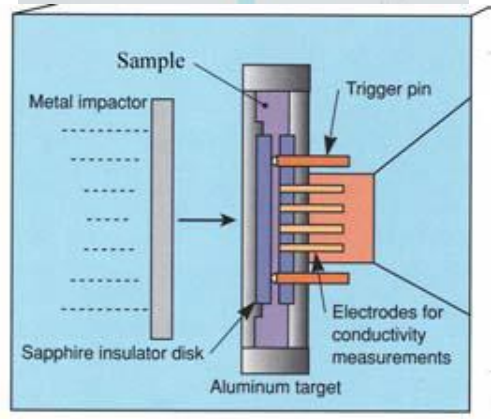
The heavier halogens (Br_2, I_2) are model systems for the study of simple molecular solids under high pressure as the necessary pressures for metallization or dissociation are typically a factor of 10 to 100 smaller than for H_2

Insulator-to-metal: example 4

Hydrogen

- The most abundant element
- The only quantum molecular solids
- Insulator at ambient
- Implication for the understanding of the interior of giant planets, such as Jupiter, that is 90% hydrogen, most of which is at ultrahigh pressures in a fluid metallic state. The results can now further assist in understanding both the luminosity of the planet and the origin of its large magnetic field, which is generally believed to be associated with fluid metallic hydrogen within the planet's mantle.



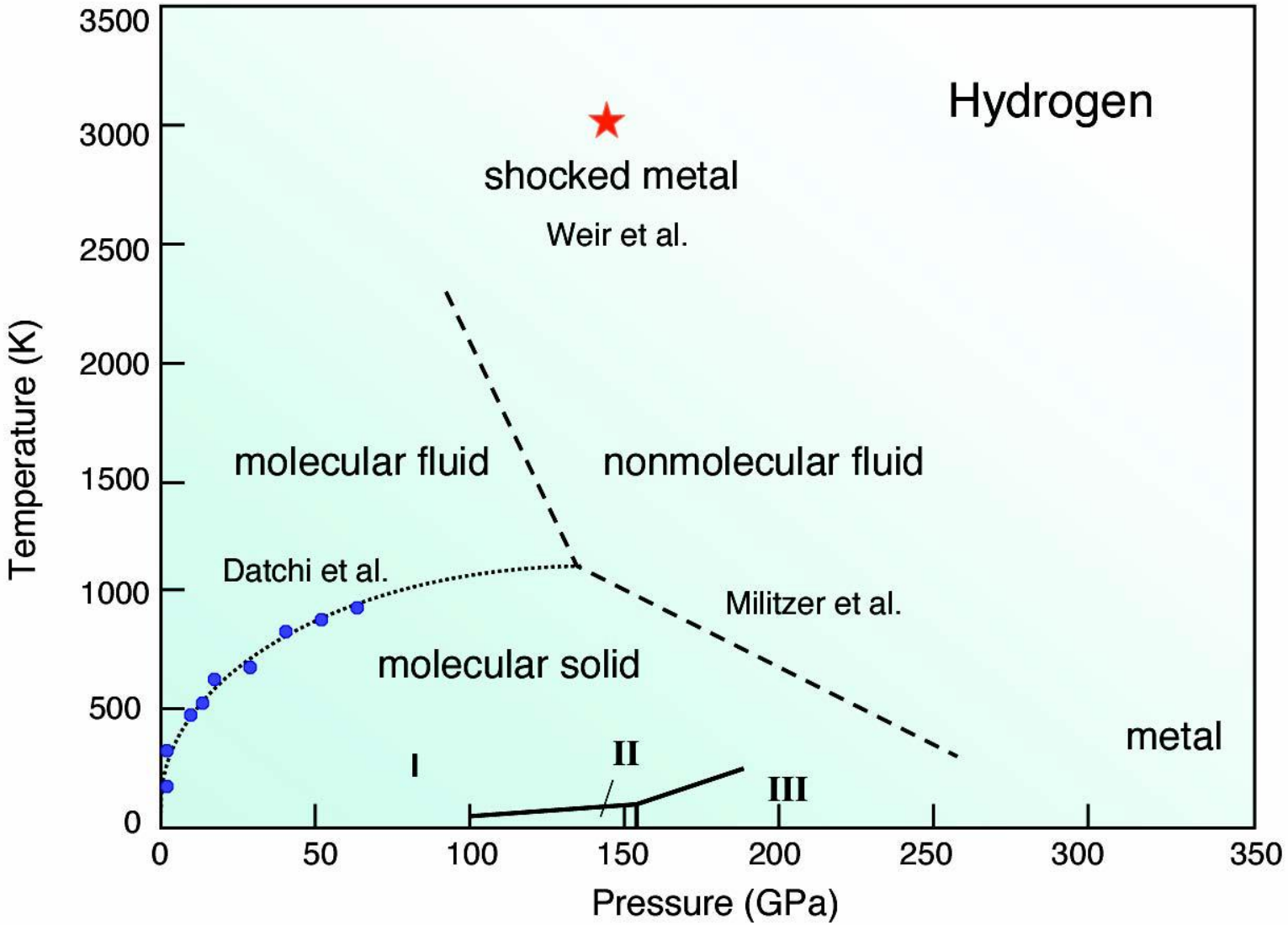


Insulator-to-metal: example 4

Hydrogen: theoretical prediction:

- Wigner and Huntington (1935): H2 molecules dissociate in favor of a monoatomic metal. Instead of discrete H_2 molecules a bulk phase would form with a solid lattice of protons and the electrons delocalized throughout
- Ashcroft (1968) suggestd that hydrogen at 400 Gpa would be liquid even at low temparture and might be superconductor up to RT

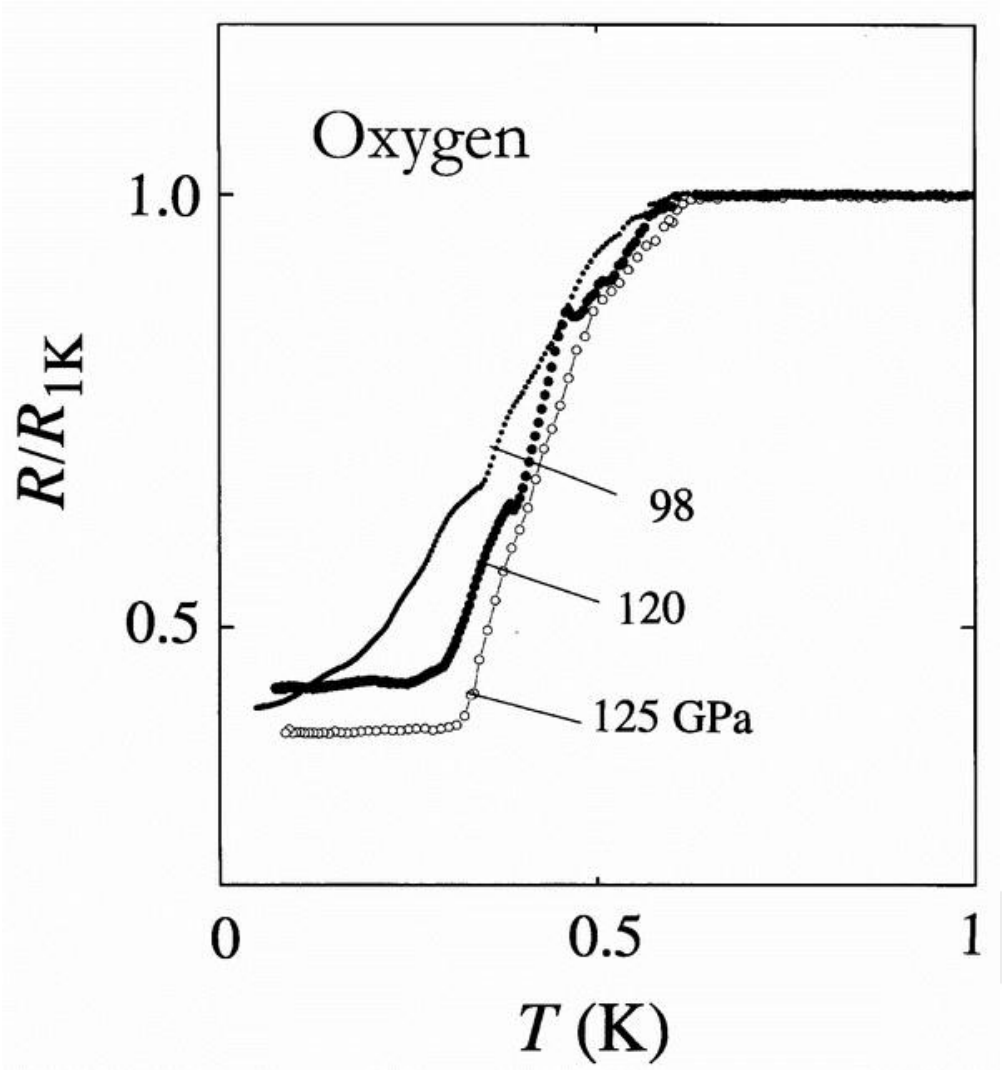
Insulator-to-metal: example 4



Insulator-to-superconductor

Oxygen

- At ~ 95 GPa, solid oxygen becomes metallic and is accompanied by a structural transition.
- At ~100 GPa solid oxygen becomes superconducting, with a transition temperature of 0.6 K. The transition is revealed by both resistivity measurements and a Meissner demagnetization signal



Metal-to-insulator

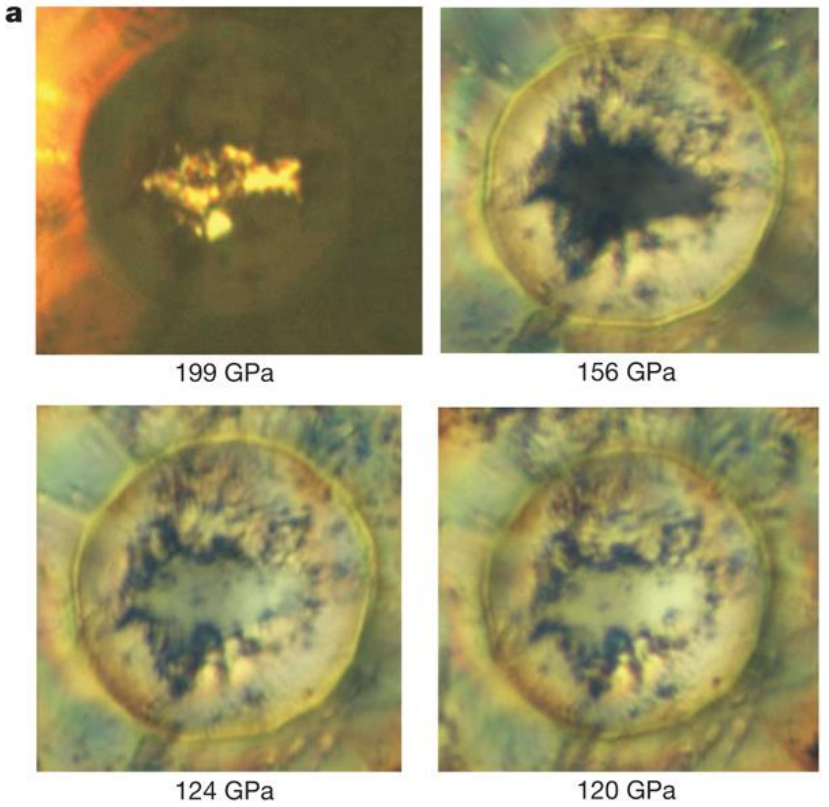
Sodium

- Intuitively, pressure produces an increase in the widths of the valence and conduction bands and hence a more pronounced free-electron-like behaviour

Metal-to-insulator

Sodium

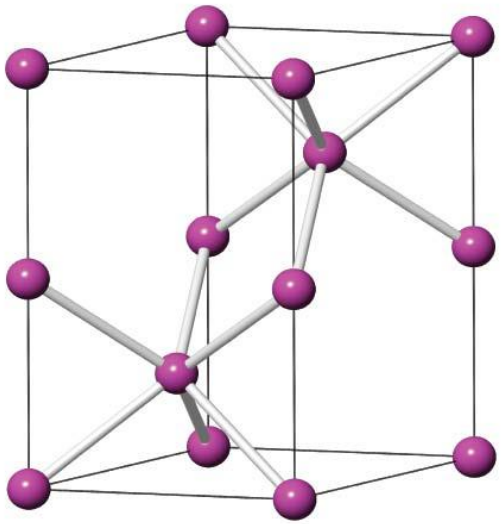
- At 200 GPa (corresponding to approximately 5.0-fold compression), Na transforms into an optically transparent phase
- Optical absorption experiments show a bandgap of 1.3 eV
- The onset of transparency coincide with a dramatic change in Raman spectra
- On decompression, the transparent phase persists to 182 GPa

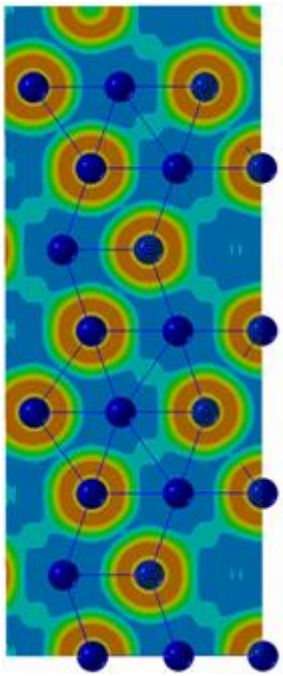


Metal-to-insulator

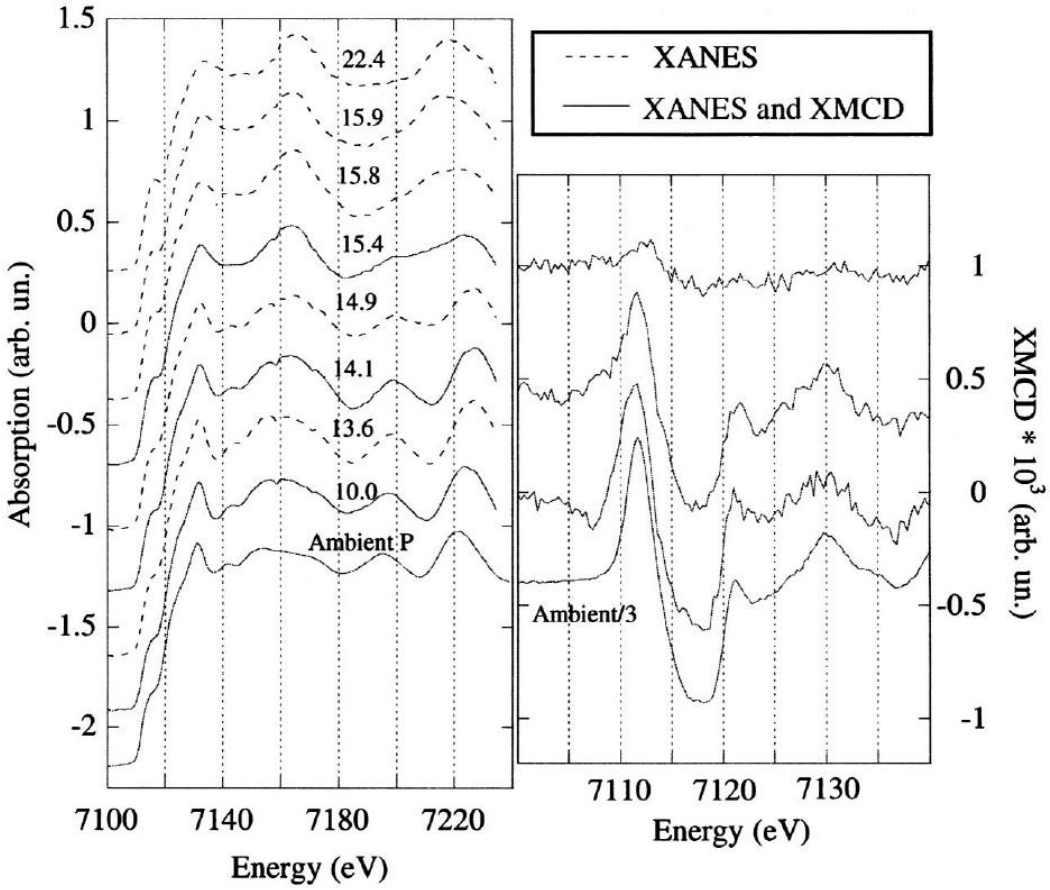
Sodium

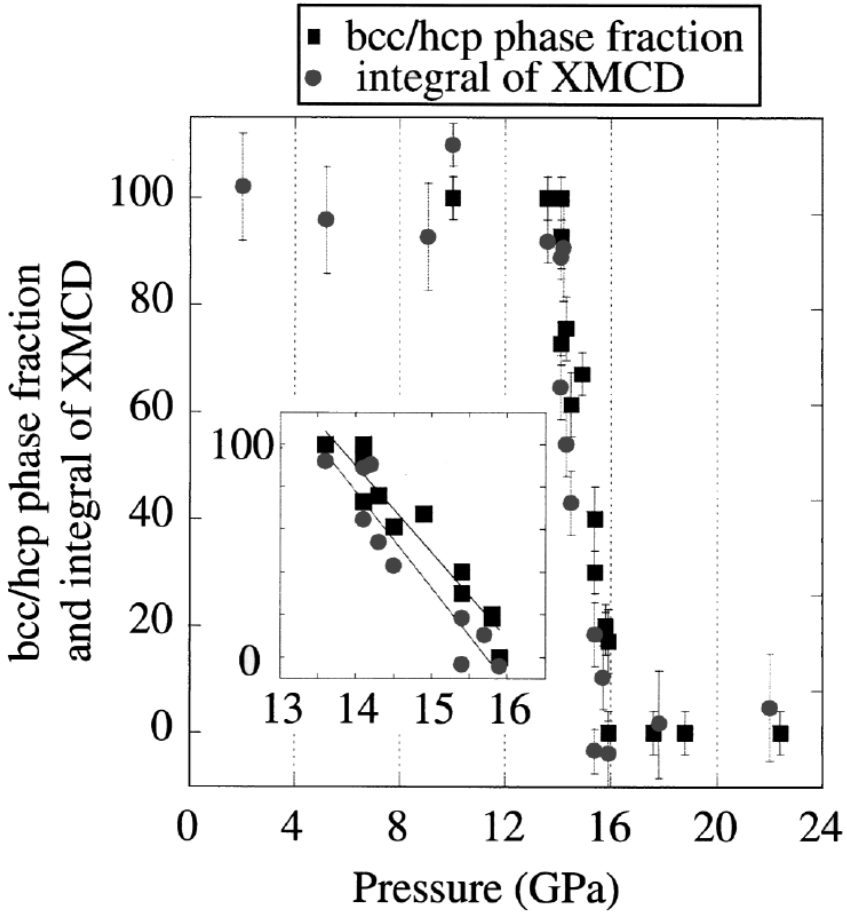
- Theoretical structure searches
- d.h.c.p. structure squeezed along c axis (hP4)
- Na atoms are 6-fold coordinated
- The electronic structure shows an insulating state
- The compression causes the 3d bands to rapidly drop in energy relative to the 3p bands and increasingly hybridize with them.
- The insulating state arises from the strong localization of valence electrons in the interstices of Na-hP4 enabled by p-d hybridization





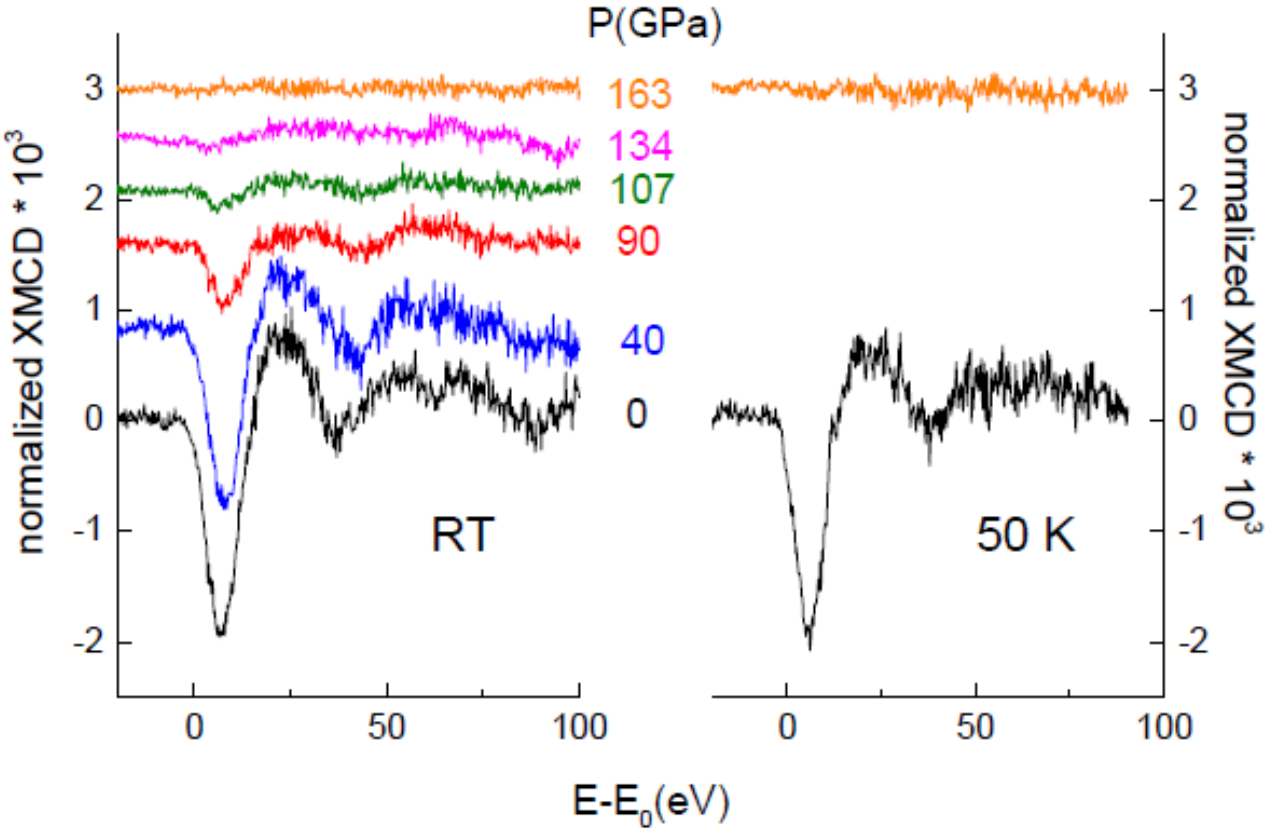
Collapse of ferromagnetism: iron





- FM bcc to non-FM hcp transition in the 13-16 GPa range
- The origin of the instability of the bcc phase can be attributed to the suppression of magnetism caused by pressure

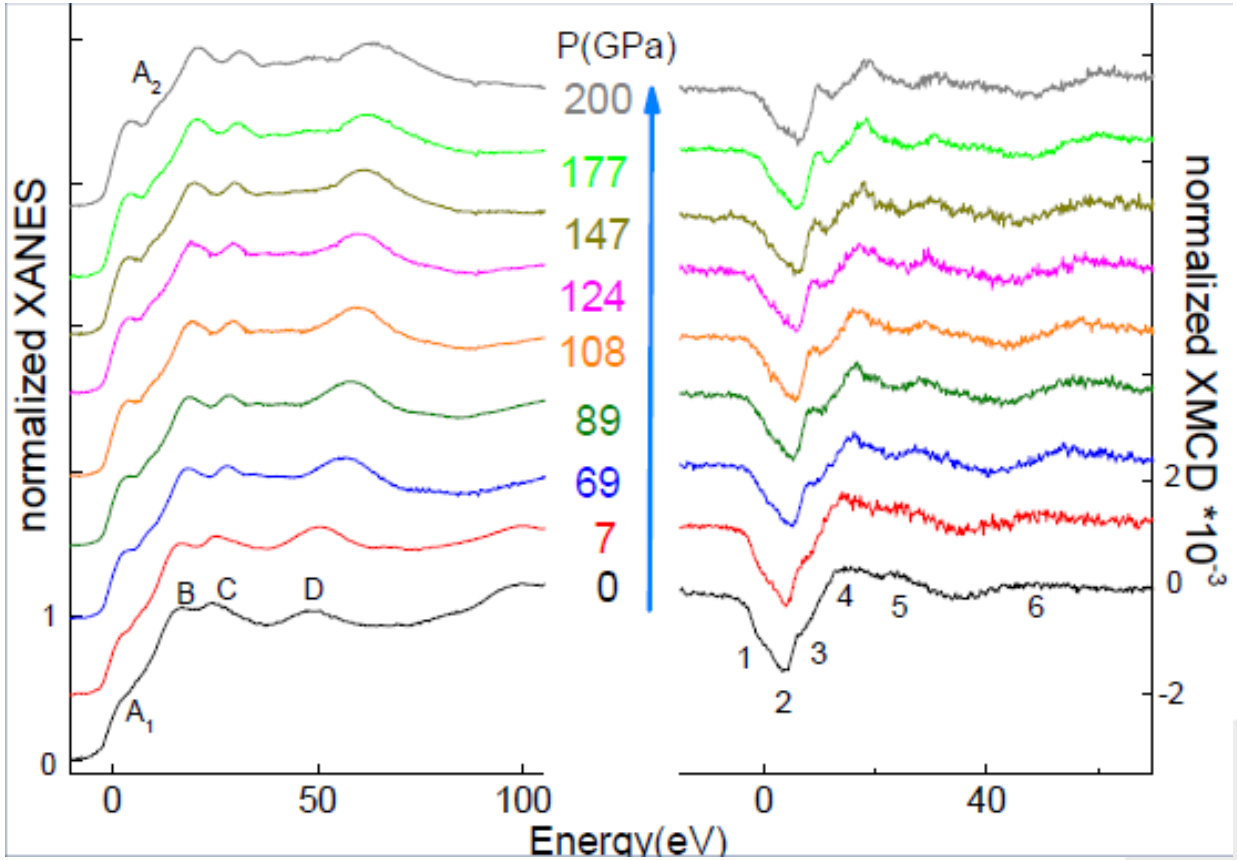
Collapse of ferromagnetism: Co



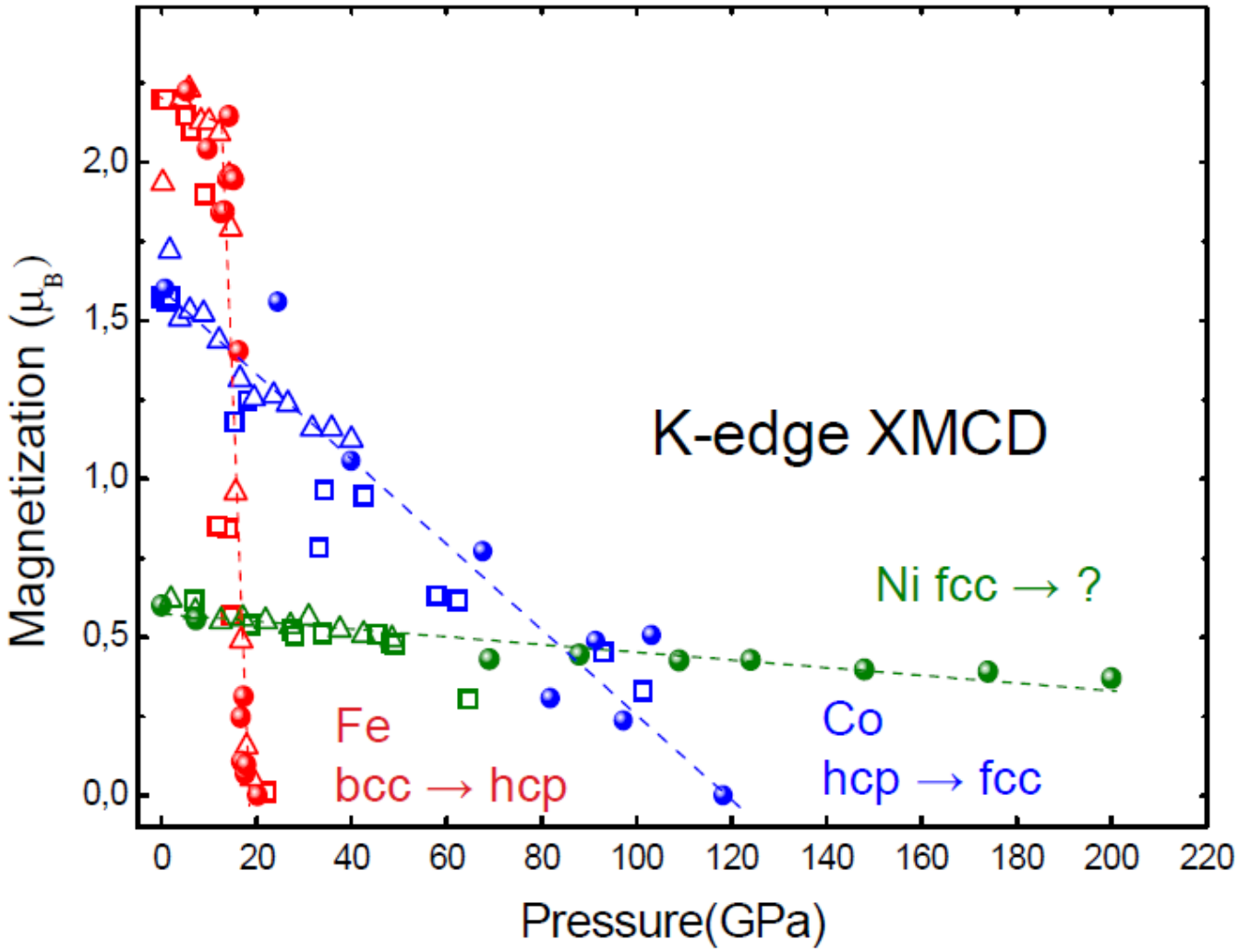
- FM is suppressed at P>130 GPa in mixed hcp-fcc phase
- No re-appearance of the signal at low temperature (50 K), indicating that the high pressure state is likely non-magnetic

Collapse of the magnetism: Ni

- No structural changes are observed up to 200 GPa
- Fcc Ni is still FM at 200 GPa
- Comparisons with DFT calculations expects a collapse of FM above 400 GPa



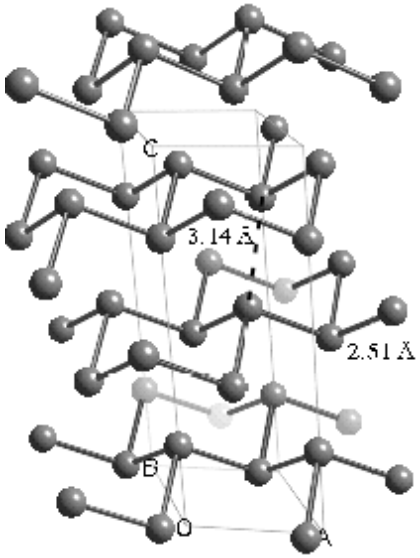
Collapse of ferromagnetism: summary



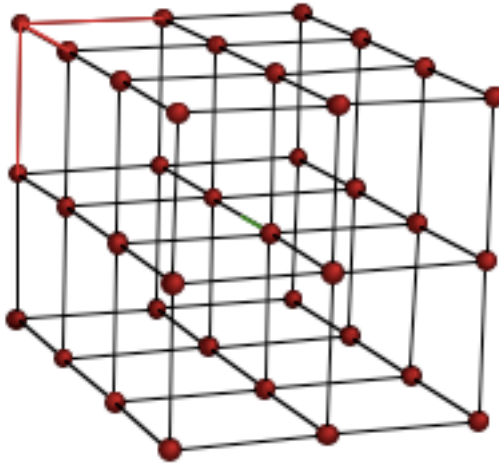
Loss of magnetism drives structural changes

Phase transitions to simpler structures

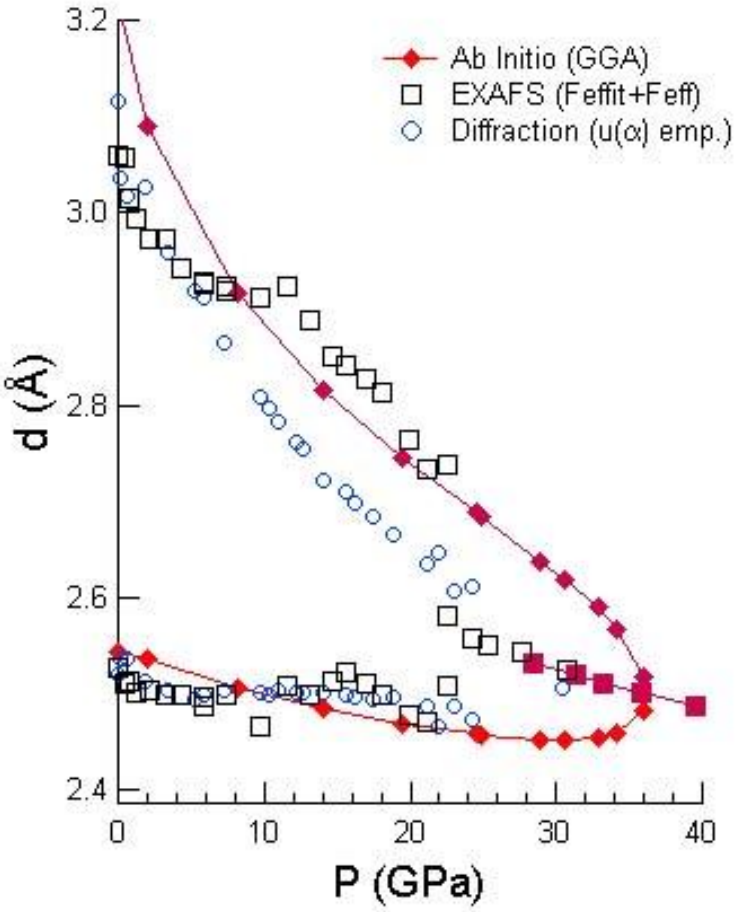
Arsenic



rhombohedral

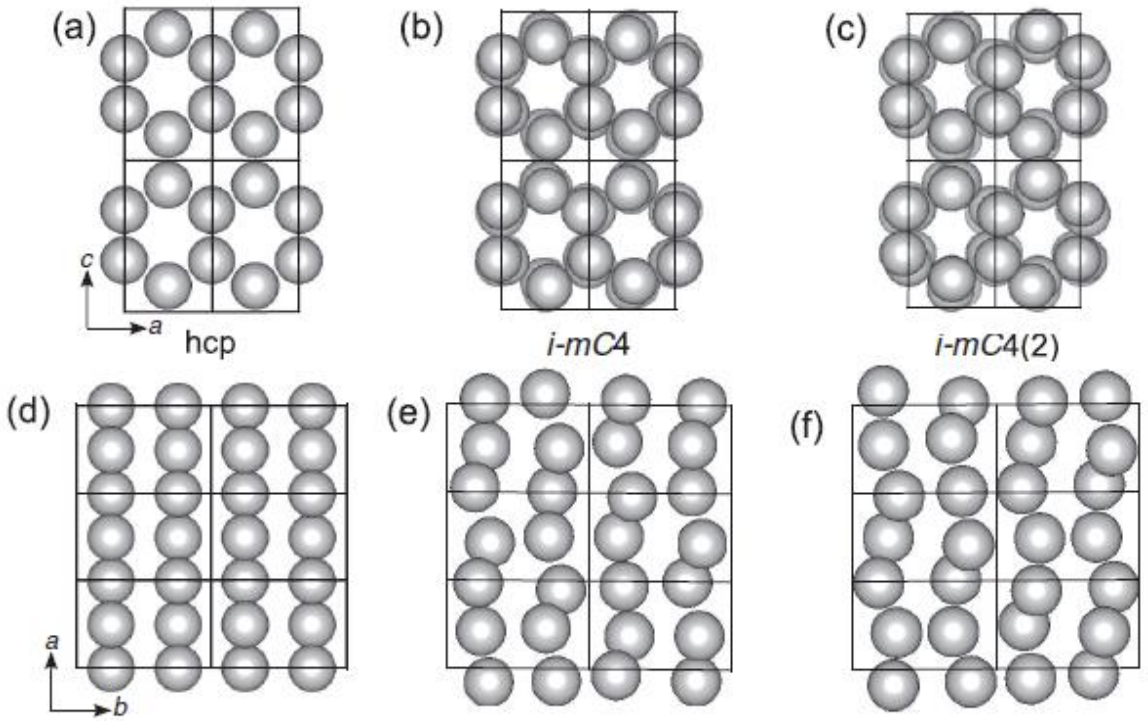


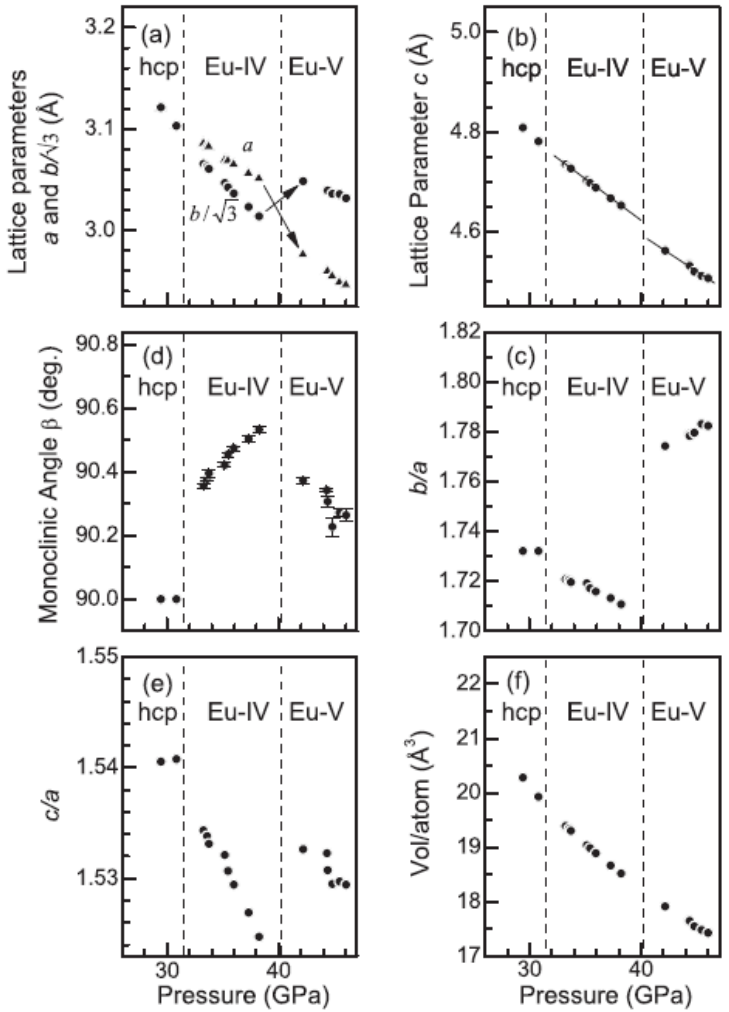
Simple cubic



Phase transitions to more complex structures

Europium: incommensurate to incommensurate phase transitions



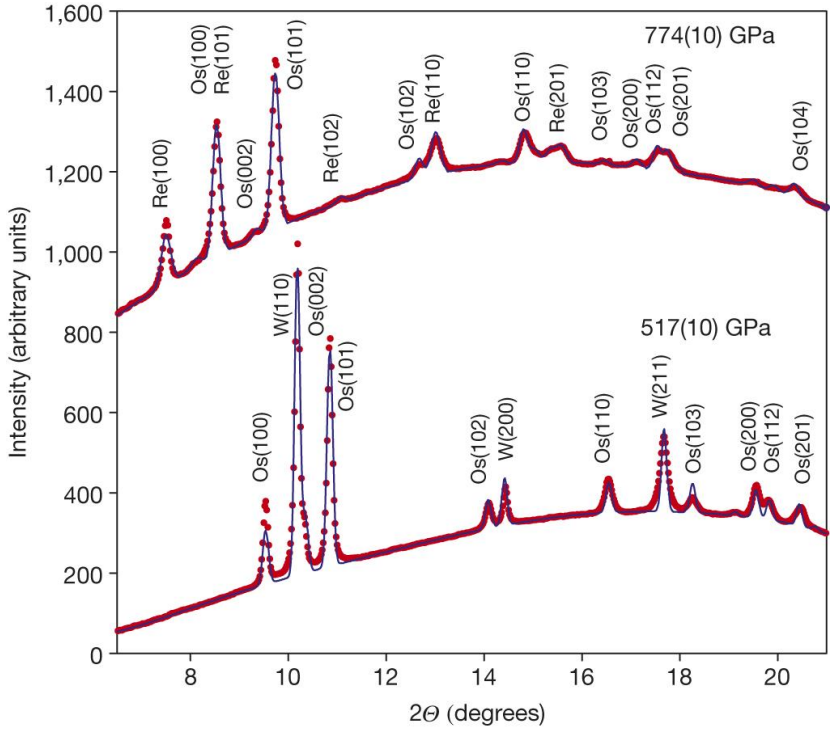


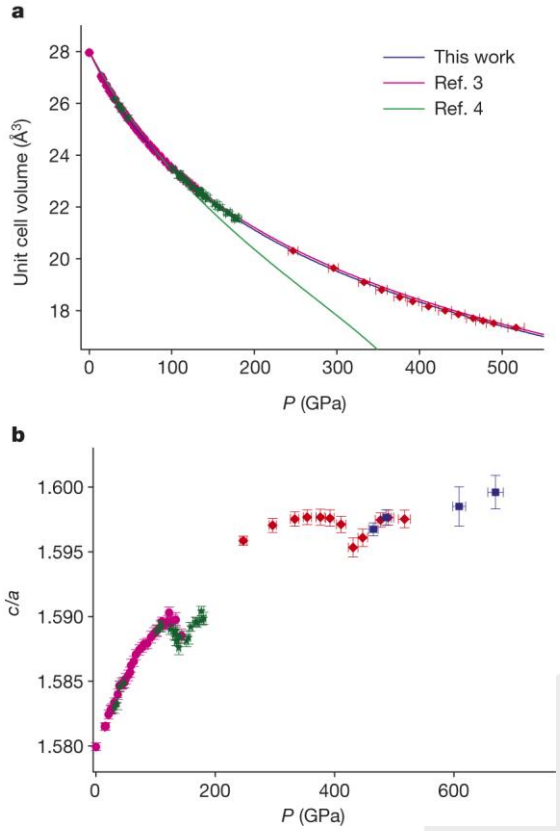
A incommensurate structure is a structure in which a superstructure is displaced with respect to the basic lattice at non simple fraction.
This gives rise to an aperiodicity.

No phase transitions

Osmium to 770 GPa

- At ambient, Os has the highest density, one of the highest cohesive energies and melting temperatures. Very incompressible
- Os retains its hexagonal close-packed structure upon compression to over 770 GPa





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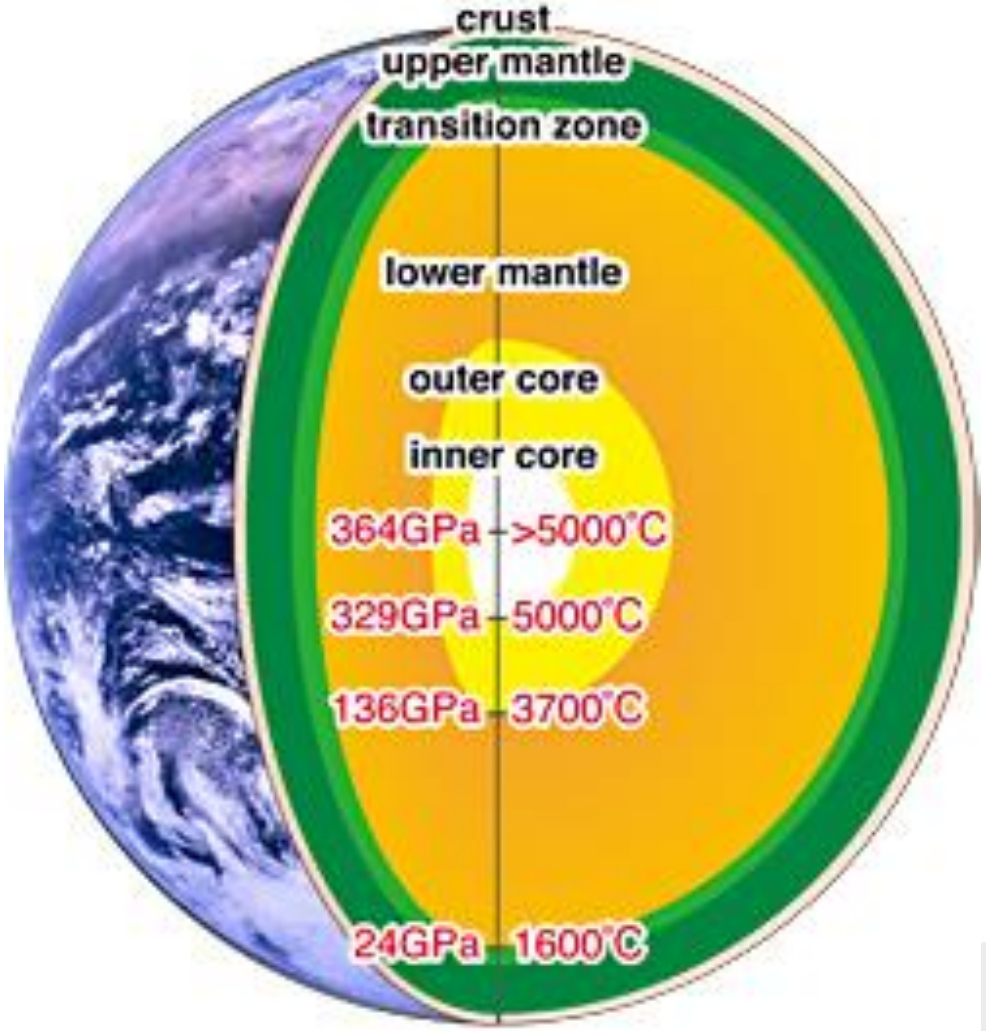
Pressures inside the Earth

10^3 atm= kbar

10^6 atm = Mbar

10 kbar= 1 GPa

1Mbar= 100 GPa



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Earth's interior activity

Earthquakes and volcanic eruptions result from chemical reactions and motions in Earth's mantle, the stony region from a few tens of km depth beneath the continents to almost 3000 km in depth.

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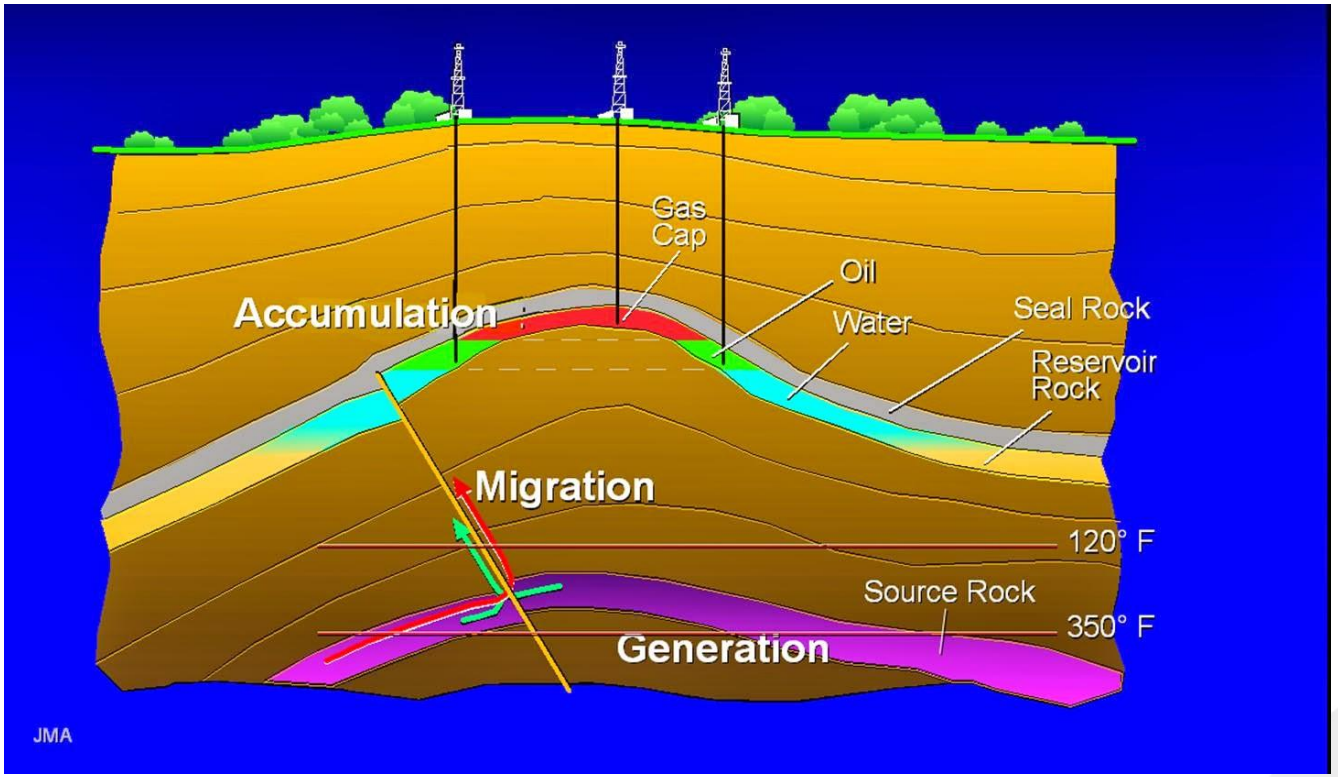
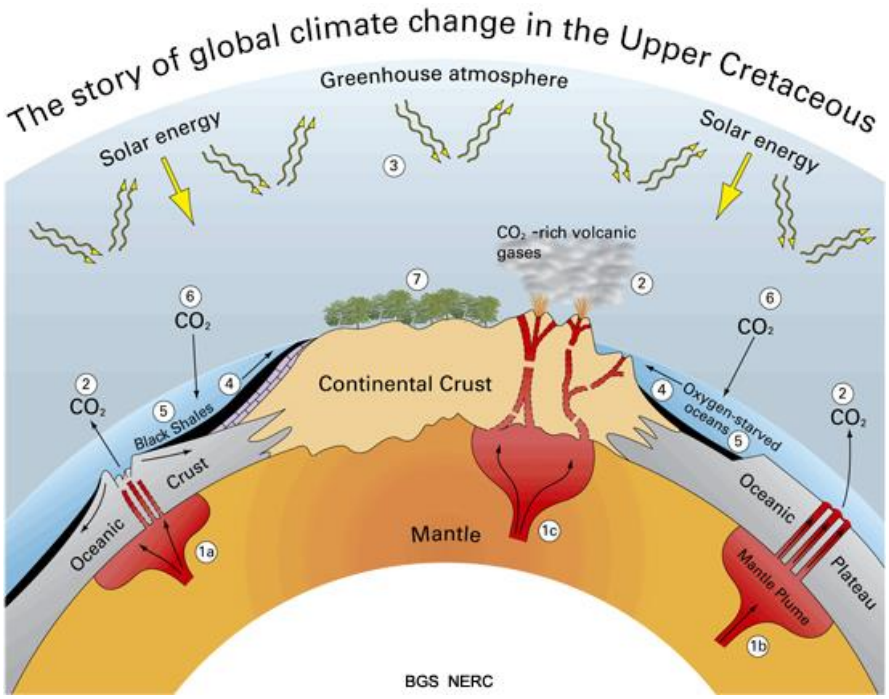
At the crust

Buried at shallow levels beneath the ocean floor and preserved by high pressures in the sediments are the greatest known deposits of hydrocarbon energy resources.



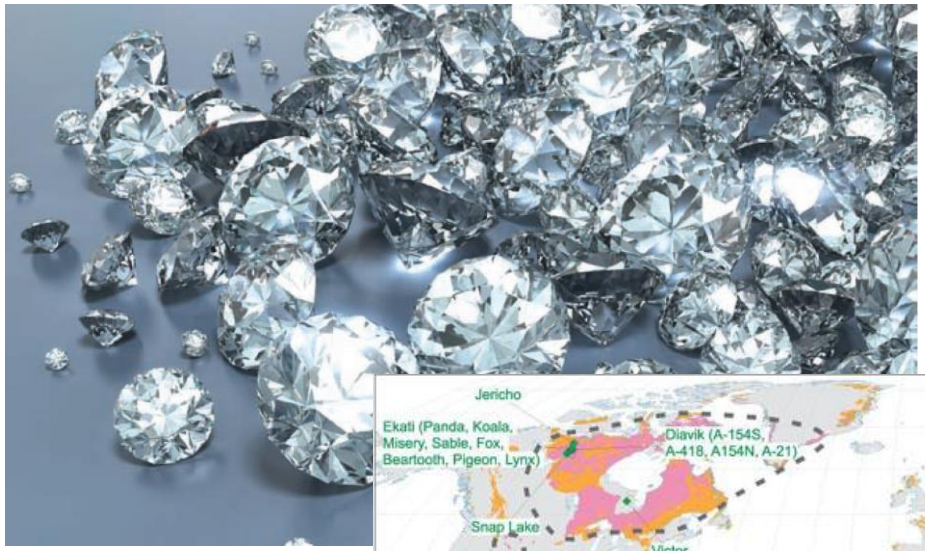
At the mantle

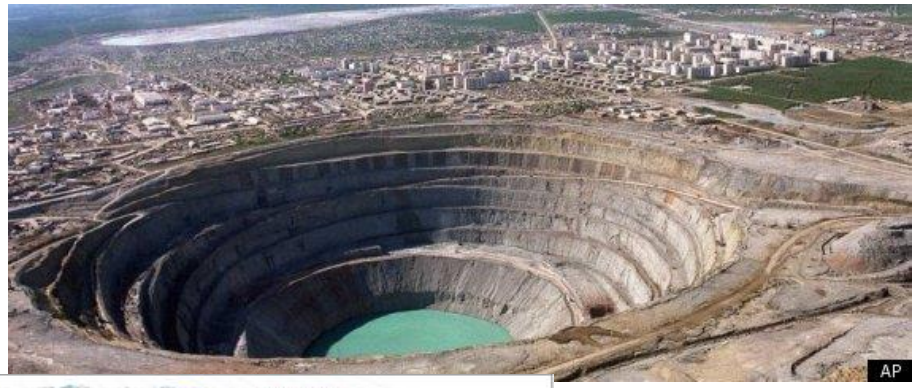


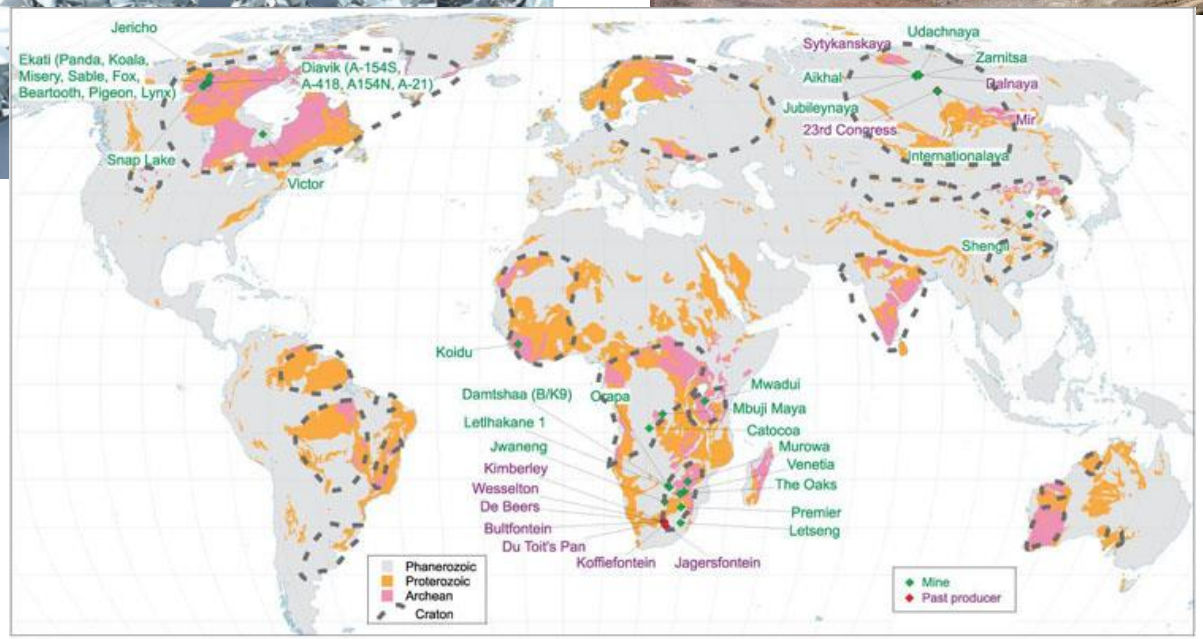
- Earth's mantle likely contains far more water and carbon dioxide than is present in all the world's oceans and atmosphere combined
- Mantle processes have probably had a strong influence on the quantity of carbon dioxide - a major greenhouse gas - present in the atmosphere

Carbon reservoir

Direct evidence of carbon reservoirs in the mantle can be seen in diamonds







Global distribution of kimberlite hosted diamond mines and major Archean cratons. *Source: Geological Survey of Canada*

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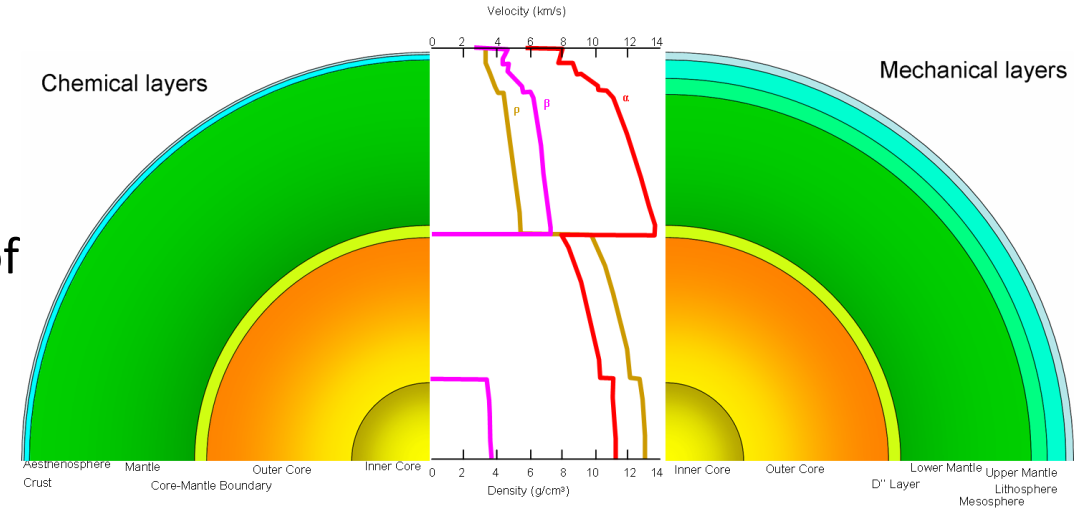
How to observe

- No borehole has ever pierced Earth's thin crust due to the high temperatures and pressures existing at depth
- Our information about the Earth's interior came from study of Earthquake shock waves, complemented by cosmochemistry and mineral physics

Volcanoes bring materials to the surface from depths of ~ 100 km

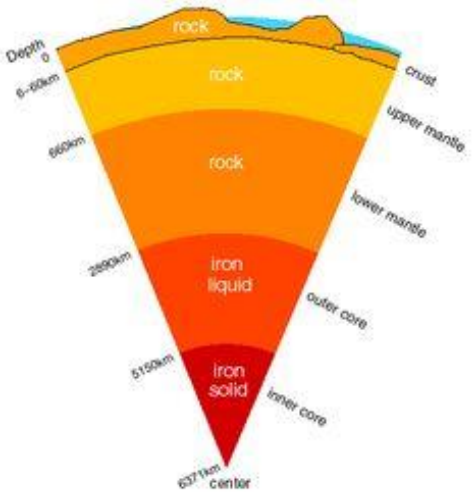


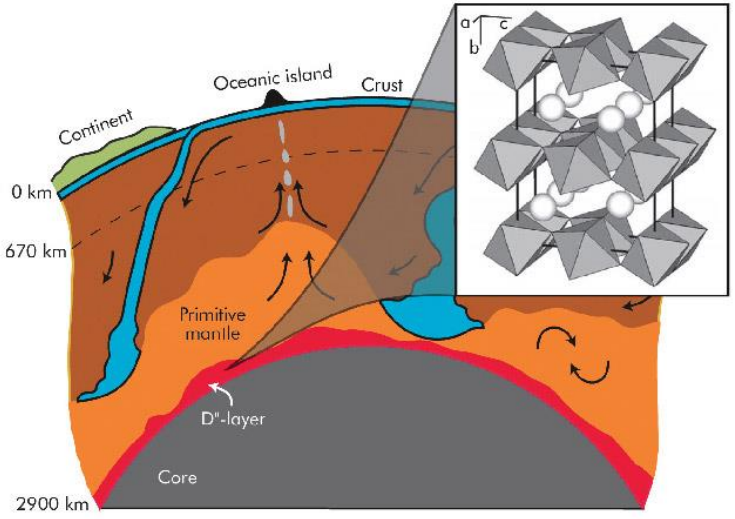
Diamonds may come from ~ 400 km

By studying how long it takes waves to pass through Earth (travel times) we worked out a model for the internal structure of the planet

Earth complexity

- The last two decades have brought unprecedented advances in understanding Earth's interior as well as other planetary bodies in our solar system and beyond
- The simple layered models depicted in textbook diagrams are being replaced with more sophisticated models that show the complexity and dynamics of Earth's interior

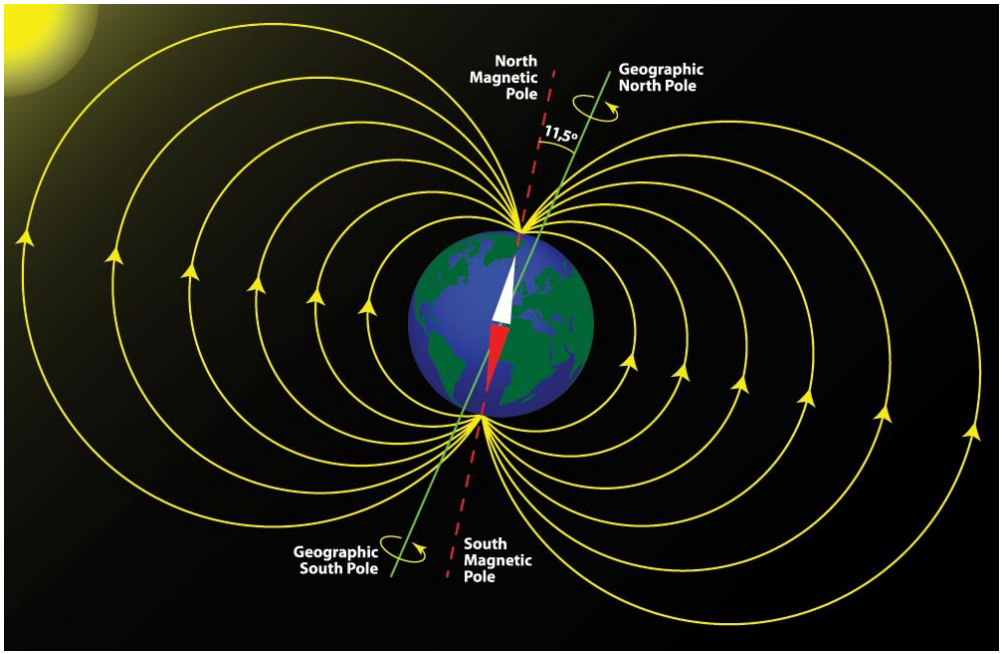


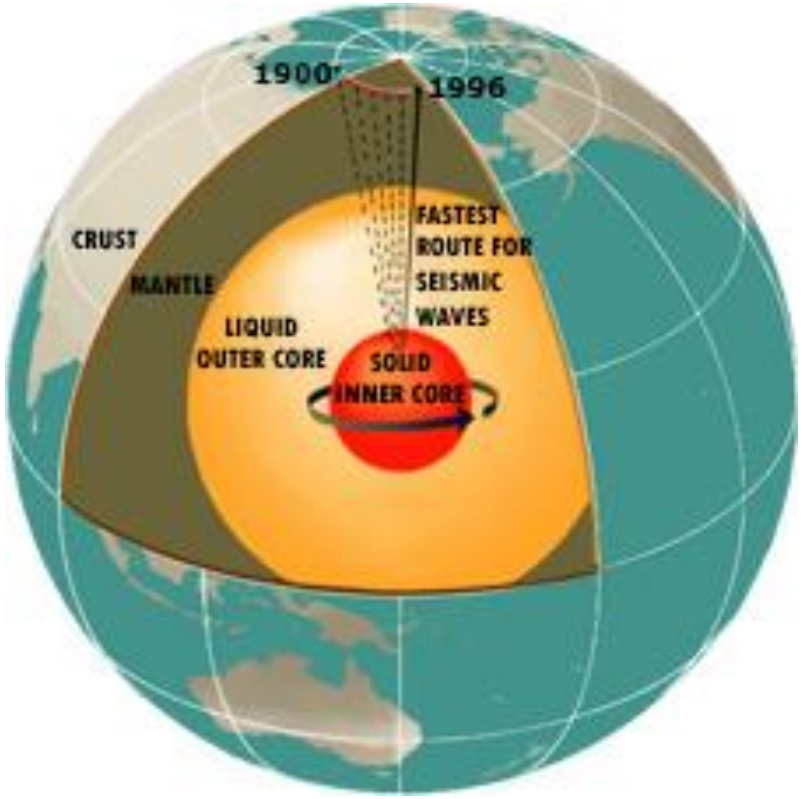


- The features of this internal system give us clues as to how the interior works – for example how material moves, how heat is transported and what it is made of – and how Earth developed to this state.

Magnetic field

We now know that motions in Earth's metallic core are responsible for the magnetic field at the surface





Computer simulations show liquid metal flow in the outer core can generate a magnetic field like Earth's

Earth's interior conditions in the lab

- One of the greatest achievements of high pressure science has been the ability to reach pressures and temperatures of Earth's core in the laboratory
- This pressure regime is from 130 GPa at the boundary between the rocky mantle and the liquid core (or Core Mantle Boundary - CMB) to 360 GPa at Earth's center
- Today not only it is possible to reach these pressures, but samples can be heated to core temperatures (~ 6000 K) using focused laser beams, while probing the atomic, electronic and magnetic structures using XRD, XAS and other SR-based techniques
- Sophisticated quantum mechanical calculations can be performed to simulate the behavior of minerals and iron at the relevant P and T conditions.

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High pressure for geophysics

- Any realistic interpretation of the geophysical observations requires accurate knowledge of the properties of candidate materials under extremely high pressures and temperatures
- For example, to understand the cause of seismic anisotropy of the inner core and how core material deforms in response to various forces, we need to know the elastic constants of iron under inner core conditions

Elastic constants

Elastic constant using Inelastic x-ray scattering

Contents lists available at ScienceDirect

Earth and Planetary Science Letters

journal homepage: www.elsevier.com/locate/epsl

Composition of the Earth's inner core from high-pressure sound velocity measurements in Fe–Ni–Si alloys

Daniele Antonangeli [a,b,*], Julien Siebert [a,b], James Badro [a,b], Daniel L. Farber [b,c], Guillaume Fiquet [a], Guillaume Morard [a], Frederick J. Ryerson [b]

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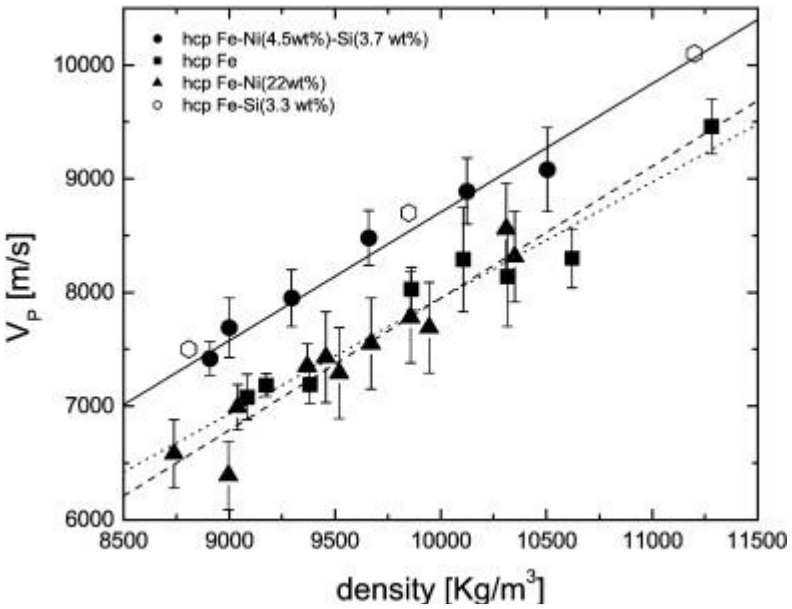

A B S T R A C T

We performed room-temperature sound velocity and density measurements on a polycrystalline alloy, $Fe_{0.89}Ni_{0.04}Si_{0.07}$, in the hexagonal close-packed (hcp) phase up to 108 GPa. Over the investigated pressure range the aggregate compressional sound velocity is ~9% higher than in pure iron at the same density. The measured aggregate compressional (V_P) and shear (V_S) sound velocities, extrapolated to core densities and corrected for anharmonic temperature effects, are compared with seismic profiles. Our results provide constraints on the silicon abundance in the core, suggesting a model that simultaneously matches the primary seismic observables, density, P-wave and S-wave velocities, for an inner core containing 4 to 5 wt.% of Ni and 1 to 2 wt.% of Si.

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Outline

- Introduction
- Effects of pressure
  - Insulator to metal transitions
  - Metal to insulator transitions
  - Effects on magnetism
  - Structural phase transitions
- High pressure and Earth's science
- Tools and methods
- Examples of high pressure studies using XAS
  - Polyamorphism in glassy GeO_2
  - Melting of iron at megabar pressures
  - Revealing Earth's interior
- Bibliography

Static compression methods

- Large volume press
  - Large sample volume (mm^3 - cm^3)
  - Bulky facilities (many tons)
  - P max ~ 60 GPa
  - T max ~ 2000 K

- Paris- Edinburgh press
  - Large sample volume (mm^3)
  - Relatively compact ~ 100 kg
  - P max ~ 30 GPa
  - T max ~ 2000 K

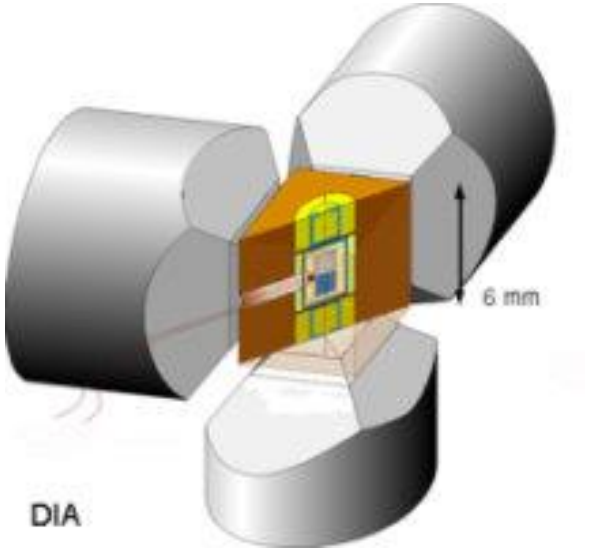
- Diamond Anvil Cell
  - Small sample volume (< 10^{-4} mm^3)
  - Compact < 1kg
  - P max ~ 800 GPa
  - T max ~ 6000 K

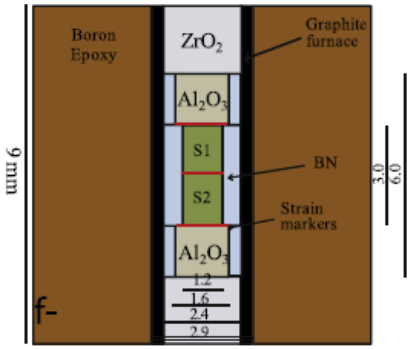
Large volume press

Id06 - ESRF

2000 Tonnes force

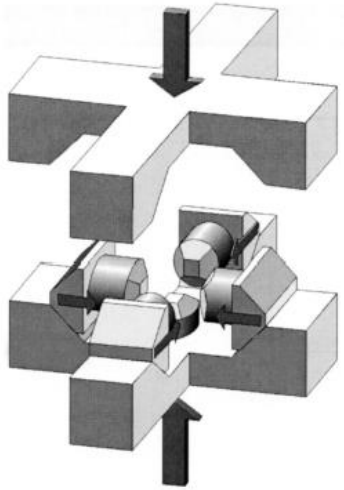
20 GPa, 2000 K





DIA module

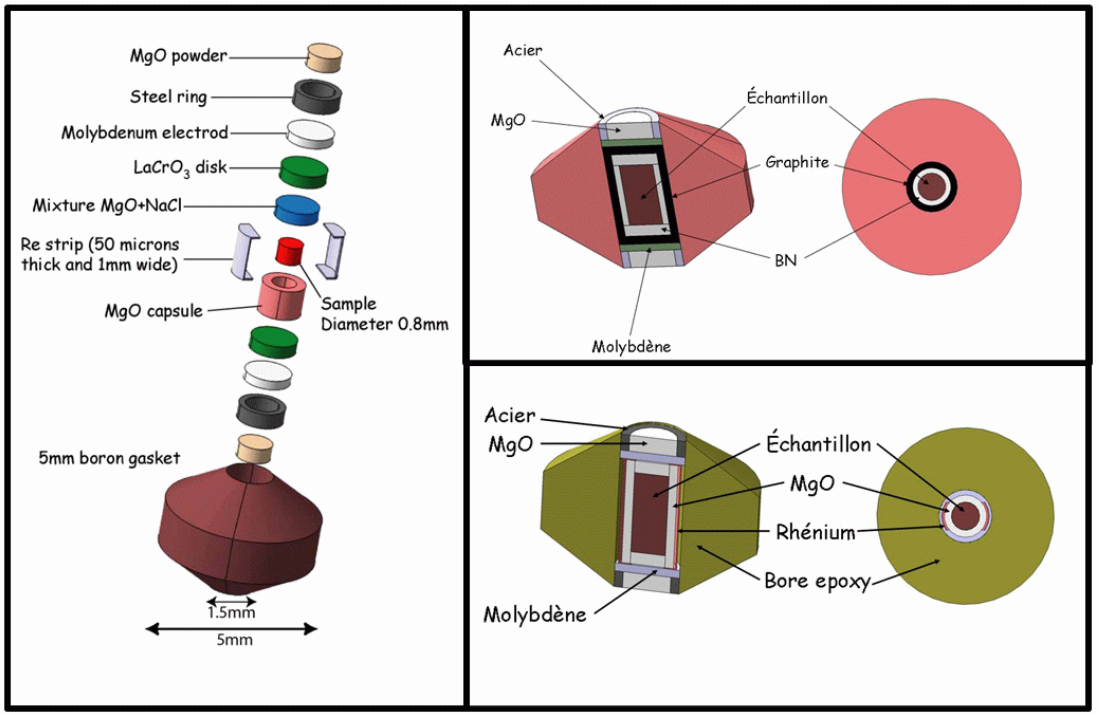
The cubic setup compressed between 6 anvils

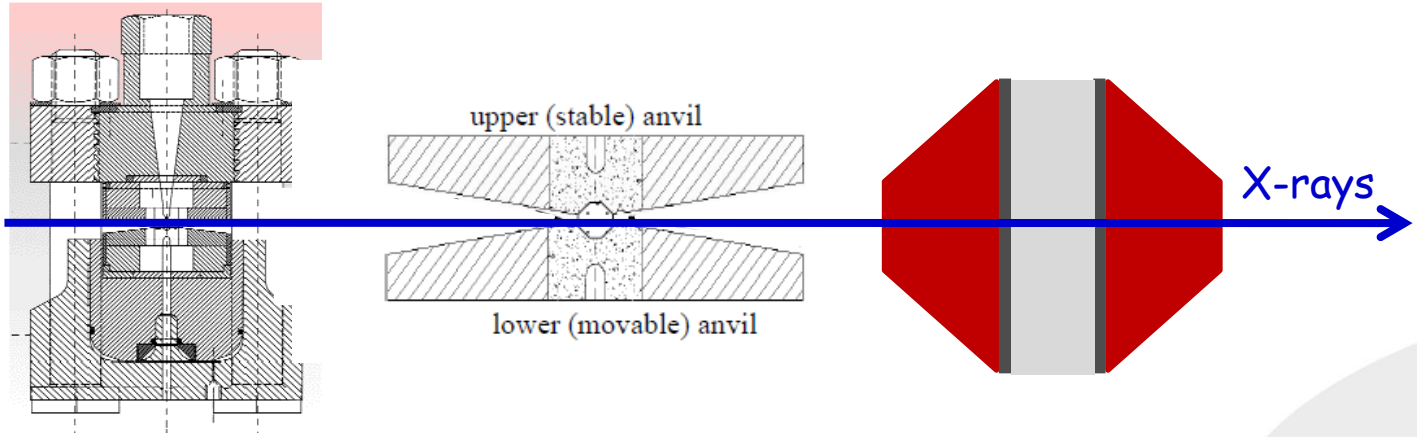


D-DIA

Top and bottom anvils can be moved independently allowing deformation experiments to be performed under upper mantle P-T conditions

Paris-Edinburgh press

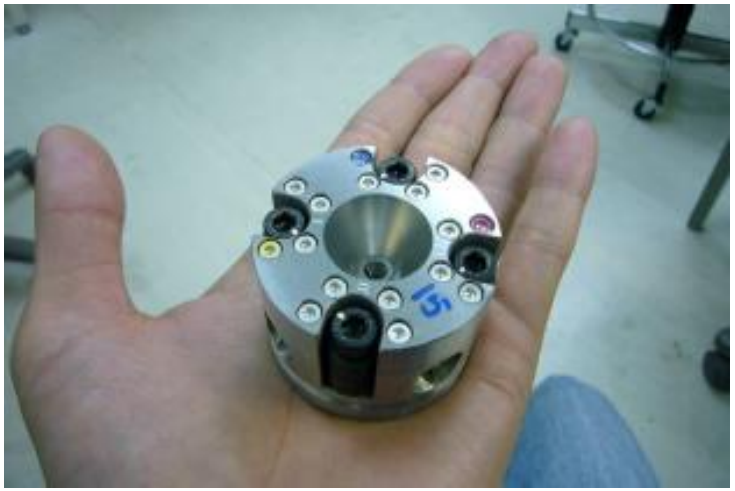


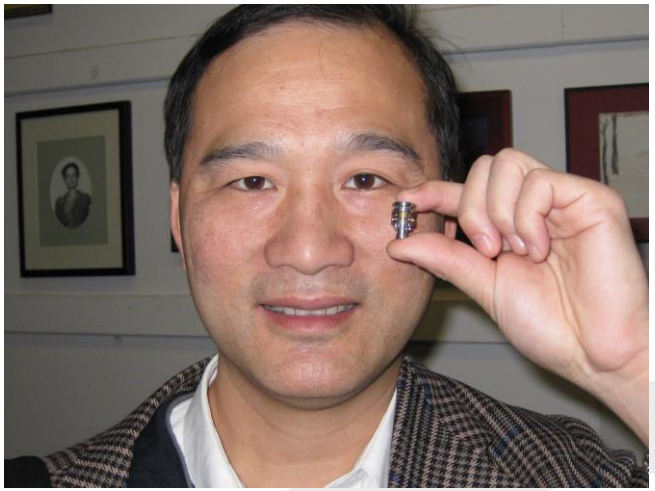


Diamond anvil cell

- The DAC allows to reach the highest static pressures
- The first DAC was designed and constructed at the National Bureau of Standard (1959)
- DAC can fit into the palm of the hand and can generate pressures above 700 GPa

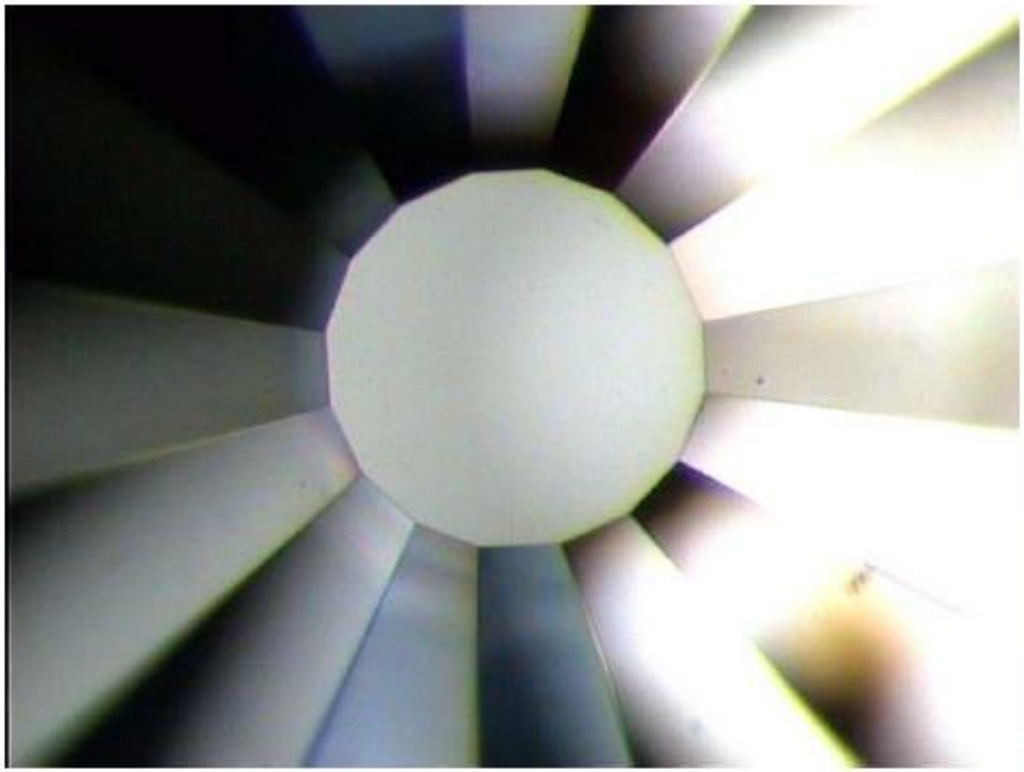
- 100 GPa in 1976
- 200 GPa in 1985
- 300 GPa in 1990
- 400 GPa in 2007
- 640 GPa in 2012
- 770 GPa in 2015

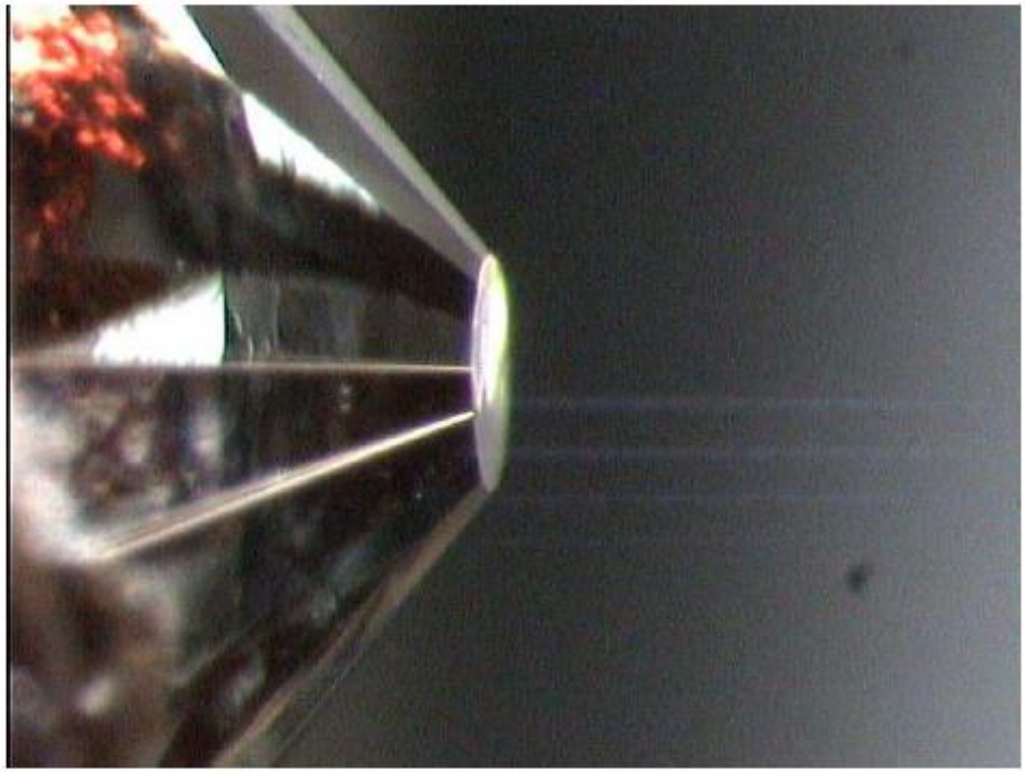




DAC: the anvils

Two gem-quality single crystal (now also polycrystalline) diamonds with flat surfaces serve as anvil faces



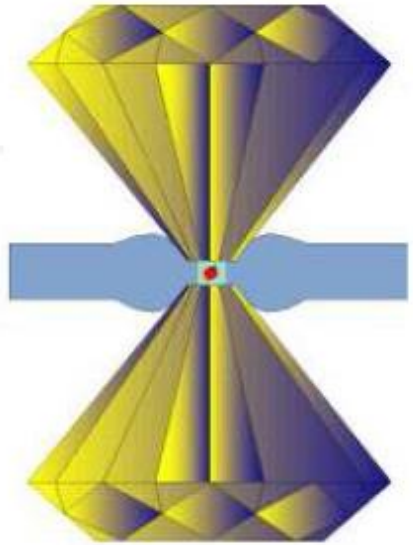


DAC: the principle

The diamonds are mounted so that the sample can be squeezed between the anvil faces

The smaller the area A of the of the anvil faces, the higher the pressure P reached by the DAC for an equivalent value of applied force F, according to $P = \frac{F}{A}$

P_{max} (GPa)	Ø flat (μm)
30	600
60	300
100	150



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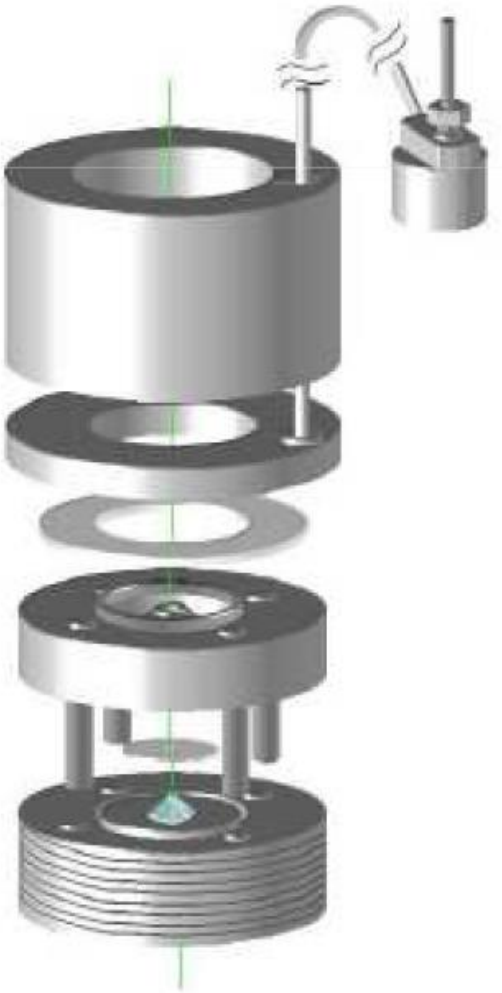
DAC: the pressure

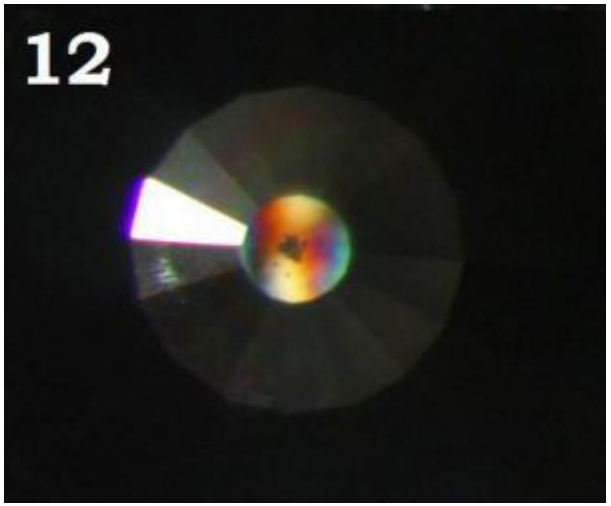


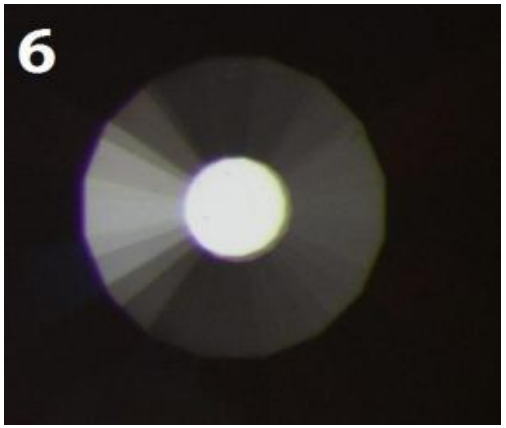
- To apply pressure, the anvils must have a high degree of parallelism.
- One of the diamond anvils is usually mounted on the end of a sliding piston, while the other is stationary
- A cylinder guides the piston so that the anvil faces meet very precisely
- The piston is pushed by a mechanical device such as a screw or a small hydraulic ram, thus driving the two anvils together

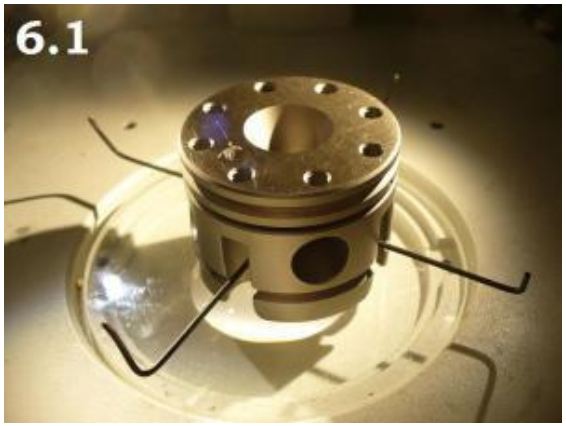
DAC: the alignment

The adjustment procedure is made under microscope

The concentricity is achieved moving the support of the piston diamond slightly to superimpose the two polygons corresponding to the faces of the anvils







The parallelism is checked by observing the interference fringes that appear when the two anvils are not parallel

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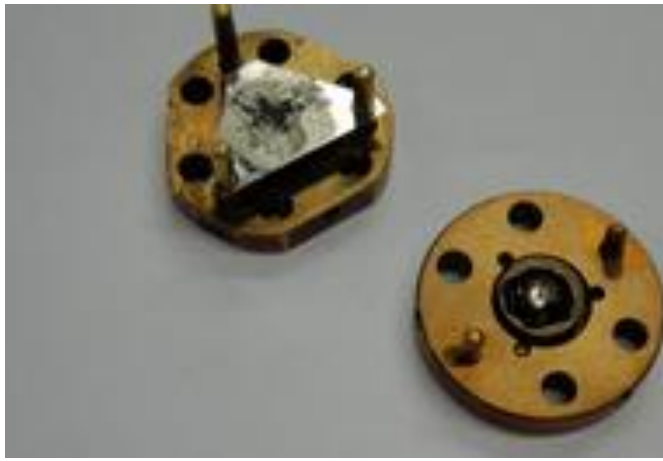
DAC: different models



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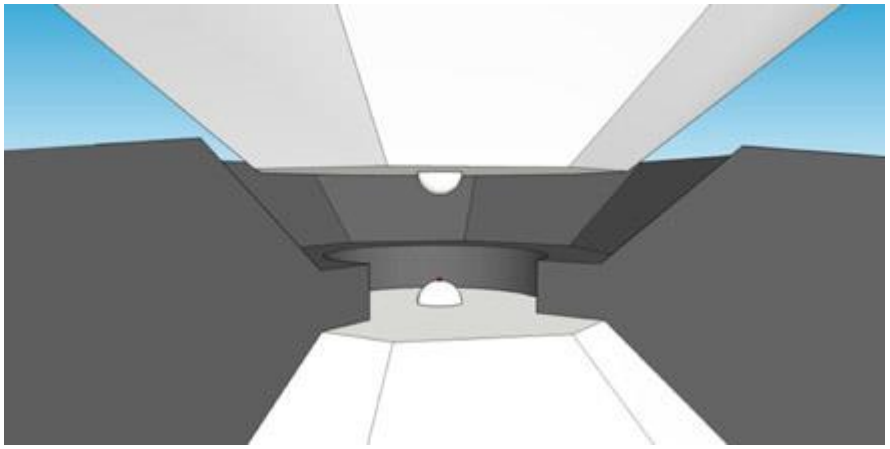
DAC for ultrahigh pressures

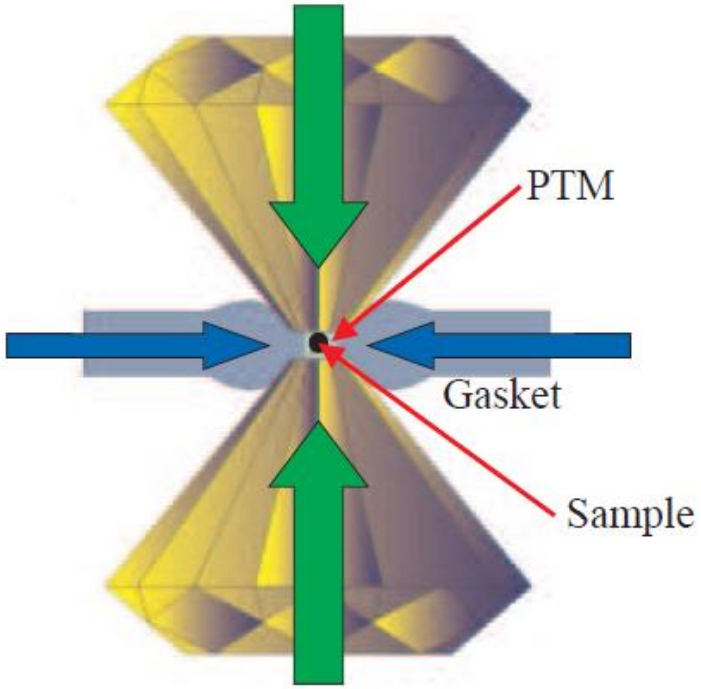
Double-stage diamond anvil cell

- Micro-anvils of 10 to 20 μm in diameter made of nanocrystalline diamonds
- These nanocrystals, which are diamond grains of a nano-size, are bound together forming a bulk micro-anvil
- The many grain boundaries make the nanocrystalline anvils even harder than single crystal diamonds, extending the range of static pressure in experiments from about 400 GPa to 770 GPa at room temperature

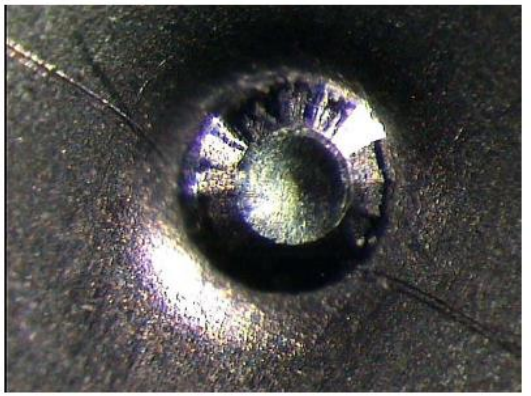


Gaskets - 1

- When the sample is placed between the anvil faces, as the anvils are forced together, the sample is trapped and develops a uniaxial pressure, whose distribution ranges from a maximum at the center to essentially zero pressure at the edge of the sample area
- In order to have an isotropic pressure distribution the sample must be embedded and confined in a pressure transmitting medium softer than the sample.
- To encapsulate the sample and the hydrostatic medium, both are placed in a small hole drilled in a metallic gasket



Gasket - 2



- The gasket consists of a metallic foil of typically 200 µm of thickness
- To increase the hardness of the metal, the foil placed between the two diamonds and is indented to about 30-60 µm.
- The higher the pressure that has to be achieved during the experiment, the higher the pre-indentation pressure and the smaller the final gasket thickness (and sample volume)

flat diameter (μ)	indentation thickness (μ)	P max (GPa)
>500	50-60	< 20
300	40-45	50-70
150	25-30	100-150
< 100	20-25	>150

- A hole in the pre-indented gasket is then drilled by electro-erosion or by a laser. The diameter of the hole depends critically on the diameter of the diamonds, and it is typically one third the diameter of the flat of the diamond

Pressure transmitting medium

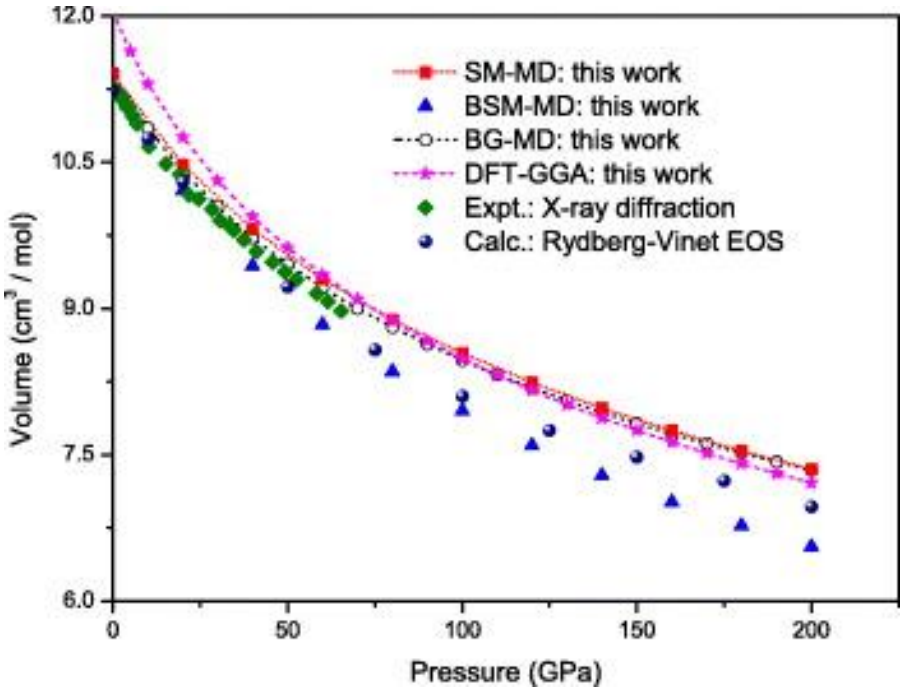
- The uniaxial compression of diamonds acts directly on the media that transmit hydrostatic pressure to the sample
- If the PTM solidifies, the hydrostatic conditions inside the cell volume are no longer achieved and the sample is subject to a pressure gradient: i.e. the stress is not uniform in all directions
- The variation of stress conditions at different points in the sample depends upon the strength of the PTM
- It is desirable to eliminate or reduce the pressure anisotropy and inhomogeneity in some HP experiments
- The PTM must not chemically react with the sample and must not interfere with the measurement of the sample

Typical pressure transmitting media

- Liquids (alcohol, alcohol mixtures (Me-Et 4:1), silicone oil)
  - Easy, fast, available
  - Low hydrostaticity limit (< 10 GPa)
- Soft solids (alkali halides, NaCl, KBr, etc)
  - Easy, good for laser heating, good insulation, can be annealed at high P, easy, available
  - Hydrostatic below 7-8 GPa, can react, hydroscopic
- Hard solids (MgO, Al2O3, etc)
  - Good thermal insulator for laser heating experiments
  - Nonhydrostatic
- Condensed gases (He, Ne, N2, Ar, …)
  - Best pressure medium for room and low temperature experiments
  - Difficult to load without gas-loading or cryogenic devices

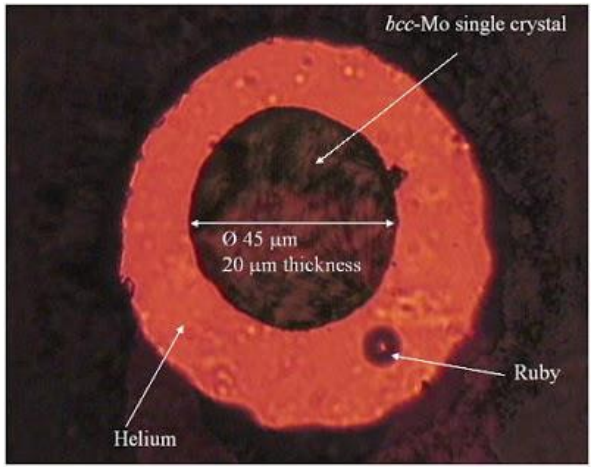
Pressure measurements in the DAC - 1

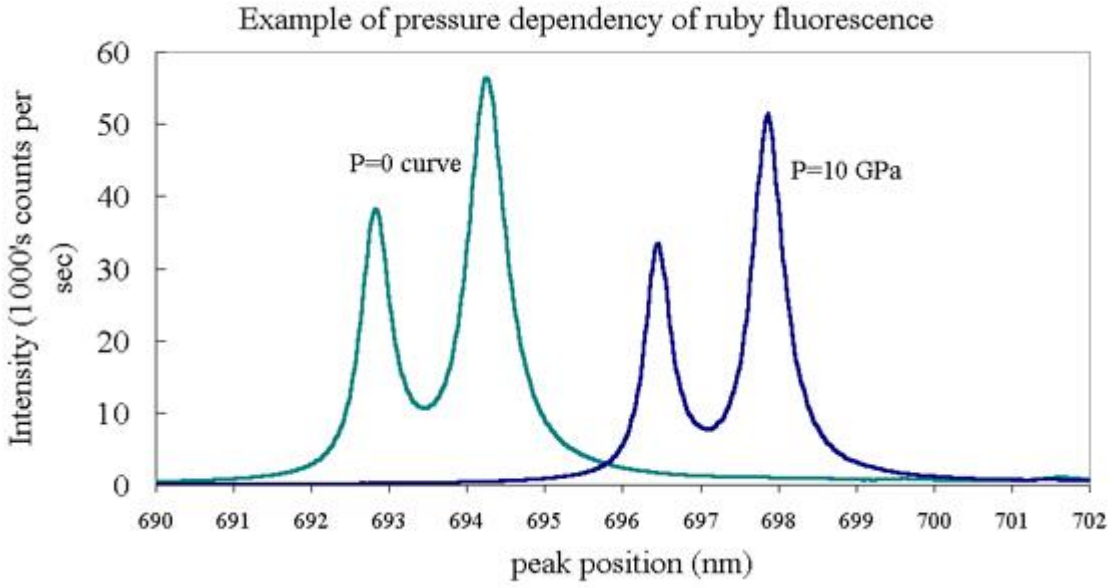
- If the experimental technique is *in situ* XRD, then the diffraction pattern of an internal standard such as NaCl or Au, can be obtained along with that of the sample
- The pressure is then determined from the lattice parameters calculated from the diffraction pattern.



Pressure measurements in the DAC - 2

- Ruby fluorescence method
- It exploits the high transparency of the diamonds to visible light





In this method a tiny chip of ruby (5-10 µm in dimensions) is placed in the pressure medium along with the sample, and its luminescence is excited by a laser. The shift in wavelength is followed as a function of pressure.

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Outline

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  - Melting of iron at megabar pressures
  - Revealing Earth's interior
- Bibliography

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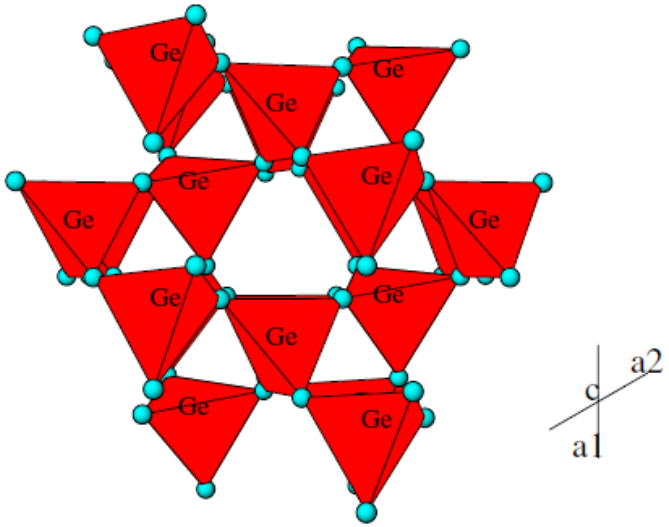
Correlation between short and intermediate range order in compressed glassy GeO_2 studied by X-ray absorption spectroscopy

Glassy GeO_2: motivation

- Chemical analogue of SiO_2
- Archetypal network-forming glass
- Pressure-driven polyamorphism



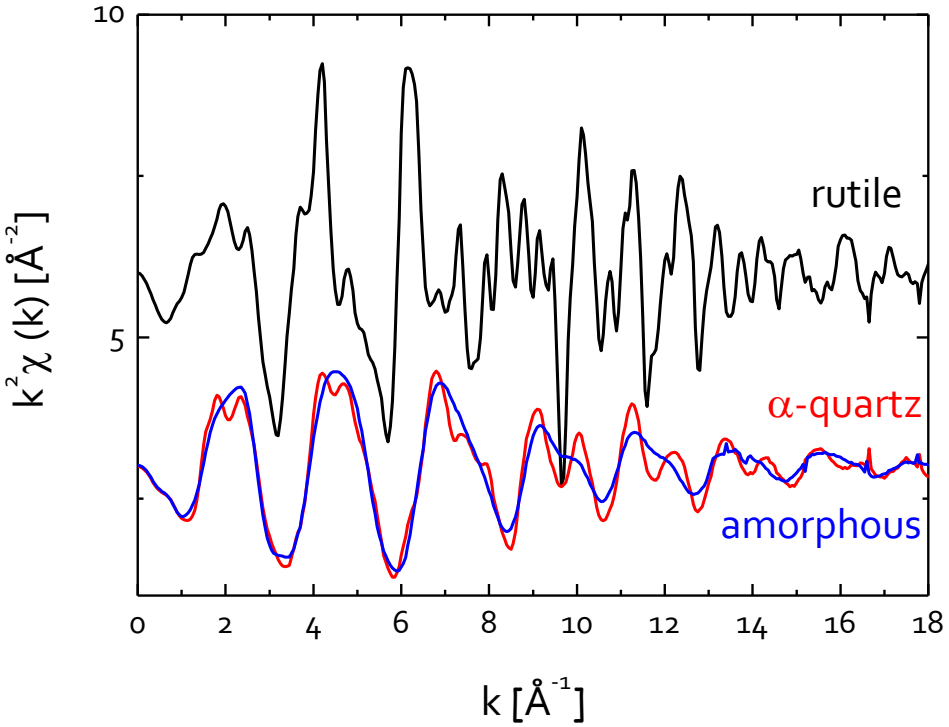


Figure 1. Projection of the α-quartz-like structure (left) and rutile-like structure (right) onto the (001) plane.

From Micoulaut, Cormier, Hendersen *JPCM* **18**, R753 (2006)

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Polyamorphism in glassy GeO_2: first evidence

VOLUME 63, NUMBER 4 PHYSICAL REVIEW LETTERS 24 JULY 1989

Pressure-Induced Coordination Changes in Crystalline and Vitreous GeO_2

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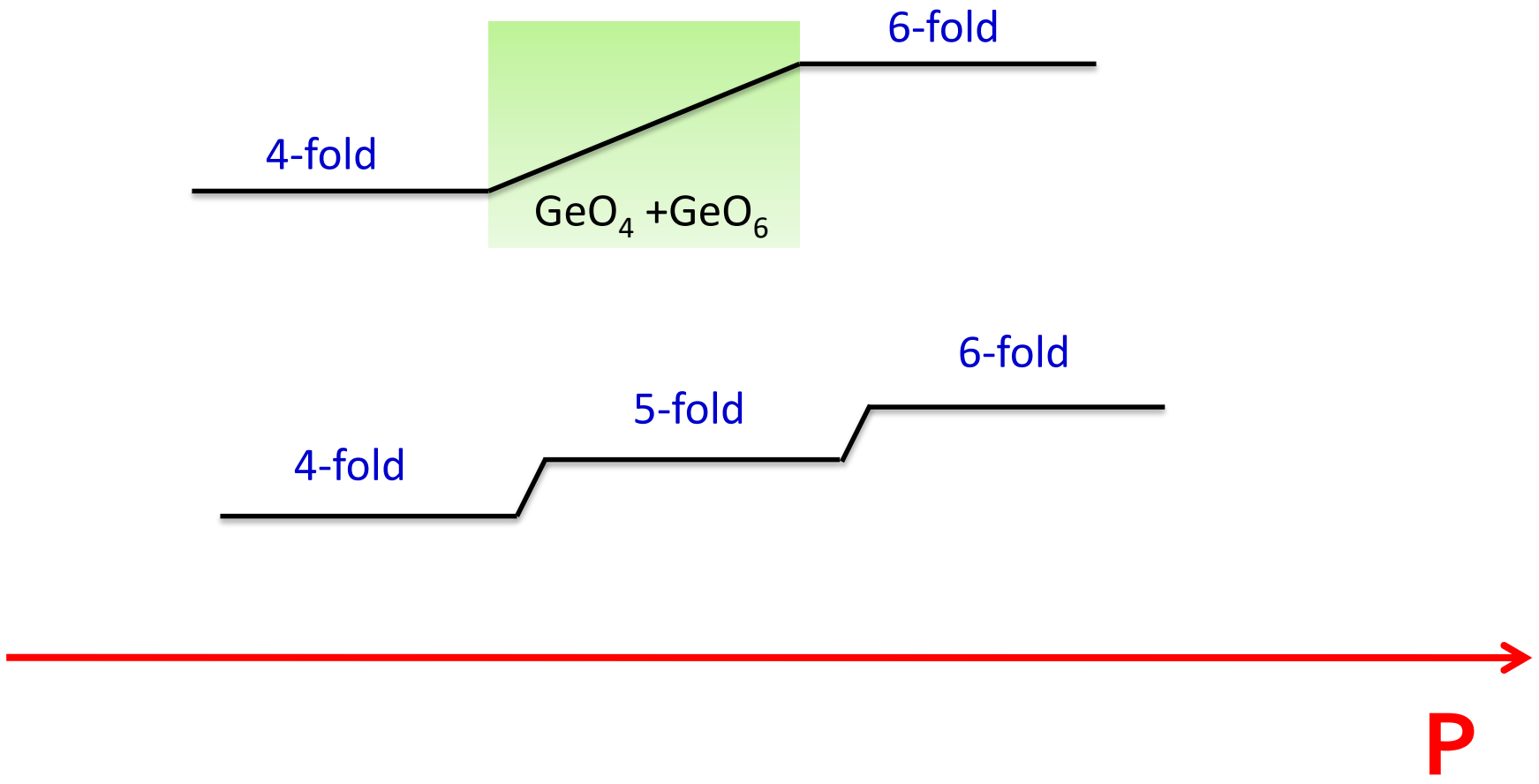
(Received 21 February 1989)

In situ high-pressure x-ray-absorption spectra have been performed on amorphous and crystalline GeO_2 using a diamond-anvil cell adapted to an energy-dispersive spectrometer. The coordination of Ge changes from fourfold to sixfold at pressures between 7 and 9 GPa. The progressive evolution of the measured Ge-O distances as well as the modification in the x-ray-absorption near-edge structure indicate two different sites rather than a progressive site modification. The phase transition observed in the amorphous phase is reversible in contrast to that observed in the crystalline form.

PACS numbers: 64.70.−p, 61.40.+b, 62.50.+p, 78.70.Dm

Compaction mechanism

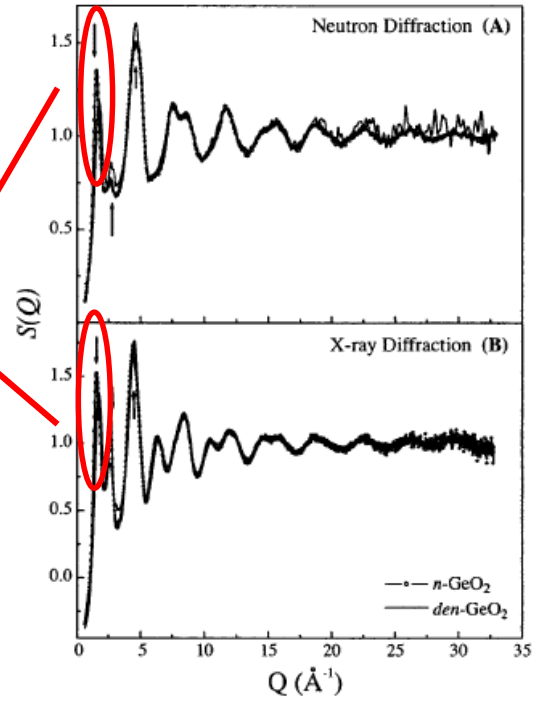


Intermediate range order

- IRO in network forming glasses with AX2 stoichiometry
- Tetrahedral units assembled in the 3D network
- Length scale periodicity: 2π/Q

At HP:

First Sharp Diffraction Peak



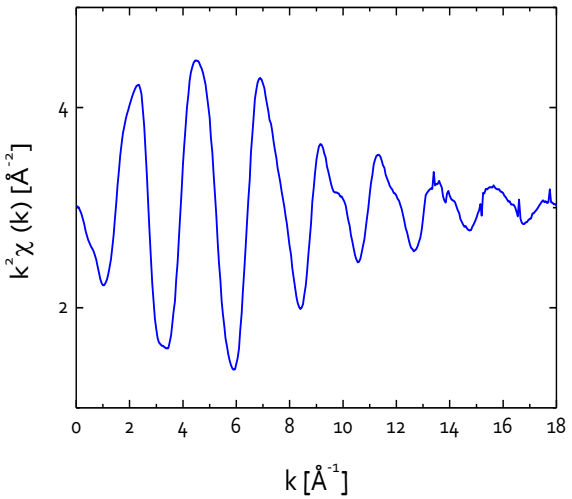
Measurements on densified glasses and in-situ

Broadening and shift to higher Q of the FSDP

Reduction of the length scale of the IRO i.e. a breakdown in the network

Correlation between intermediate and short range order

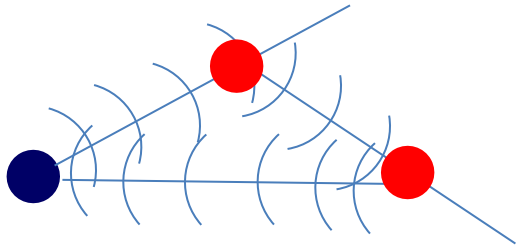
XAS beyond single scattering



$$\chi(k) = \frac{\sigma(E) - \sigma_0^t(E)}{\sigma_0}$$

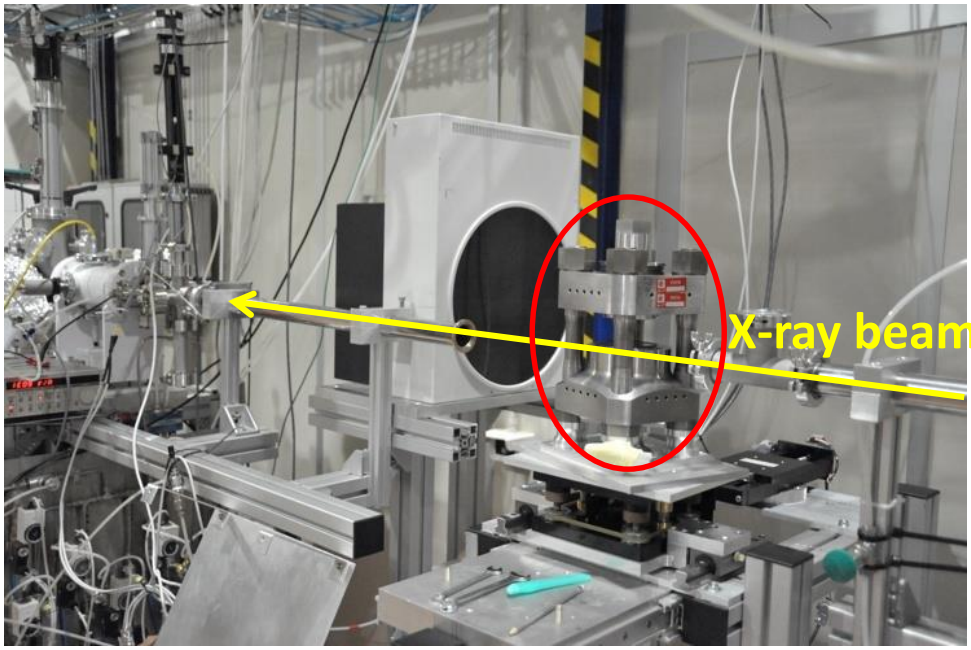
$$k = \sqrt{\frac{2m(E - E_0)}{\hbar^2}}$$

$$A(k)\sin[2kR + \phi(k)]$$ ➡ Fourier transform analysis

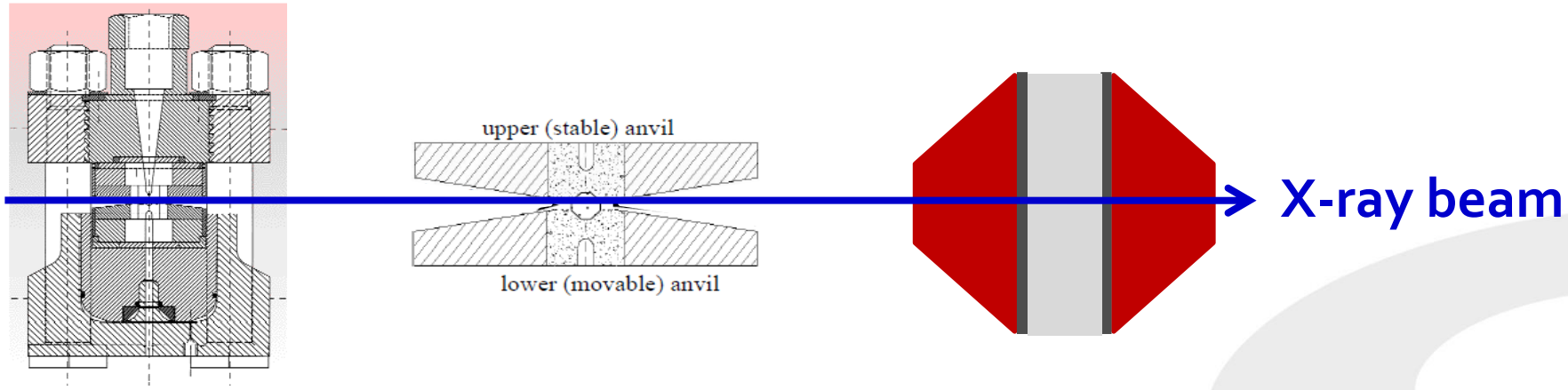


XAS is sensitive to atomic arrangements involving more than two atoms at the same time through ***multiple scattering*** processes

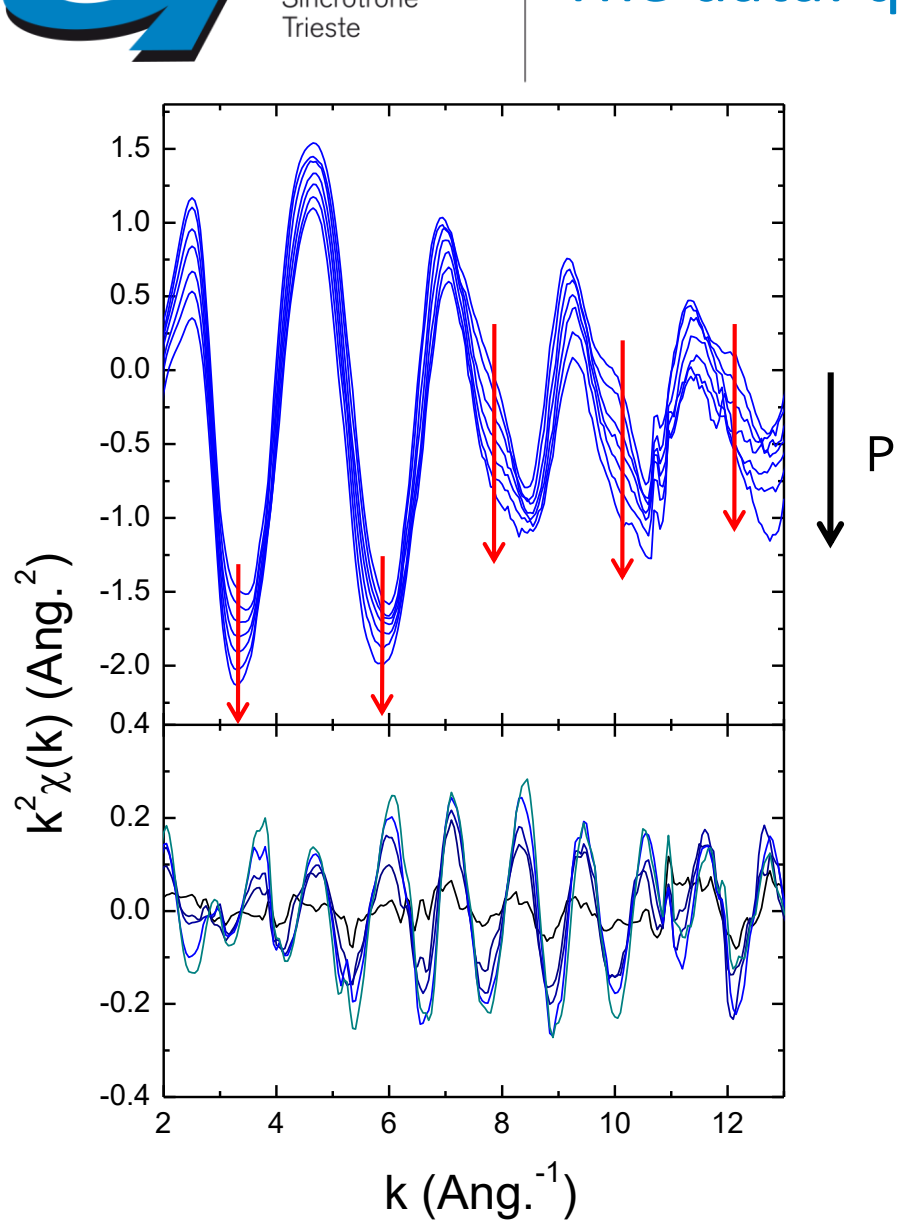
Experiment at XAFS at Elettra

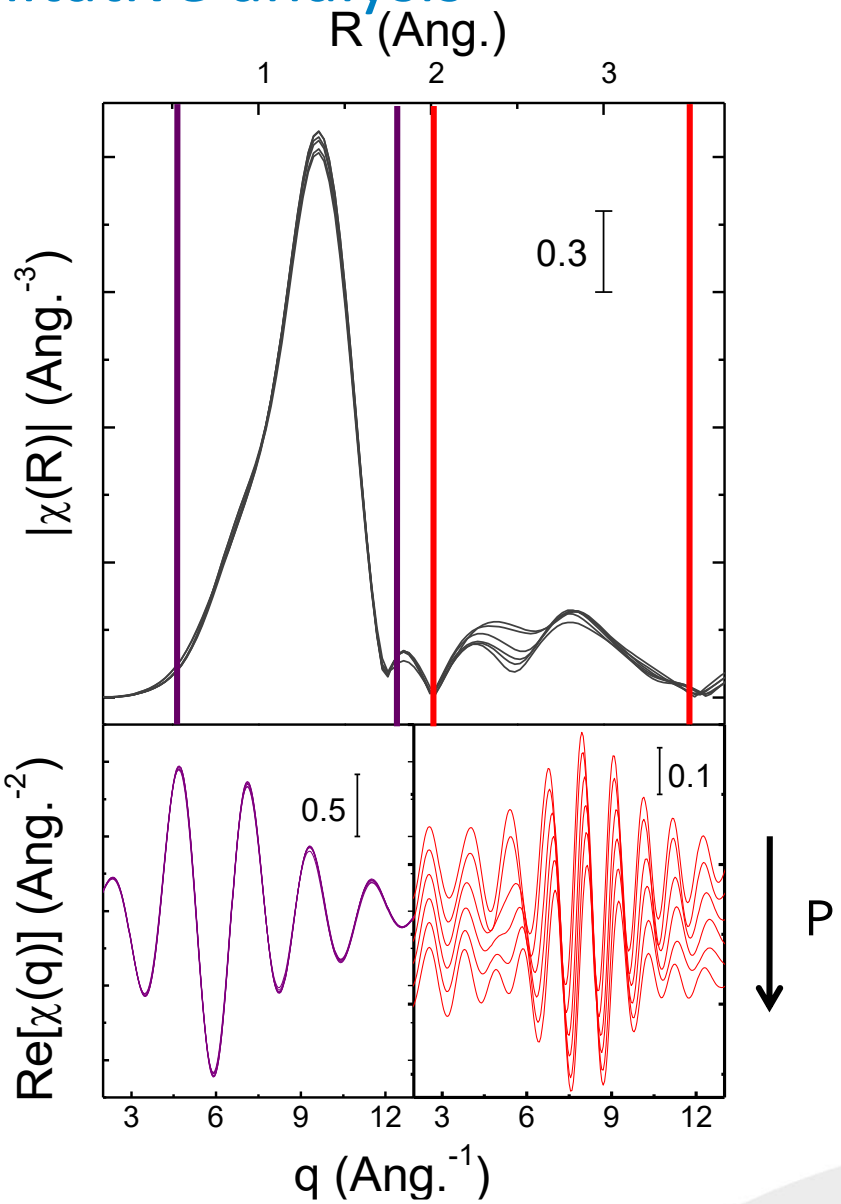


- Ge K – edge
- glassy GeO_2 mixed with BN
- Image plate for ADXRD (E = 15 keV)
- 7 mm boron epoxy gasket
- P from ambient to 5.1 GPa

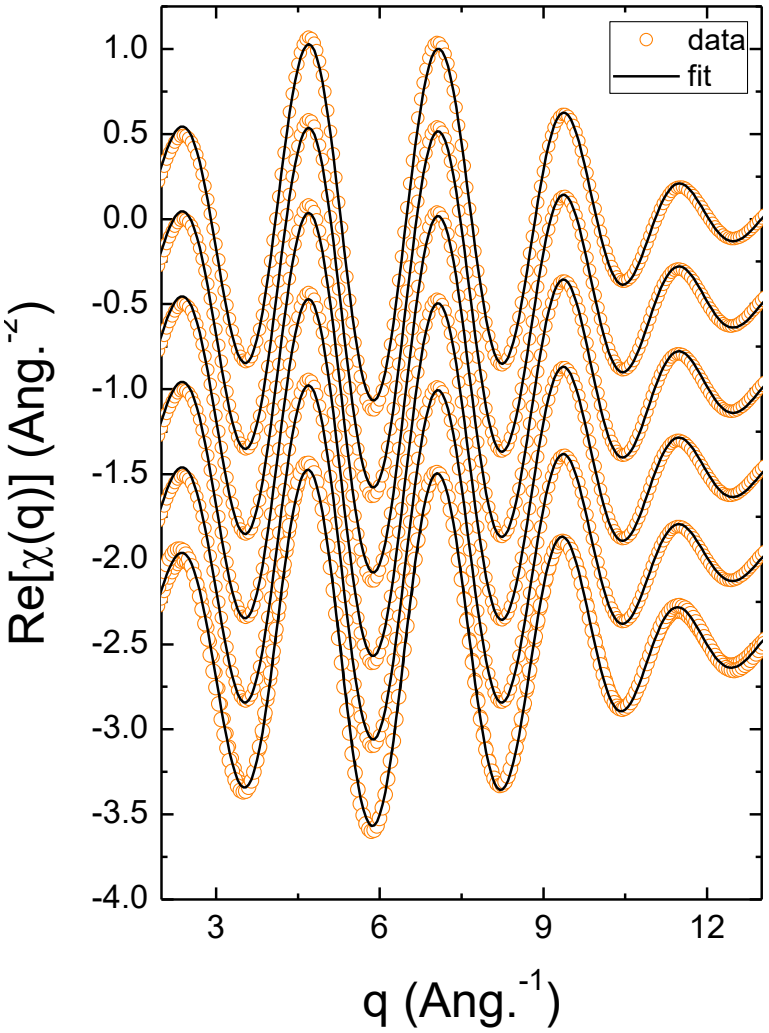


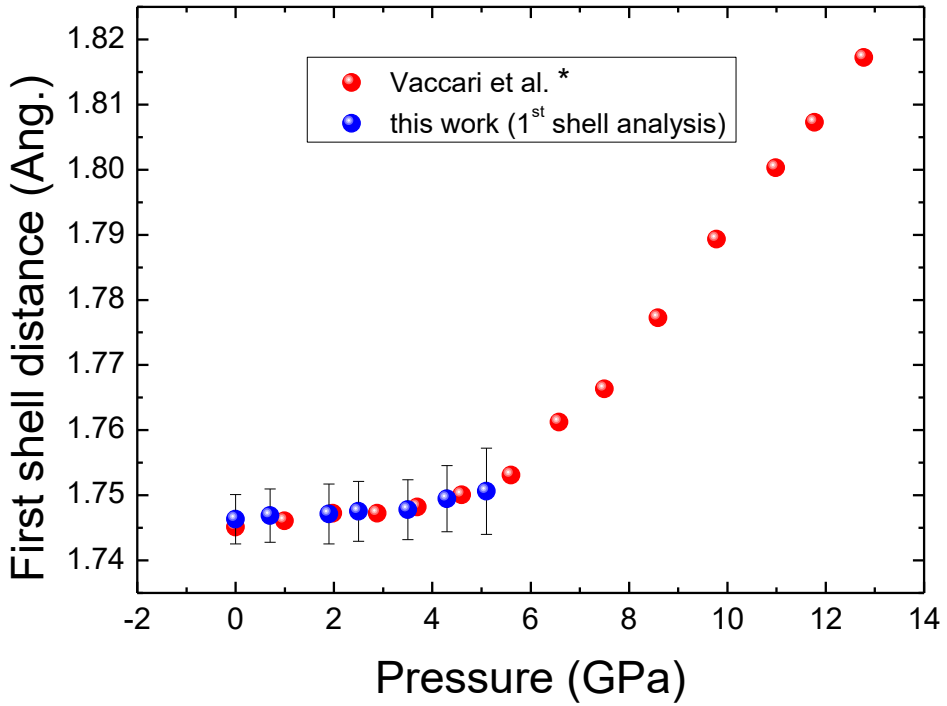
The data: qualitative analysis





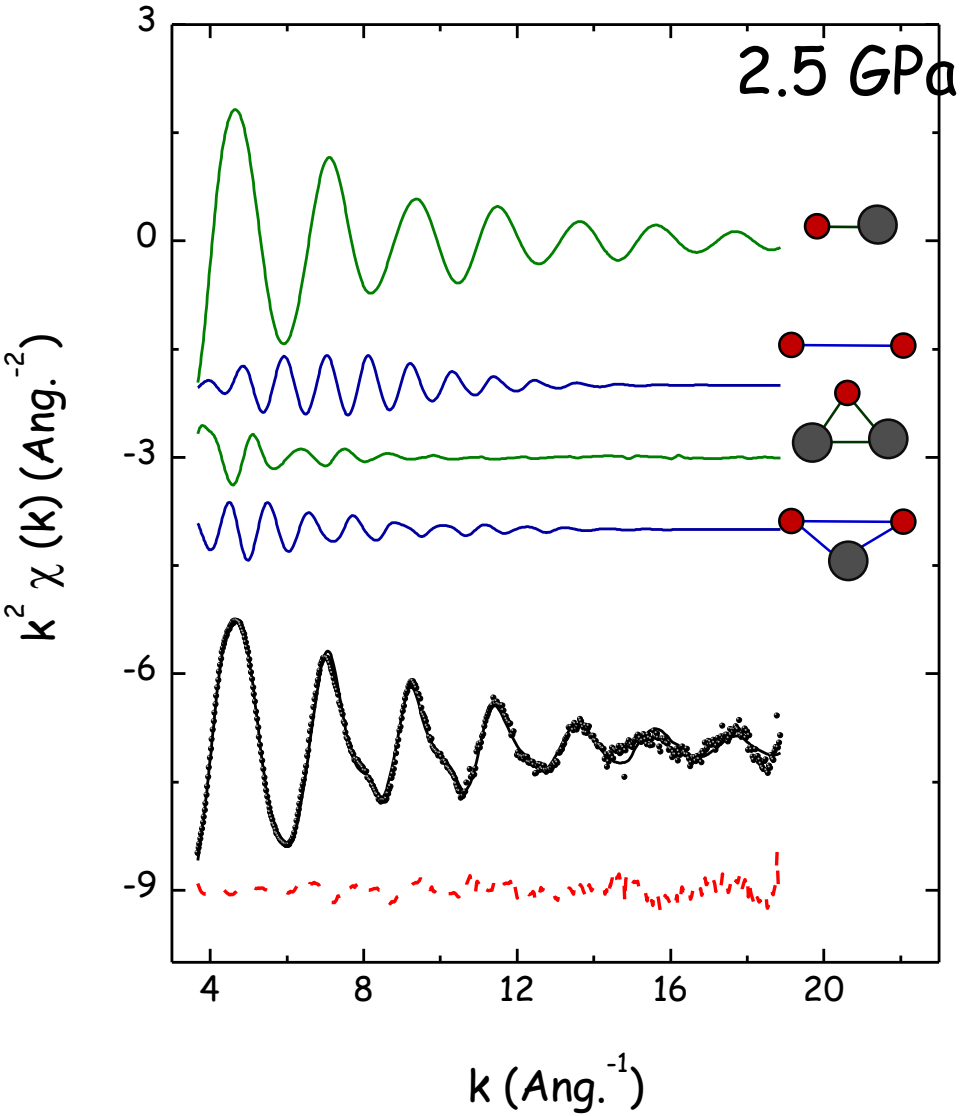
First shell analysis

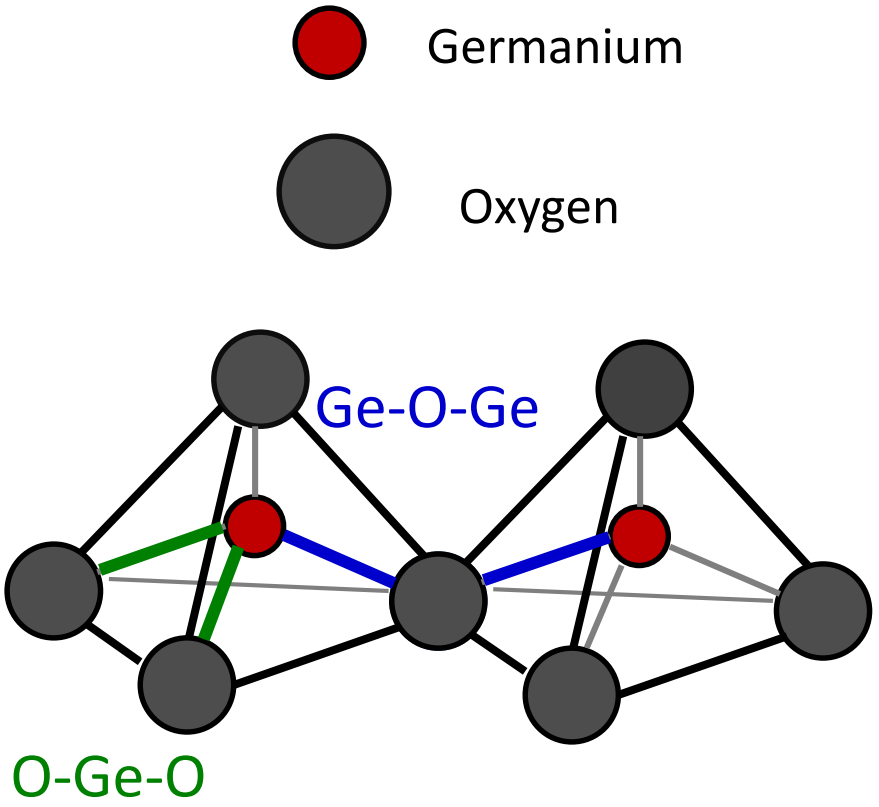




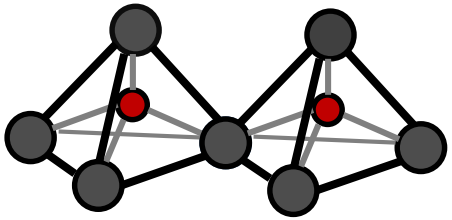
* M. Vaccari *et al.*, J.Phys.Cond. Matt. **21**, 145403 (2009)

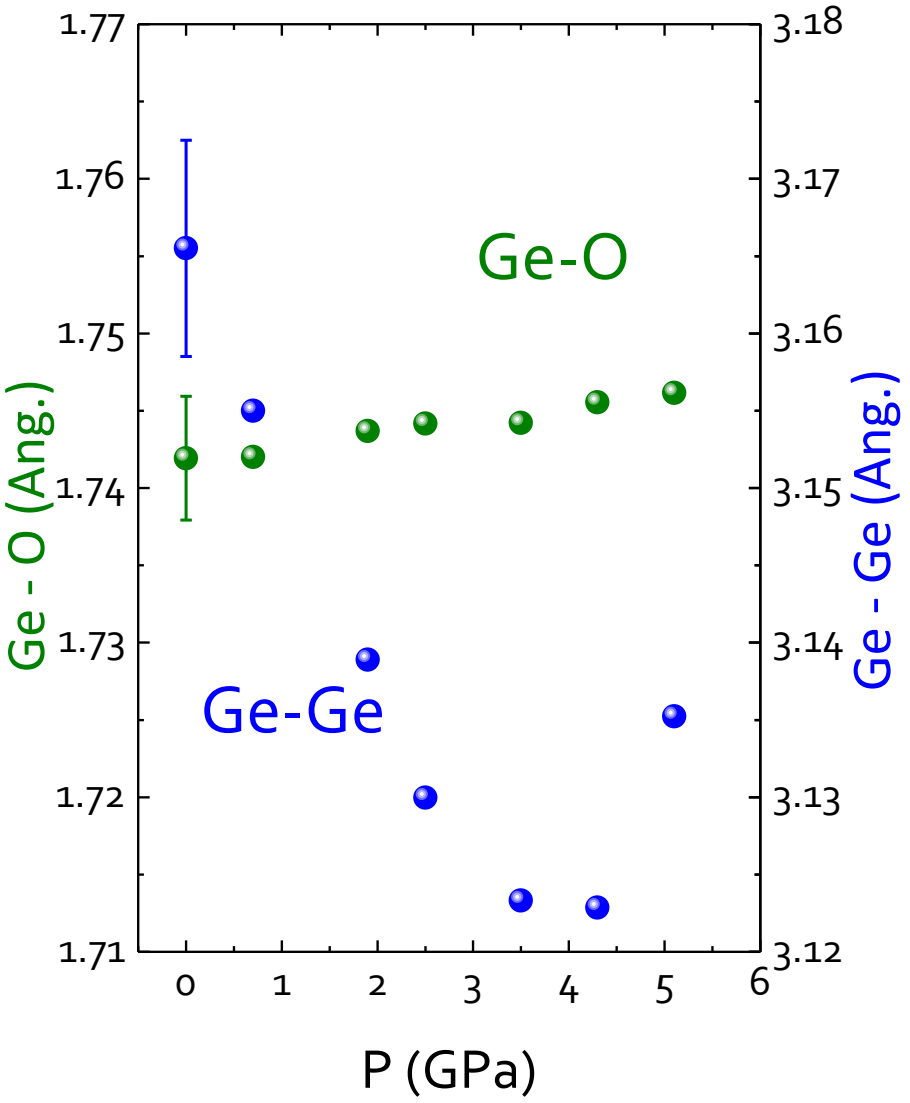
N-body analysis

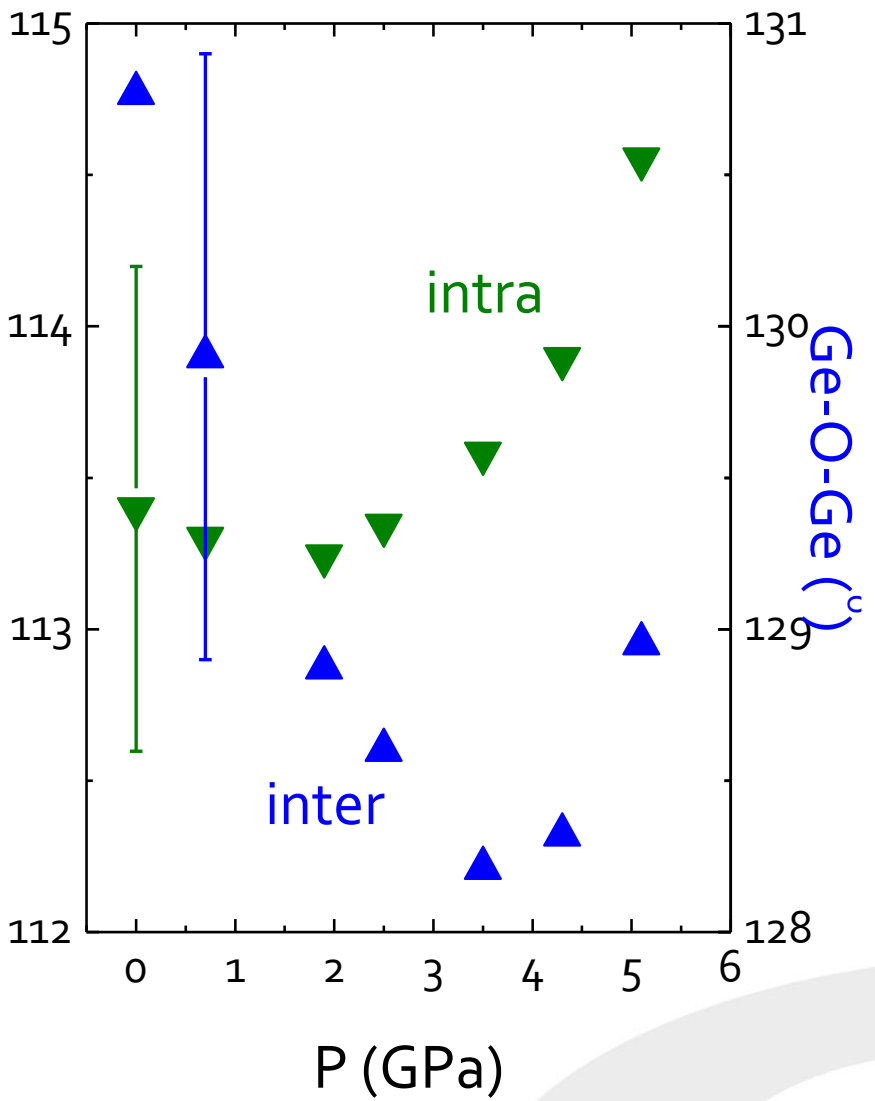




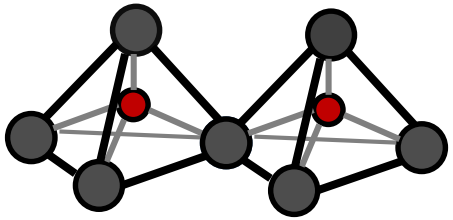
Results: distances and angles

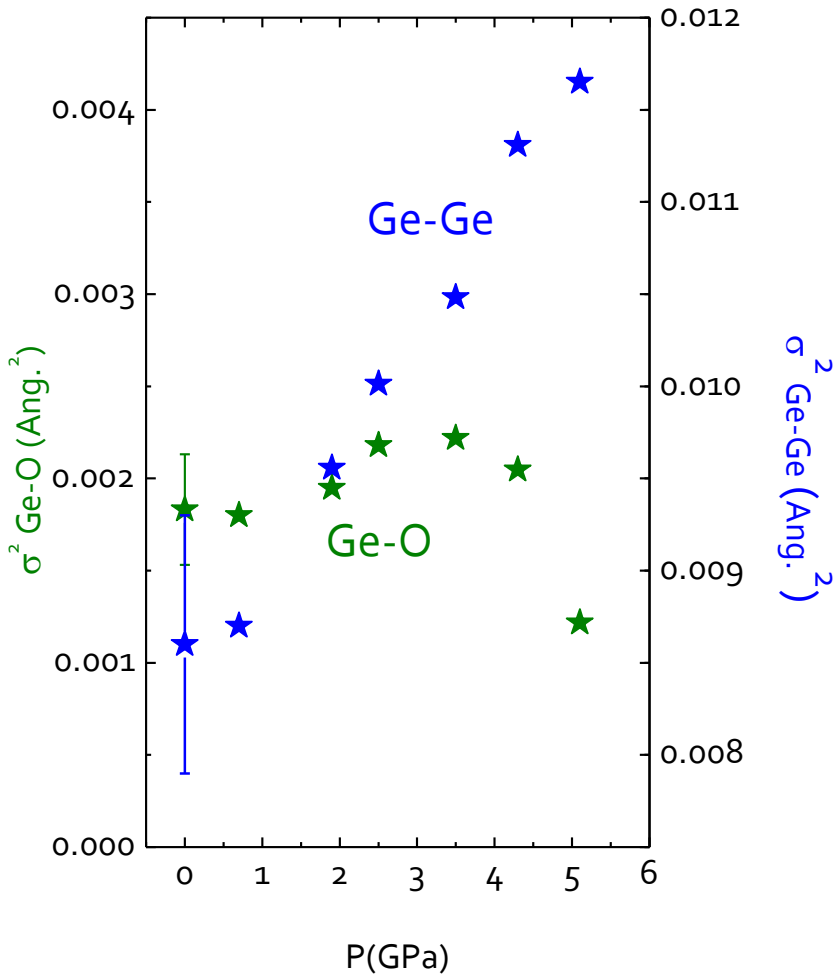


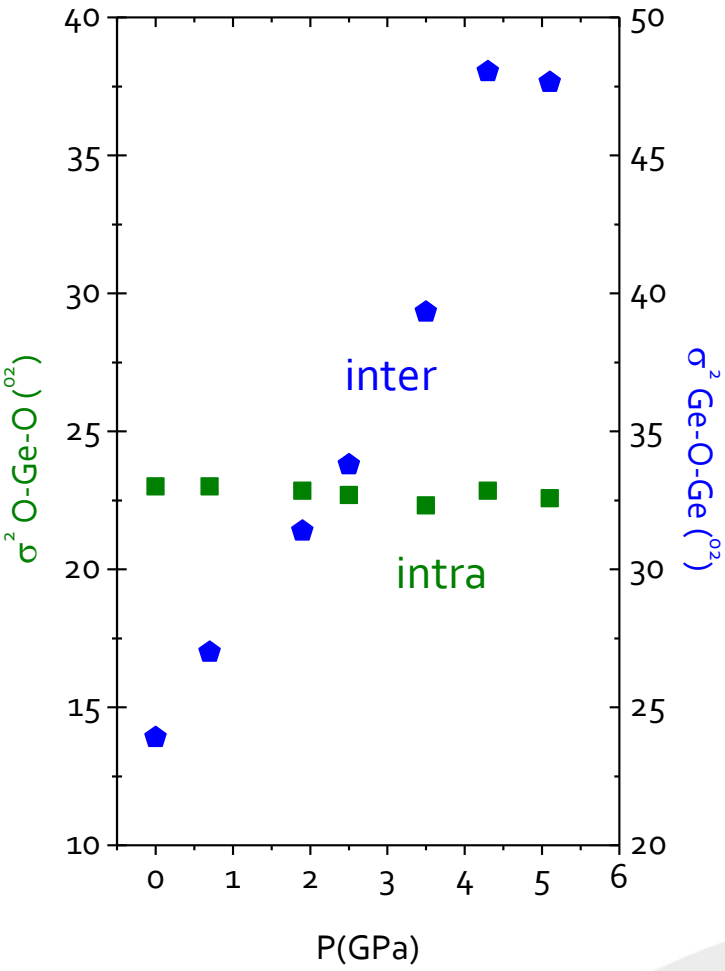




Results: variances







Summary and Conclusions

- Multiple scattering approach has been applied to EXAFS data of compressed glassy GeO_2
- Angular distributions have been determined as a function of pressure

- A change of the IRO occurs as soon as the pressure is applied
- It is the relative position between the tetrahedra that plays the major role in the of the IRO although the basic units deform to some extent
- The pressure induces an increasing disorder both at the Ge-Ge distance distribution and at the Ge-O-Ge (intertetrahedra) angular distribution

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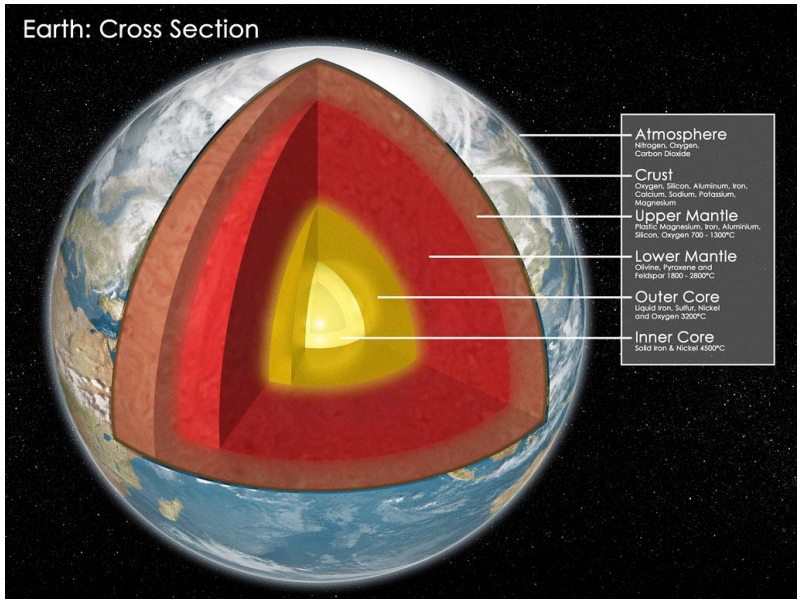
Melting of iron at extremes pressures

Introduction



- Fe is the principal component of the Earth's core
- The knowledge of the melting curve is a major concern in geophysics
- The melting temperature of iron at ICB (330 GPa) constraints the thermal gradient and thus the heat fluxes
- This is fundamental to understand the Earth's dynamo and its implications to the terrestrial magnetic field
- Discrepancies as large as 2000 K at the ICB (800 K at 100 GPa)

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XAS to detect melting

- XAS (XANES) is used to detect melting on iron compressed to over 100 GPa
- XAS maintains the same accuracy and sensitivity regardless the physical state of the investigated sample
- Similarly to diffraction techniques, XANES may distinguish different crystallographic phases, but gives in addition information on electronic structure
- The XANES spectra contain solely the signal relative to the absorbing element, without any interference of the container or experimental environment

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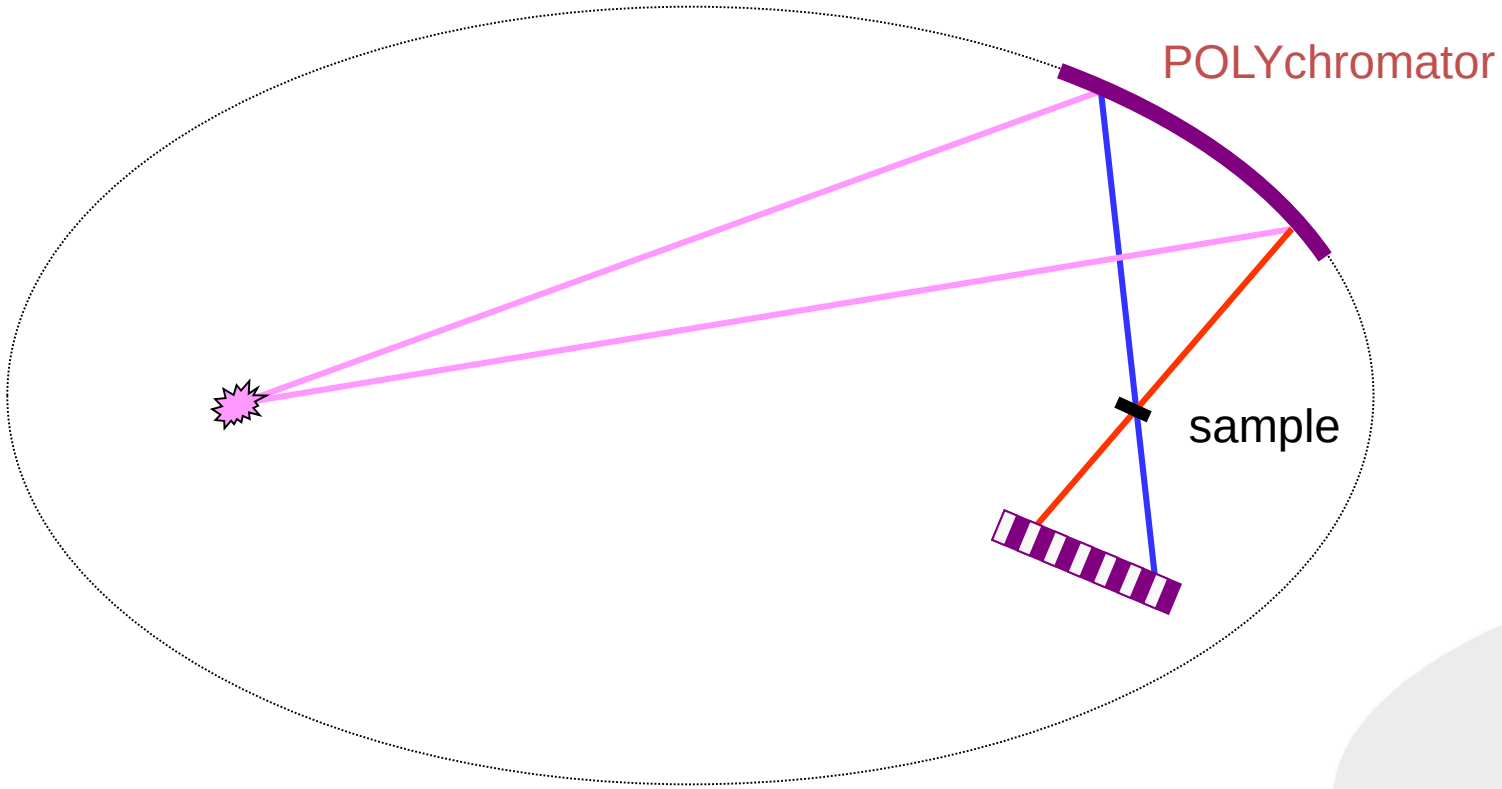
EDXAS to detect melting

EDXAS allows fast (from ns to few s) acquisition of the whole spectrum with a small (< 5mm) x-ray focal spot



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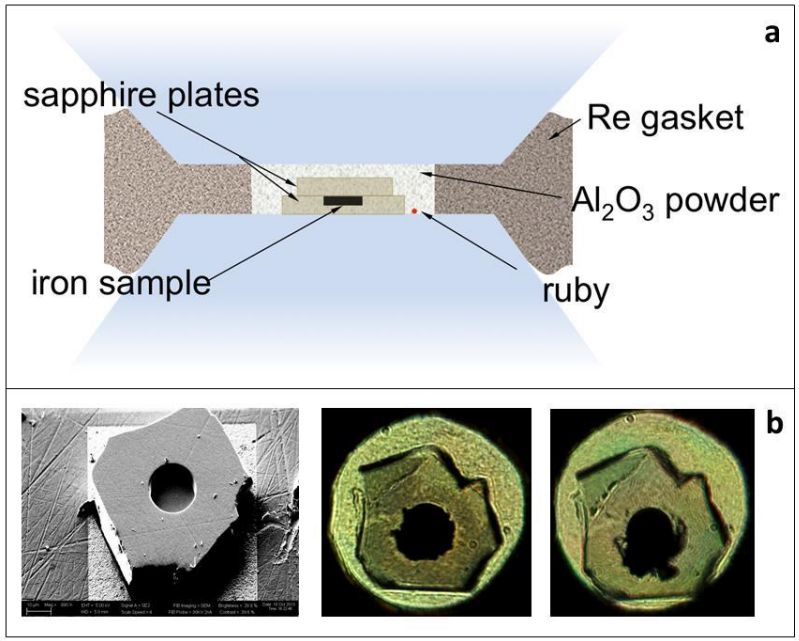
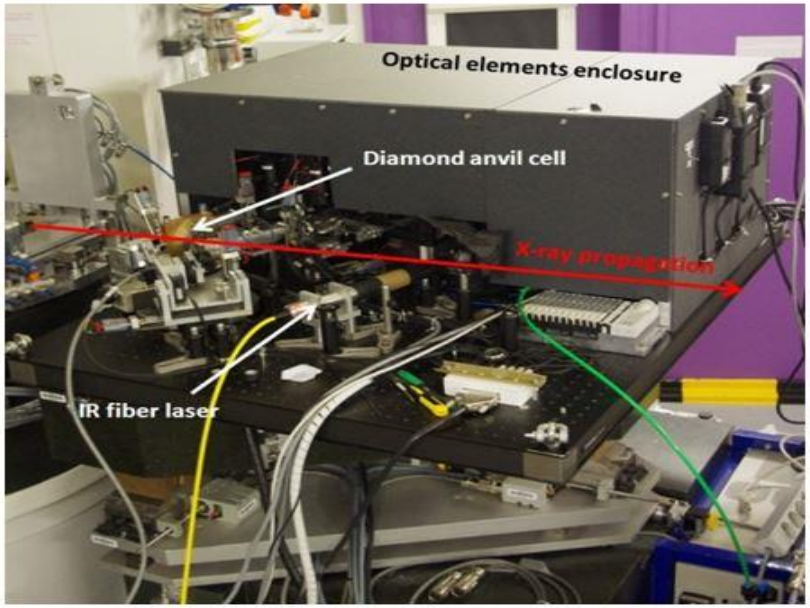
Sample preparation

- Novel sample encapsulating technique
- The sample container consists of two sapphire plates manufactured using a combination of micro polishing and focused ion beam milling
- The cavity dimension: 18 µm diameter and 6 µm depth



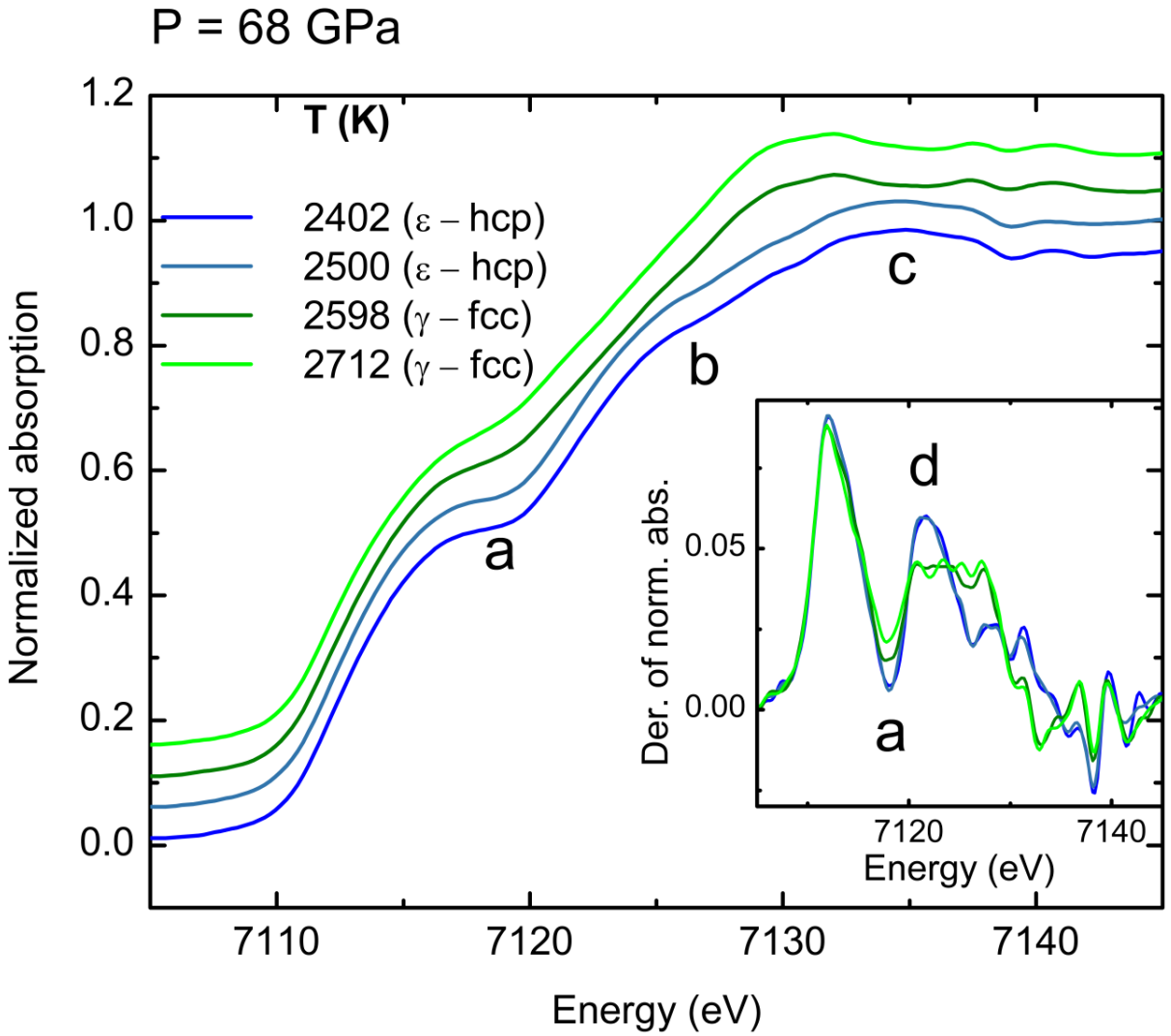
- All is embedded in a very fine grained Al_2O_3 powder which molds around the capsule to prevent fracture during loading and after laser heating

XANES measurements at ID24 (ESRF)



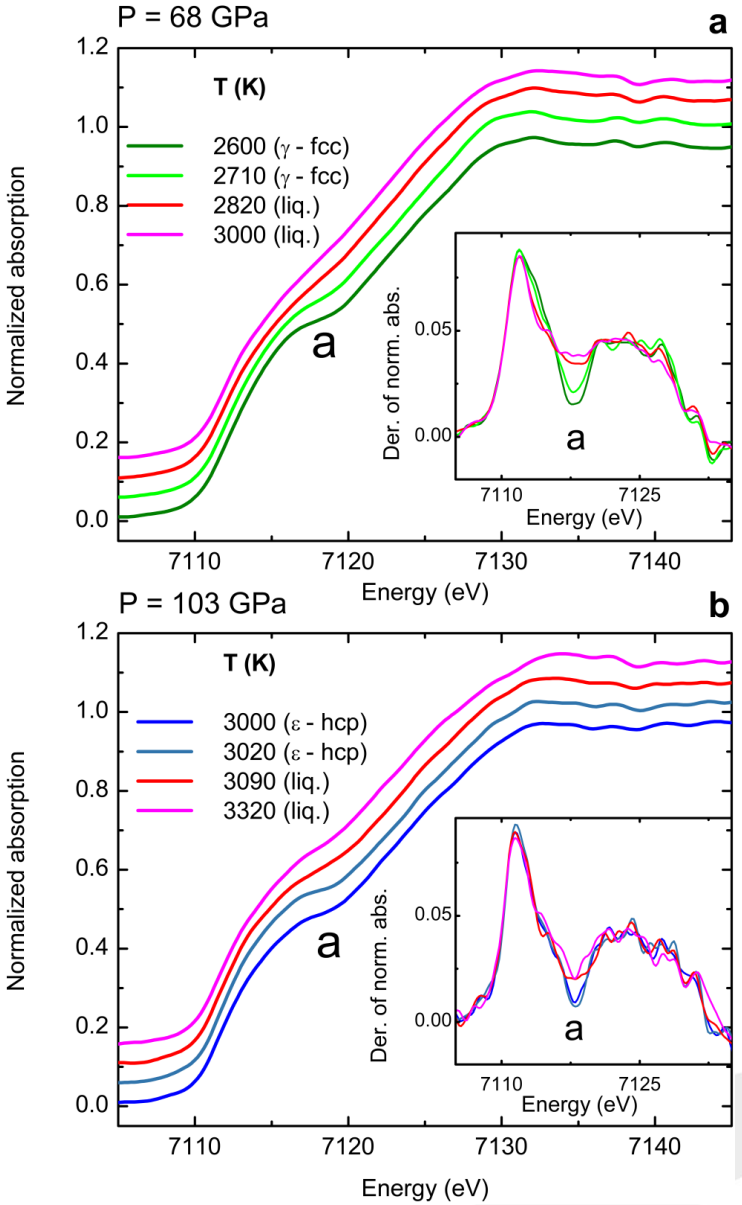
- X-ray beam size: 5 x 5 μm^2
- XANES spectra collected every few seconds before, during and after heating
- Four different runs from 63 to 103 GPa and temperatures up to 3530 K
- For each heating cycle, the laser power is ramped up incrementally and kept constant for several seconds to record the XAS spectrum and light emission to measure the temperature.

hcp to fcc phase transition



Solid to liquid phase transition

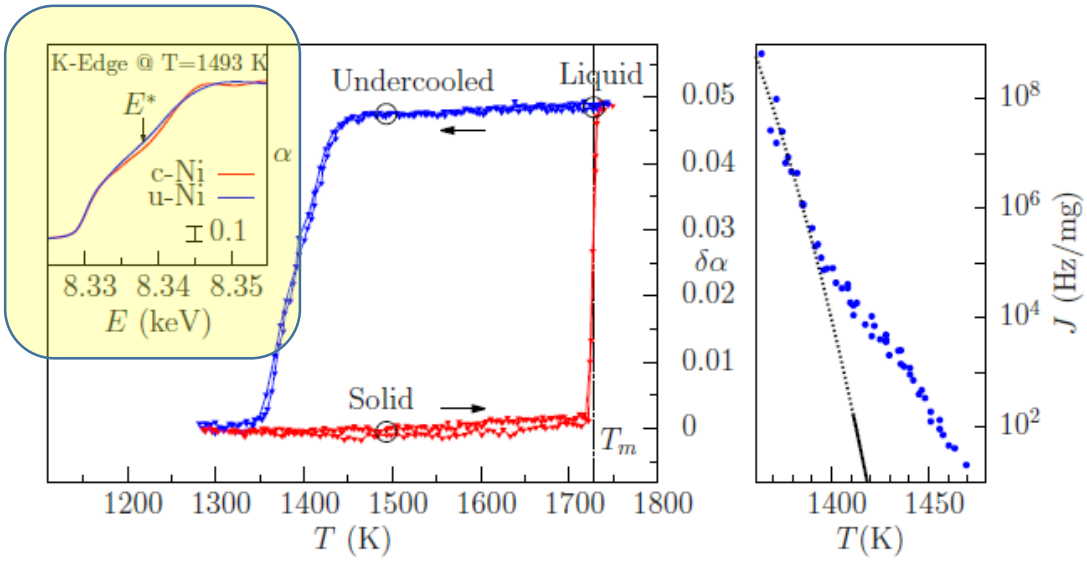
- The modification of the onset of absorption can be used as a signature for the solid to liquid phase transition
- The data show a discontinuous (although subtle) behavior
- The derivatives of the XANES highlight this change with the minimum ‘a’ flattening abruptly



Discussion

- The XAS experiment provides continuous monitoring of the changes of both the atomic and electronic structure as a function of temperature
- The melting criterion here adopted is based on changes occurring in the XANES that is known to be less affected by thermal damping and by the noise associated with extreme experimental conditions
- The detection of the new phase does not appear gradually as a weak background superimposed to a much larger signal as in XRD methods, but as a discontinuous change in the XANES signal which has similar amplitude with respect to that in the solid phase.

Other transition metals

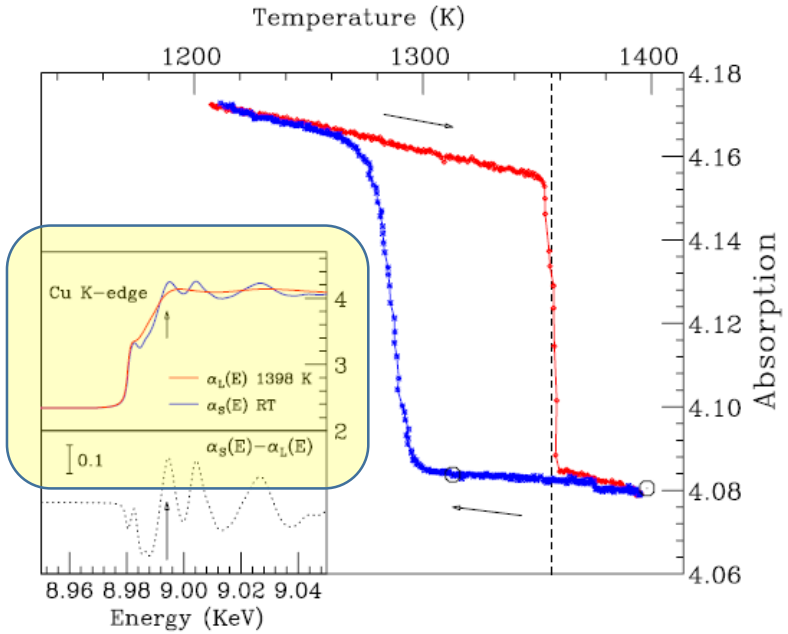


Nickel

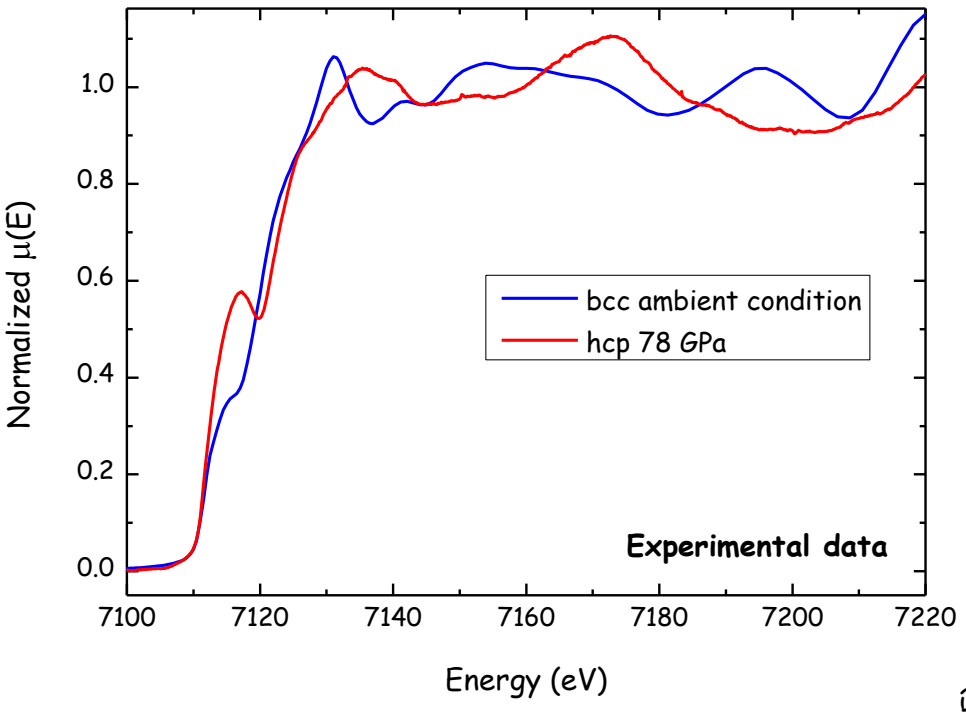
A. Di Cicco ,F. Iesari et al.,
PRB **89** (2014) 060102

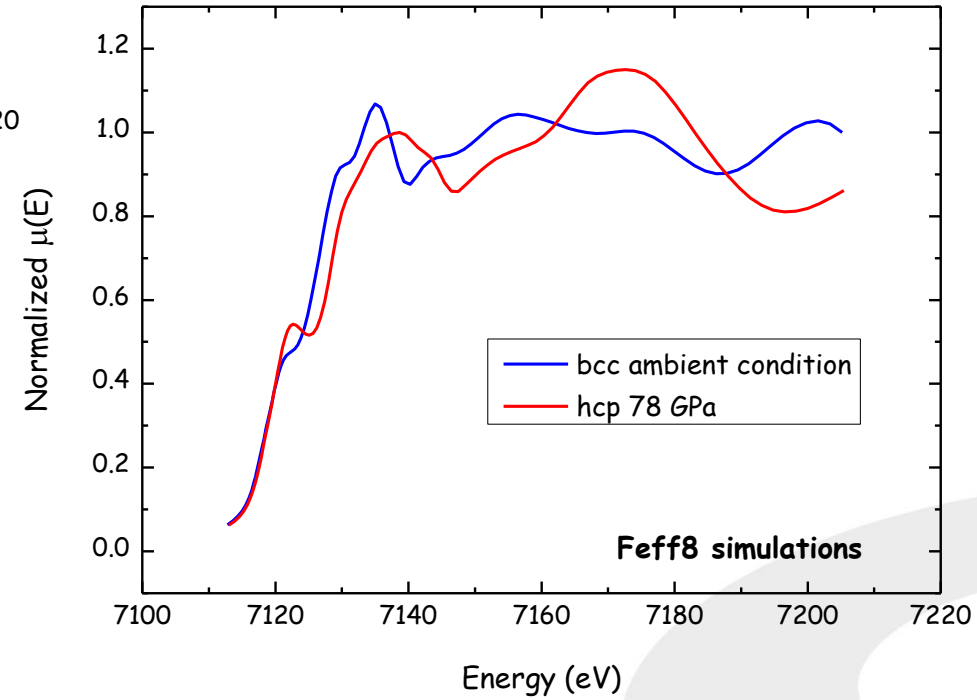
Copper

A. Di Cicco and A. Trapananti
J. Non Cryst. Sol. **353** (2007) 3671

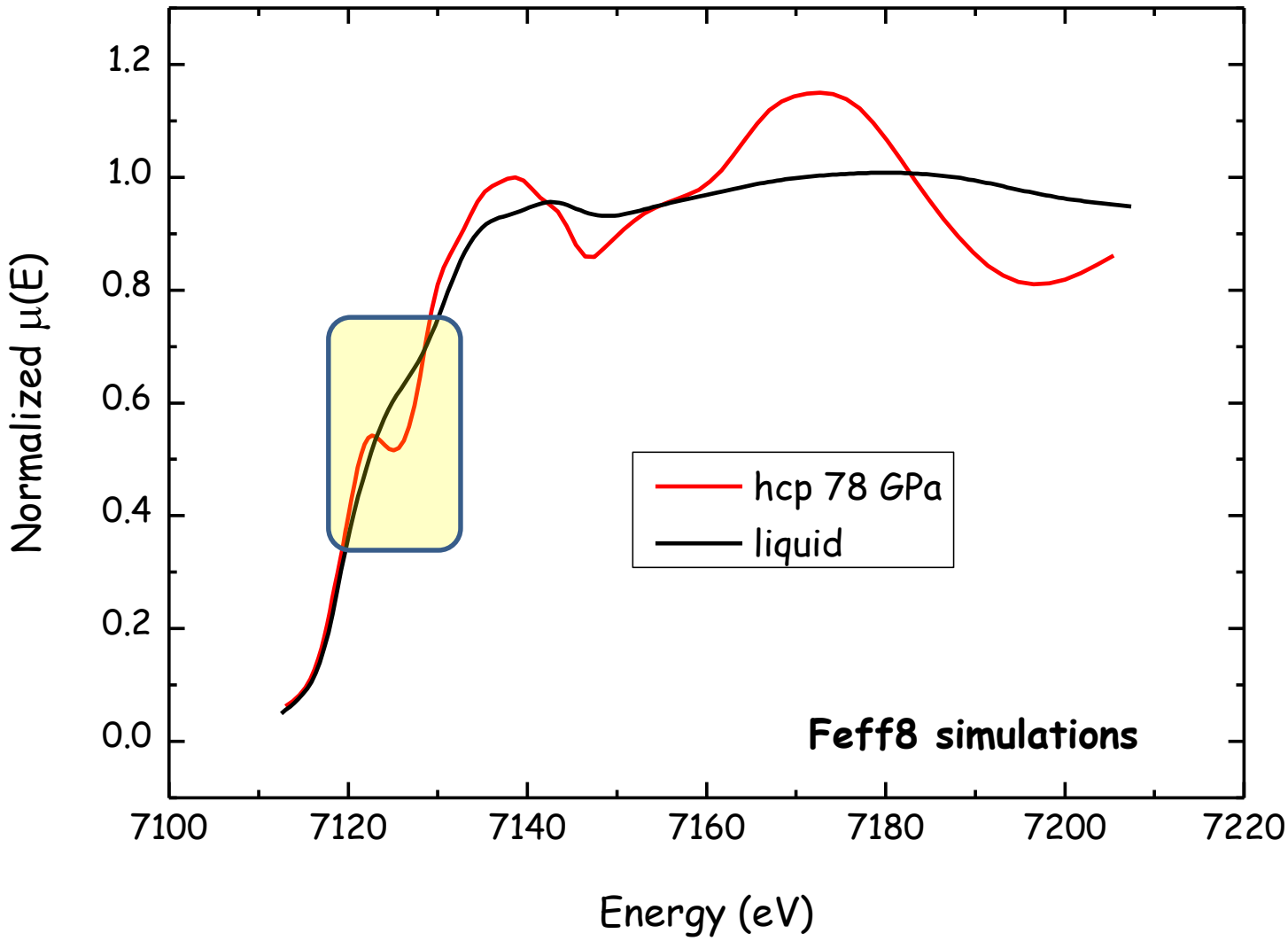


XANES simulations

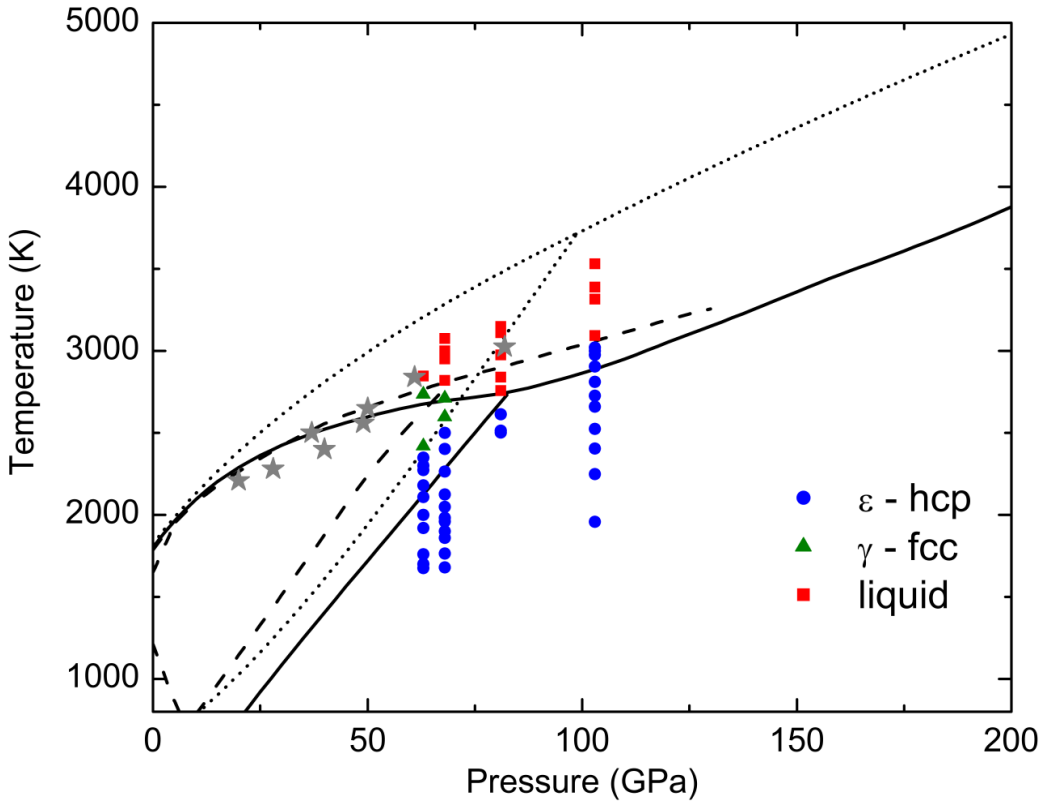




Simulations for the liquids - 2



Phase diagram and results



- Excellent agreement for the hcp -Fe to fcc-Fe transition reported earlier
- Flat melting curve near 3000 K at 100 GPa
- Melting temperature at ICB near 5000 K

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Decomposition of ringwoodite at high P and T

Introduction

At 660 km below the Earth's surface (P=23 GPa, T=1600 ^{o}C), the properties of the Earth's mantle change abruptly

- increase of density
- increase of transmission speed of seismic waves

$$[\gamma - (\mathrm{Mg,Fe})_2\mathrm{SiO_4}] \rightarrow (\mathrm{Mg,Fe})\mathrm{SiO_3} + (\mathrm{Mg,Fe})\mathrm{O}$$

ringwoodite perovskite magnesiowüstite

Pv and Mw form the most abundant assemblage in the Earth

$K^{Fe}_{Mw/Pv}$ is crucial for:

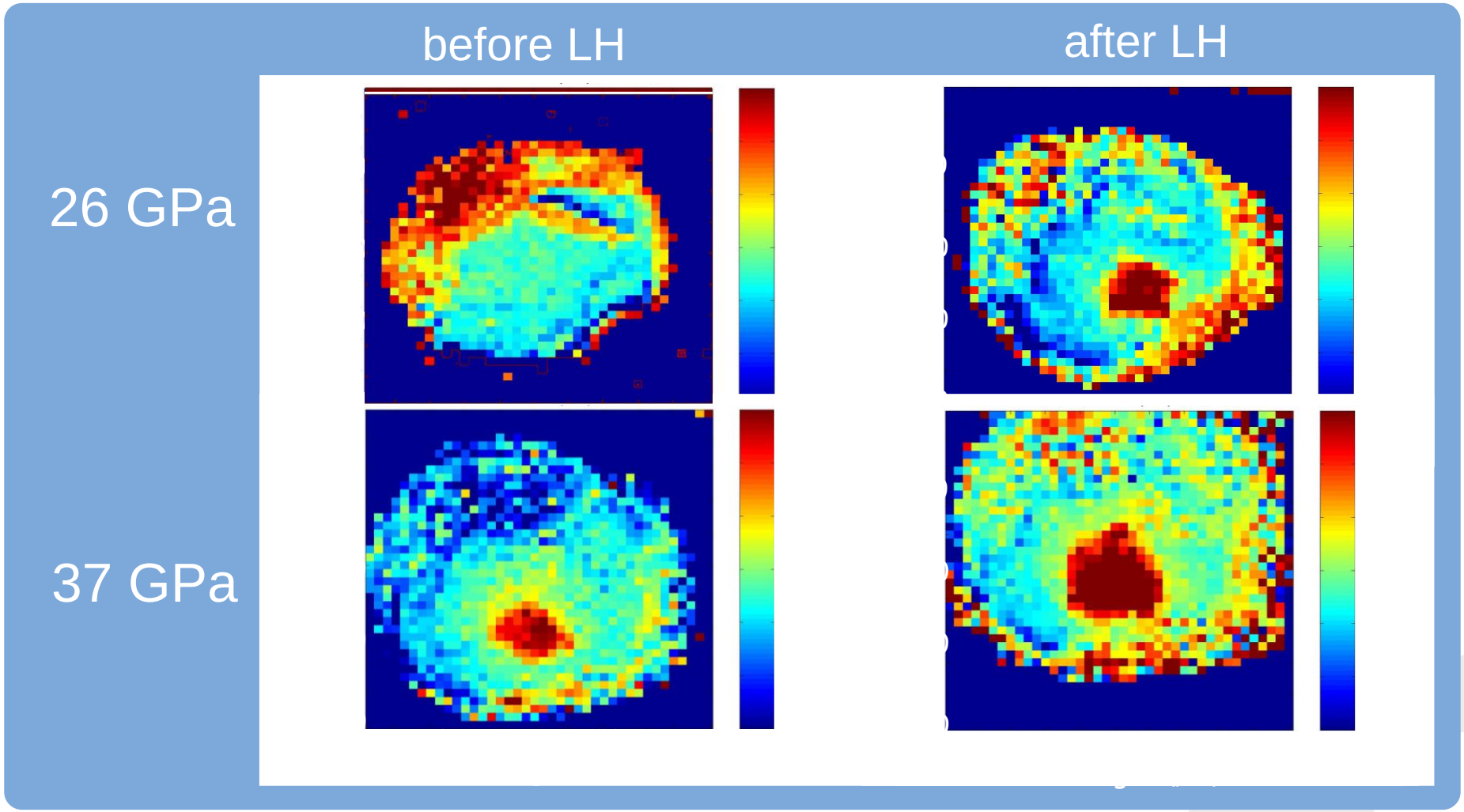
- composition and physics of the lower mantle
- interaction between the lower mantle and the liquid core
- stability field of Pv and Mw

Experiment

- Fe K-edge (7112 eV) XANES maps
- In transmission mode in a DAC
- As a function of pressure up to ~ 40 GPa, before and after laser heating
- Each map: 200 x 200 μm^2 with 5 μm spatial resolution 1600 spectra in ~ 3 hours
- The spectra are automatically treated using a Matlab program performing the basic operations of normalization and the information are stored in 2D matrices
- Different kinds of maps can be produced:
  - absorbance at a given energy
  - edge position
  - absorption jump intensity

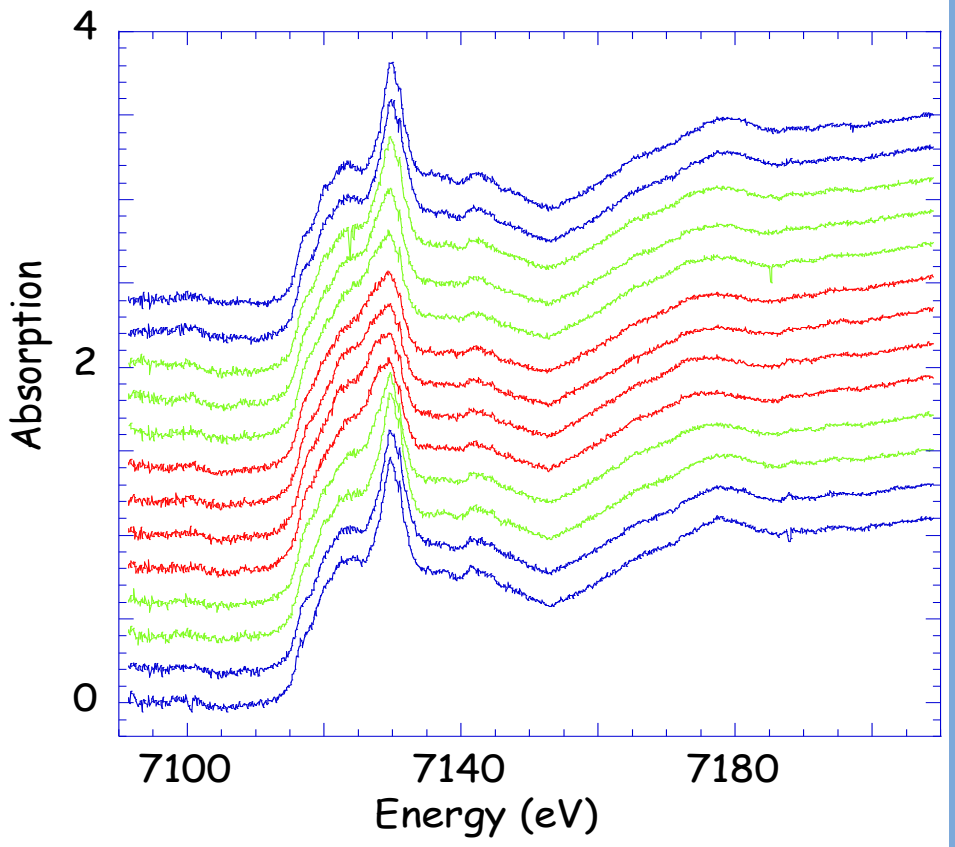
Maps

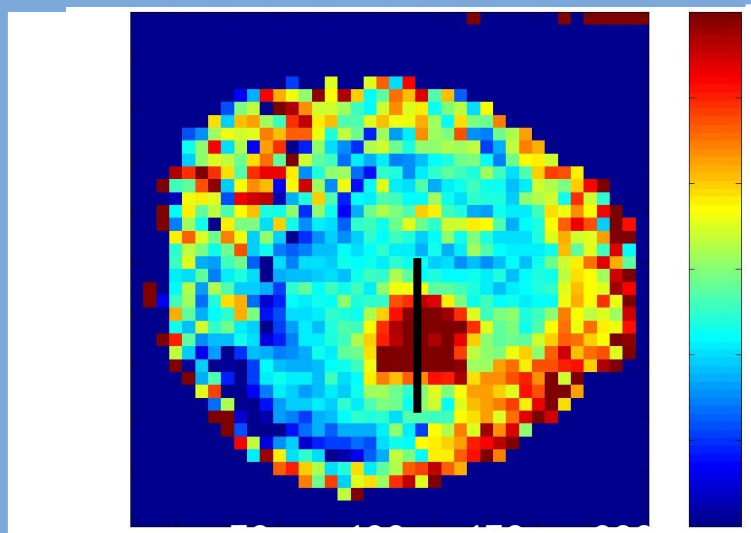
Absorbance at 7125 eV



Maps and XANES spectra

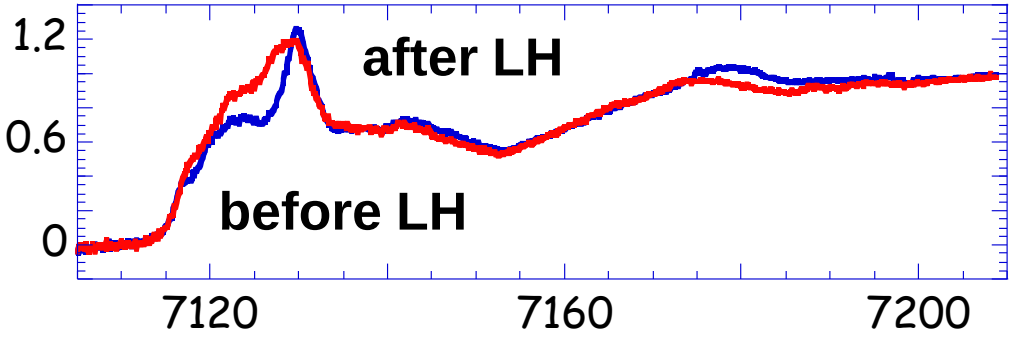
- Fe K-edge XANES spectra recorded every 5 mm through the hot spot
- Fe speciation is modified upon laser heating, i.e. with temperature





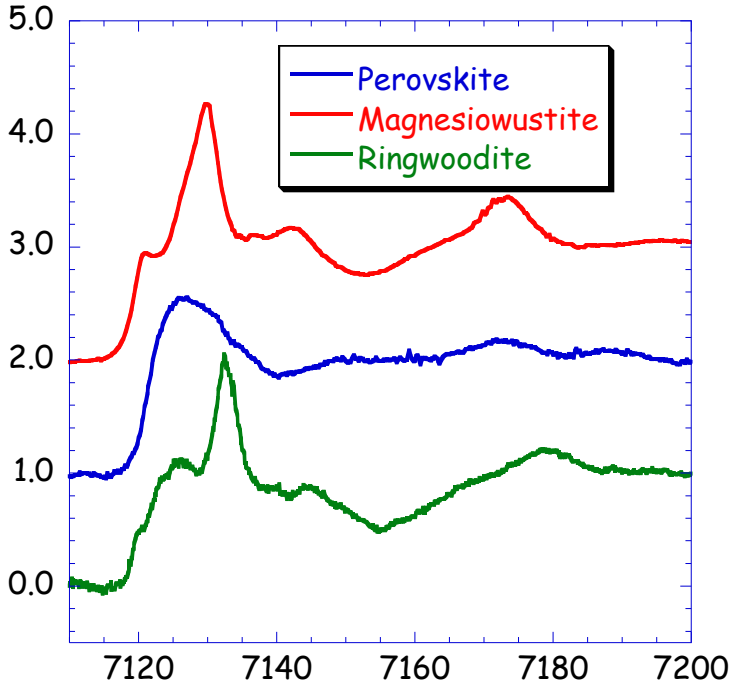
26 GPa after LH

Discussion



- The sample at the hot spot is a mixture of Rw, Pv and Mw
- The spectra at the hot spot contain a sum of the three contributions

- The sum decomposition can be done using model spectra
- The relative intensity of each characteristic signal will directly inform on the $K^{Fe}_{Mw/Pv}$



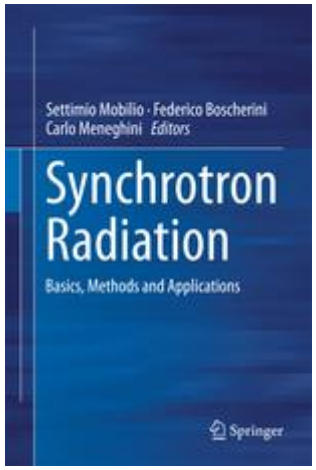
Elettra Sincrotrone Trieste

Outline

- Introduction
- Effects of pressure
  - Insulator to metal transitions
  - Metal to insulator transitions
  - Effects on magnetism
  - Structural phase transitions
- High pressure and Earth's science
- Tools and methods
- Examples of high pressure studies using XAS
  - Polyamorphism in glassy GeO_2
  - Melting of iron at megabar pressures
  - Revealing Earth's interior
- Bibliography

Bibliography

- Chapter 29 of



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