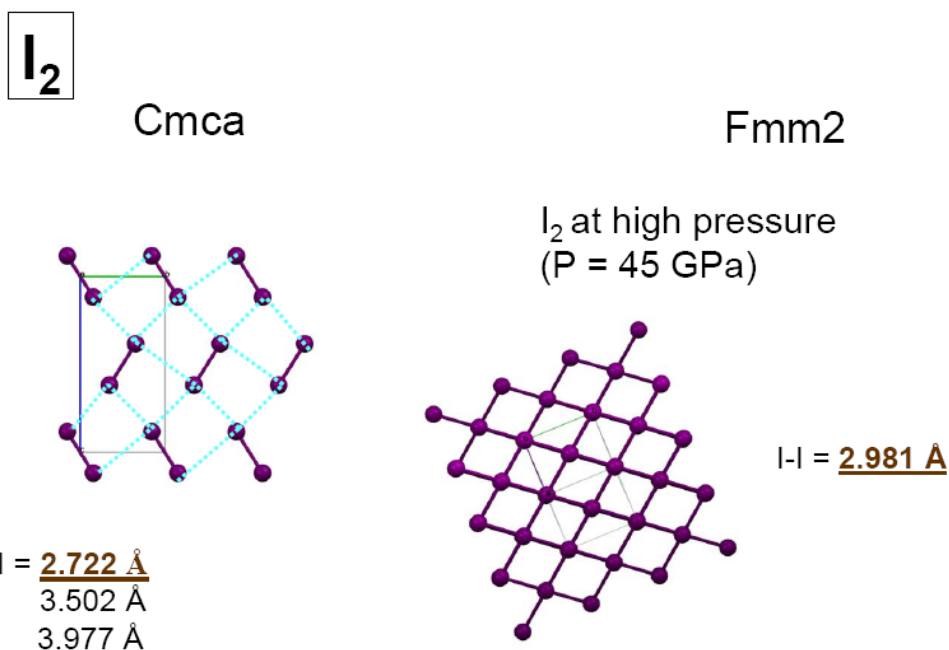
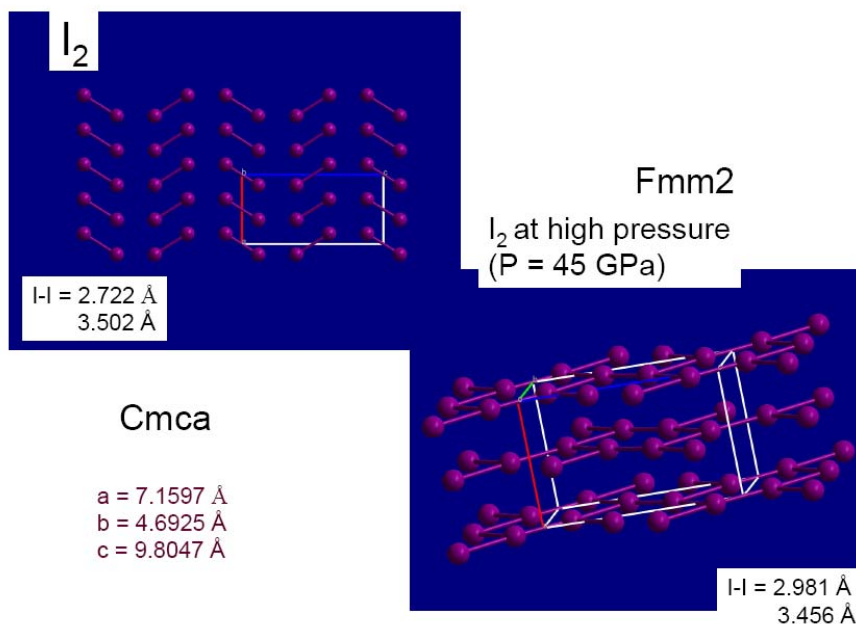


Appendix B. Selected slides to lecture presentations

Figure 1. Iodine. The data on cell parameters and space groups are not shown at the first lectures, when the structures are considered "as given", without a crystallographic analysis. Only the interatomic distances are given. At the later lectures, we come back to the same slides showing the unit cells and analyzing the symmetry. Figures are prepared using Mercury [http://www.ccdc.cam.ac.uk/free_services/mercury/] (Bruno *et al.*, 2002; Macrae *et al.*, 2006) based on data from Takemura *et al.*, 2003, 2004 a,b (refs are in Appendix C).

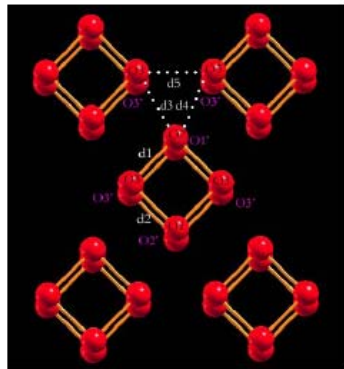


Intramolecular bonds expand at high pressure, but as a result an infinite 2D-polymeric structure is formed, in which the difference between the intra- and inter-molecular bonds does not exist any longer

Figure 2. Oxygen. The data on space symmetry are not given at the first lectures. We first consider the interatomic distances only and discuss the chemical bonding; the concept of the isosymmetric phase transition is also introduced at a later stage. The slide is composed based on J. Tse & E. Boldyreva (2010), in: Electron Charge Density Analysis, Ed. by P. Macchi and C. Gatti

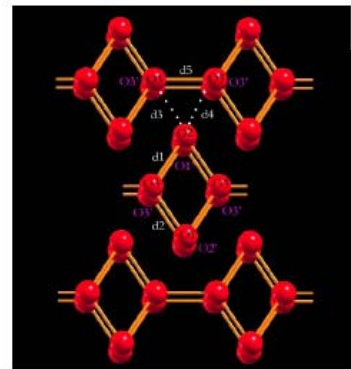


High-pressure phases of O₂



24 GPa

ε - form, C2/m, red,
diamagnetic, 8 – 96 GPa



105 GPa

ζ - form, C2/m, superconducting,
metal, 96 GPa – 250 GPa?

O-O: 1.2 Å & 2.34 Å (10 GPa),
2.17 Å (17 GPa)

Isosymmetric phase transition

Intramolecular O-O distances (Å):
1.207 (isolated molecule), 1.180 (β-O₂, R-3m, 5.5 GPa),
1.175 (δ-O₂, Fmmm, 9.6 GPa), 1.20 (ε-O₂, C2/m, 17 GPa)

Figure 3. Sulphur. The symbols of space groups are not shown at the first lectures, and are introduced later. Figures are prepared using Mercury [http://www.ccdc.cam.ac.uk/free_services/mercury/] (Bruno *et al.*, 2002; Macrae *et al.*, 2006) based on data from ICSD ([<http://cds.dl.ac.uk/cds/help/icsd.html>]) (Allmann and Hinek, 2005; Belsky *et al.*, 2002; Bergerhoff and Berndt, 1996; Kaduk, 2002) (refs are in Appendix C)

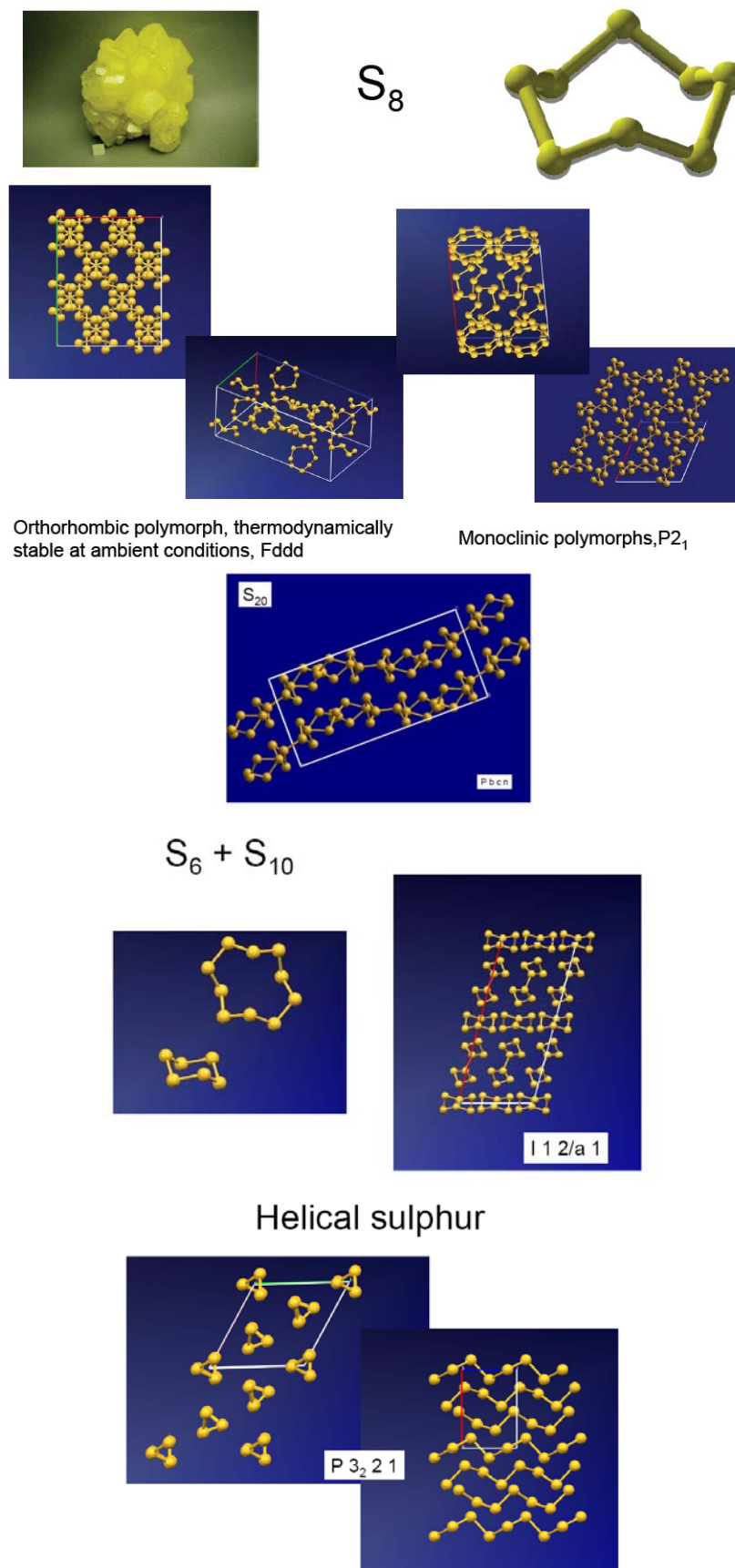


Figure 4. Effect of pressure on the crystal structures of As, Sb, Bi. The Pearson symbols are not given at the first lectures and are introduced later. The slide is a courtesy of Dr. Olga Degtyareva.

Structural sequences under pressure in group V elements

As	$hR2$	$\xrightarrow{25}$	$sc, cP1$	$\xrightarrow{48}$	monocl. h-g	$\xrightarrow{97}$	bcc < 122 GPa
Sb	$hR2$	$\xrightarrow{8.0}$	monocl. h-g	$\xrightarrow{8.6}$	tetr. h-g	$\xrightarrow{28}$	bcc < 65 GPa
Bi	$hR2$	$\xrightarrow{2.5}$	$mC4$	$\xrightarrow{2.7}$	tetr. h-g oC16 (>210°C)	$\xrightarrow{7.7}$	bcc < 220 GPa

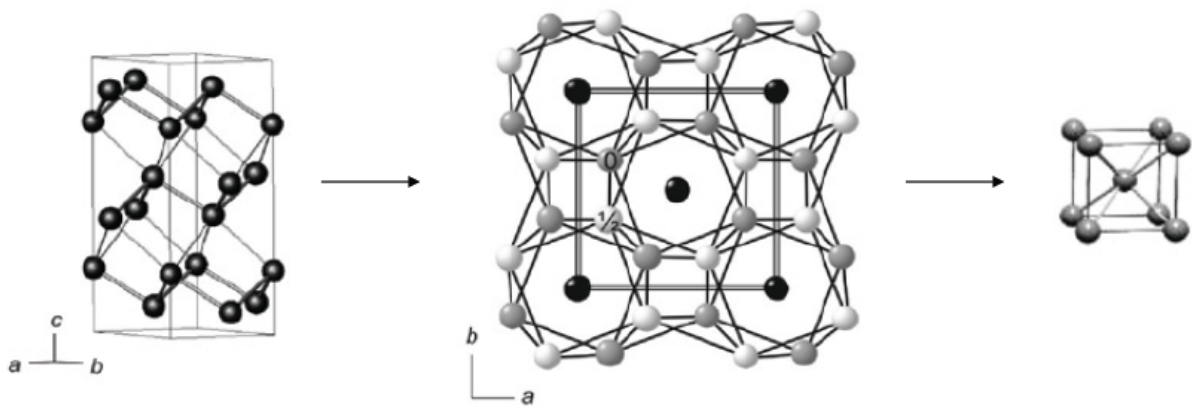
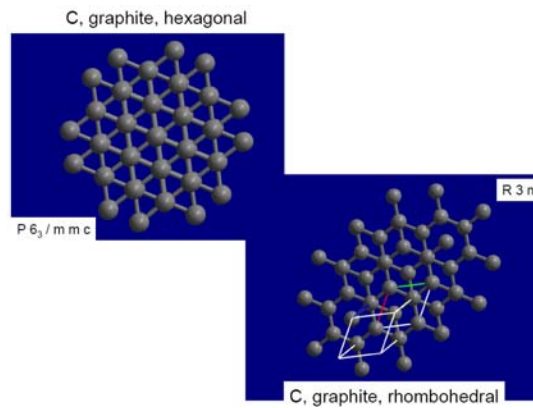
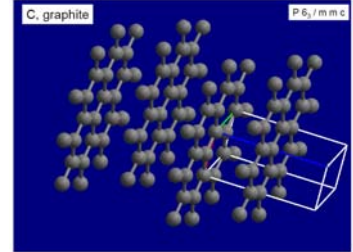
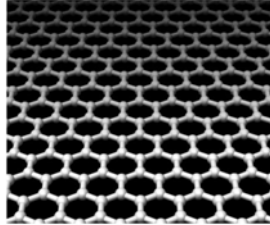


Figure 5. Carbon. The space symmetry and cell parameters are not shown and not discussed at the first lectures. The figures are borrowed from Geim. & MacDonald, 2007 (graphene), drawn using Mercury [http://www.ccdc.cam.ac.uk/free_services/mercury/] (Bruno *et al.*, 2002; Macrae *et al.*, 2006), kindly provided by Prof. A. Oganov (high-pressure polymorph of C) (refs. are in Appendix C)

Graphene (a 2D-crystal)



Superhard Monoclinic Polymorph of Carbon

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Tian Cui,¹ Ho-Kwang Mao,^{4,‡} and Guangtian Zou¹

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(Received 30 December 2008; published 29 April 2009)

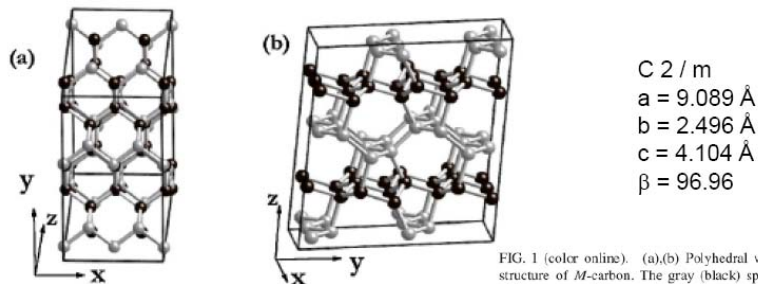


FIG. 1 (color online). (a),(b) Polyhedral views of the crystal structure of *M*-carbon. The gray (black) spheres represent the different warped layers. At zero pressure, lattice parameters of *M*-carbon are $a = 9.089 \text{ \AA}$, $b = 2.496 \text{ \AA}$, $c = 4.104 \text{ \AA}$, and $\beta = 96.96^\circ$ with four inequivalent crystallographic sites, occupying the $4i$ (0.4428, 0.5, 0.1206), (0.4419, 0, 0.3467), (0.2858, 0.5, 0.9406), and (0.2715, 0, 0.4149) positions, respectively.

Figure 6. Evolution of Si crystal structure with increasing pressure. From J. Tse, E. Boldyreva (2010), in: *Electron Charge Density Analysis*, Ed. by P. Macchi and C. Gatti, in the press (Appendix C). The slide is the courtesy of J. Tse.

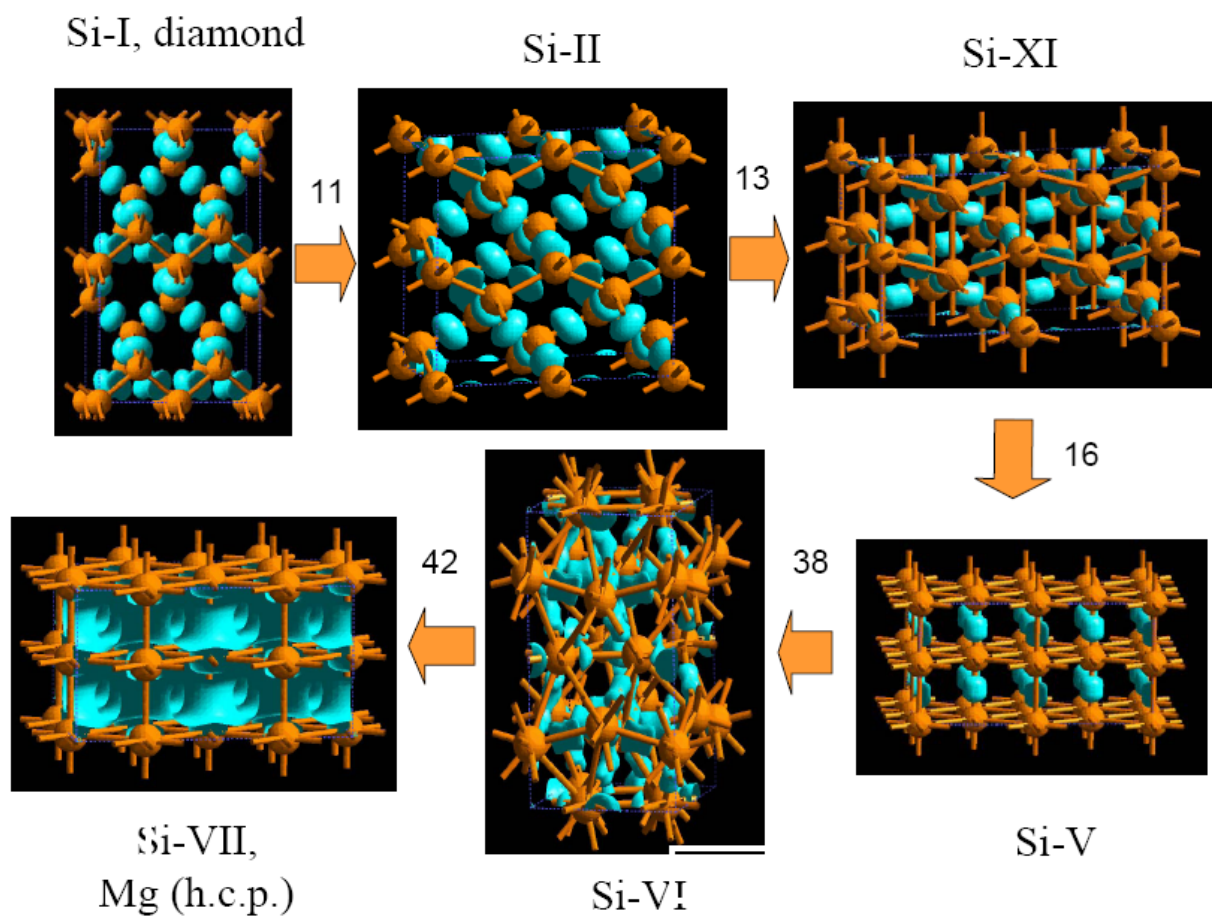


Figure 7. Allotropes of B. The space groups are discussed at later lectures. The plots are borrowed from Wikipedia.

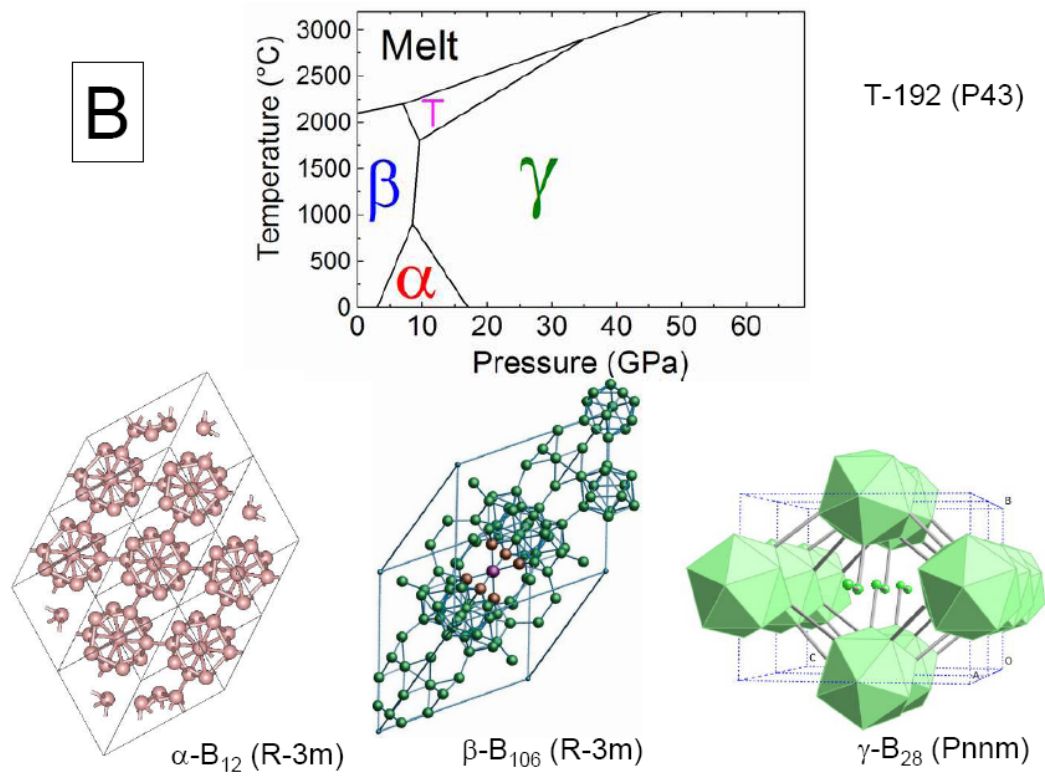
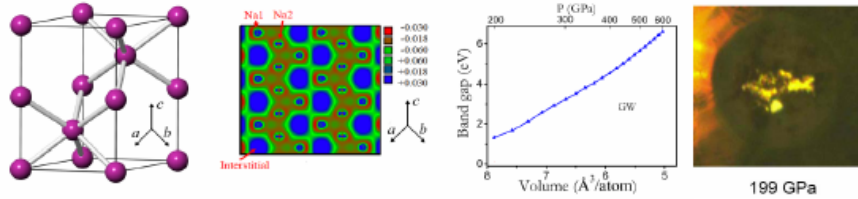


Figure 8. Sodium. These slides have been prepared and kindly provided to us by Prof. A. Oganov. We use them several times during the course - for the first introduction into the crystal structures, when discussing symmetry, when discussing electronic structure of solids

Sodium is an alkali metal, at normal conditions well described by the nearly free electron model

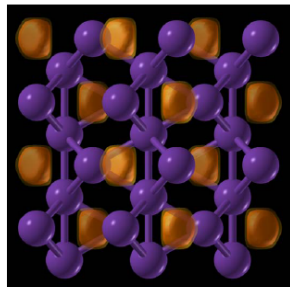
Sodium becomes transparent at ~200 GPa (Ma, Eremets, Oganov et al., *Nature* 2009)



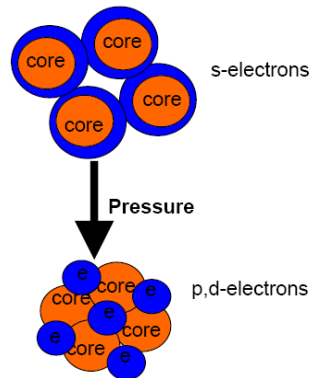
Localized interstitial electron pairs make Na insulating. Structure – close packing of interstitial electron pairs!

hP4-Na structure: elemental analog of the NiAs structure.

The new structure is a strongly squeezed close packing with valence electron pairs occupying interstitials



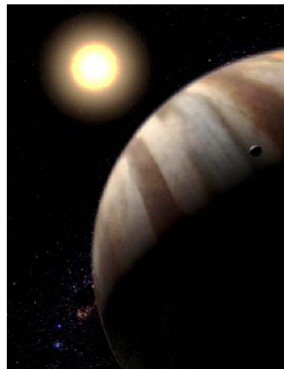
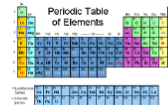
Electron localization function shows strongly localized behavior of electrons in the „empty space“ in Na



An „electride“, a compound made of ionic cores and strongly localized interstitial electrons. What type of chemical bonding is this?

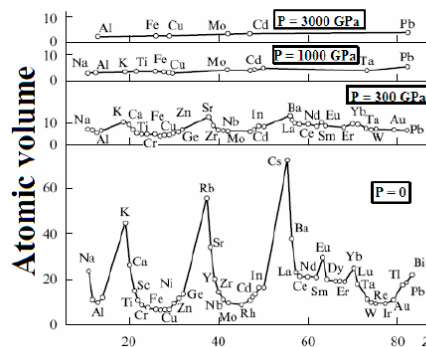
Similar model was first proposed for Li by Neaton & Ashcroft (1999)

Food for thought...



How common are electride states inside giant planets and stars?

Their poor electrical conductivity can affect planetary magnetic fields



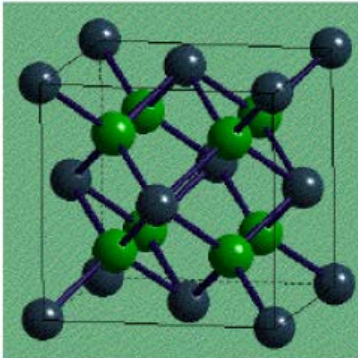
Becoming an insulator, sodium breaks traditional view of the periodic table.

Generally, the Periodic Law becomes invalid at ultrahigh pressures

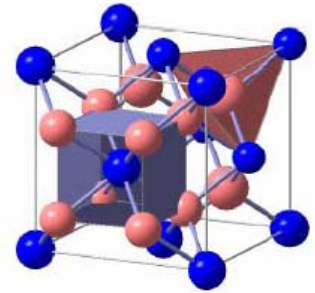
Figure 9. Examples of the crystal structures of inorganic compounds. The figures are borrowed from Wikipedia and Shaskolskaya 1976/1982 (Appendix C)

Structural type CaF_2 (fluorite)

c.c.p.



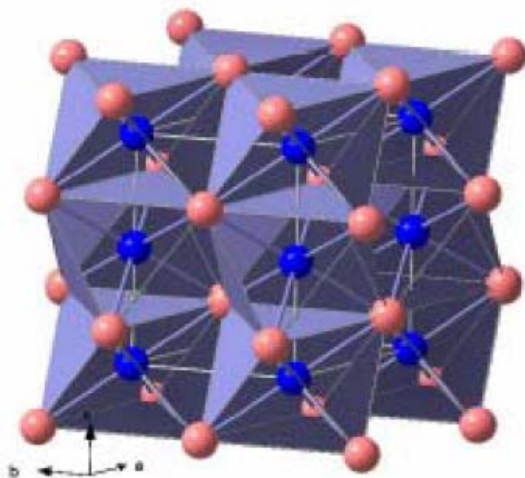
Ca :
c.n.= 8,
coordination - cube



F :
c.n.=4,
coordination - tetrahedron

All the tetrahedral interstitials occupied

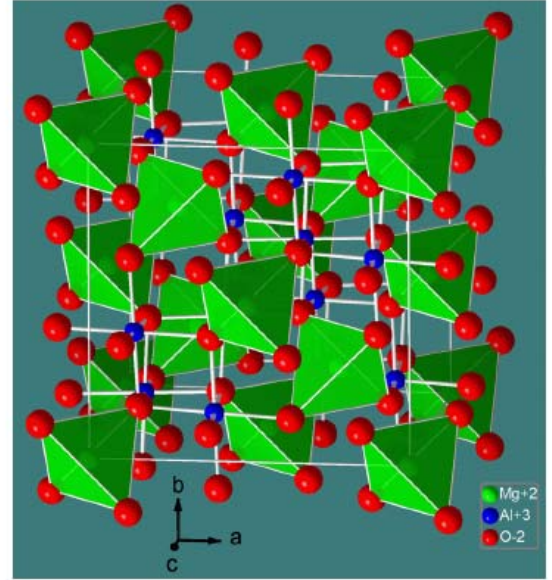
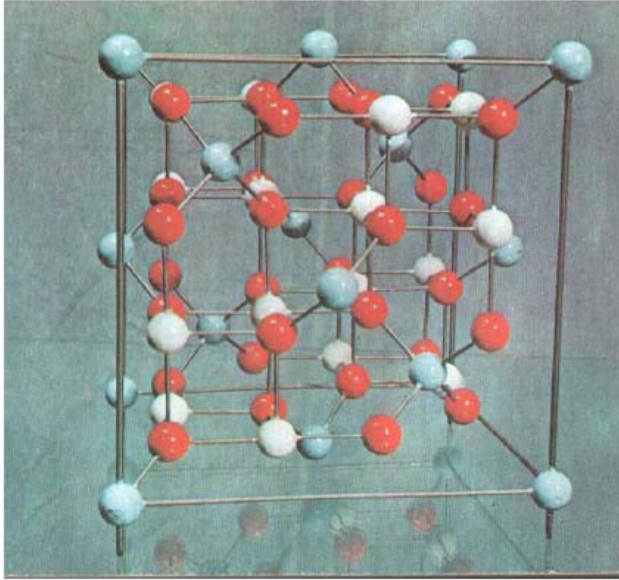
Structural type NiAs



h.c.p.

All the octahedral
interstitials occupied

Spinel $MgAl_2O_4$



Perovskite $CaTiO_3$

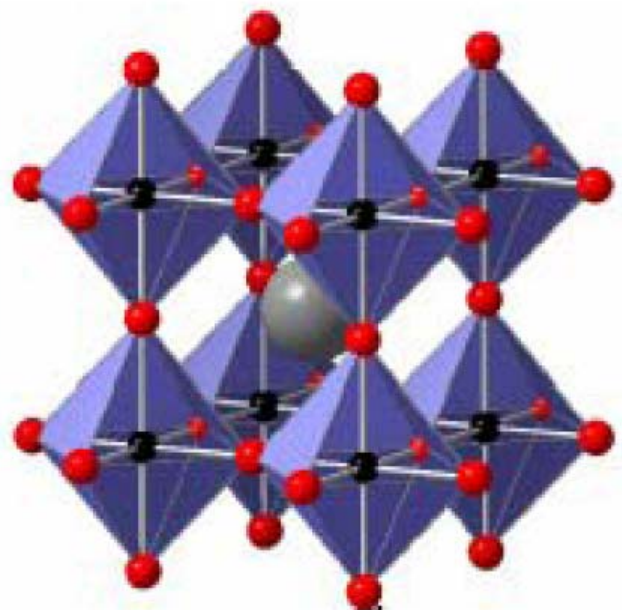
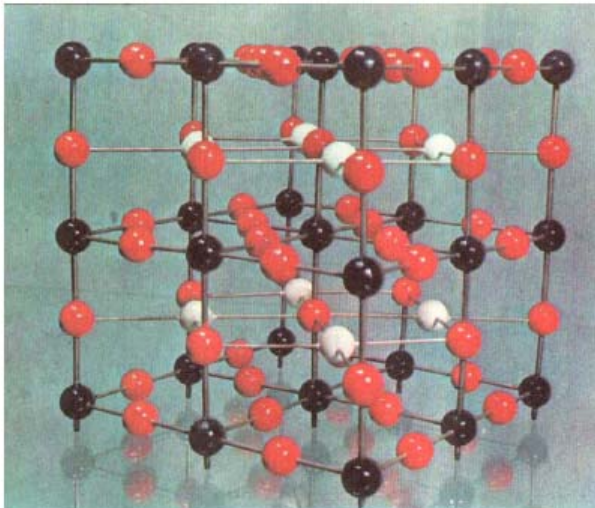
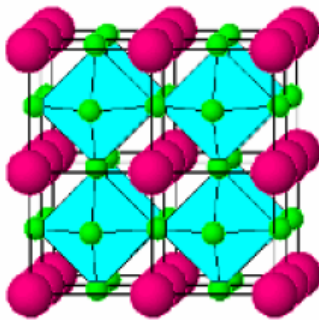


Figure 10. Structures of the "perovskite family" as a "theme" and "variations". The slides are based on the illustrations from: <http://wikis.lib.ncsu.edu/index.php/Perovskite>

Perovskite family (theme and variations)

Theme:



Ideal cubic
Perovskite,
 SrTiO_3 (Pm-3m)

Variations:

Tilt of octahedra

Distortion of octahedra

Distortion of the cube (trigonal, tetragonal, orthorhombic)

Displacement of cations inside the octahedra

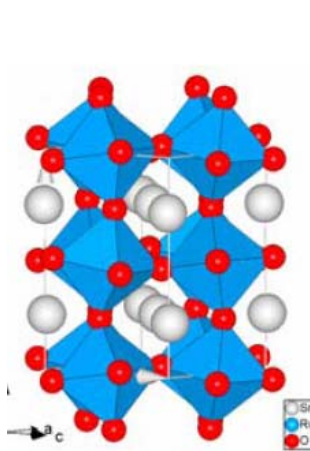
Oxygen deficiency

Inserts of the fragments from other structural types

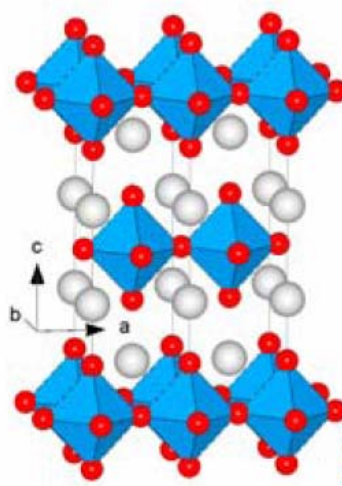
Partial isomorphous substitution of cations accompanied by distortions

Variations

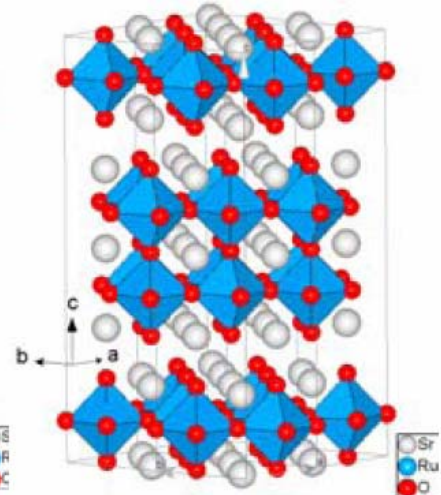
(Ruddleson-Popper, Aurivillius and Dion Jacobson phases)



SrRuO_3
Pnma

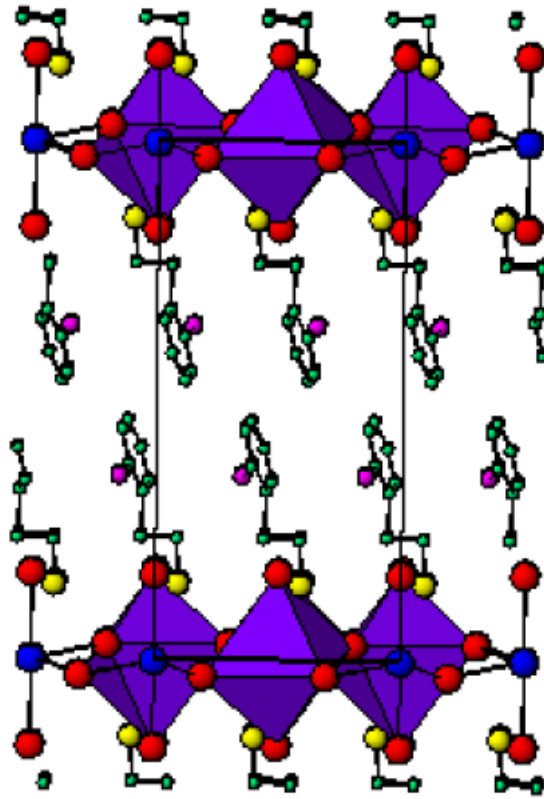


$\text{Sr}_2\text{Ru}_2\text{O}_7$
I4/mmm



$\text{Sr}_3\text{Ru}_2\text{O}_7$
Bbcb

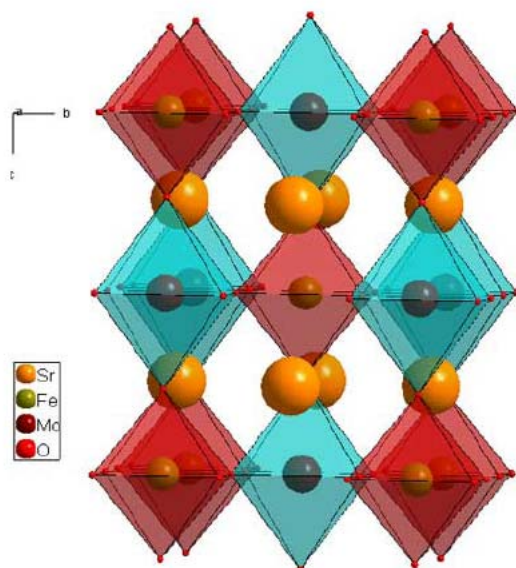
Layered perovskites



Organo-inorganic hybride materials

“Variations”

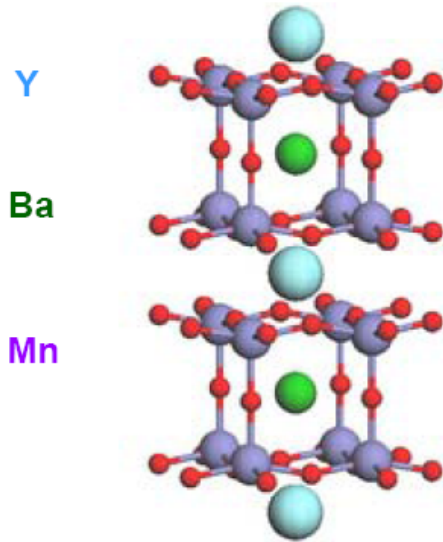
«Double perovskite»



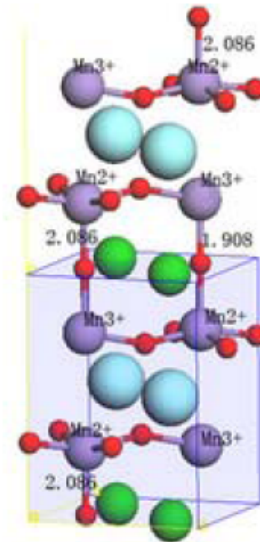
Fe and Mo are alternating regularly inside the octahedra

“Variations”

«Oxygen-deficient perovskites»



YBaMn_2O_5
P4/mmm



YBaMn_2O_5
P4/nmm

High-temperature superconductors

- $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ ($T = 92 \text{ K}$)
- $\text{Hg}_{12}\text{Ti}_3\text{Ba}_{30}\text{Ca}_{30}\text{Cu}_{45}\text{O}_{127}$ ($T = 138 \text{ K}$)

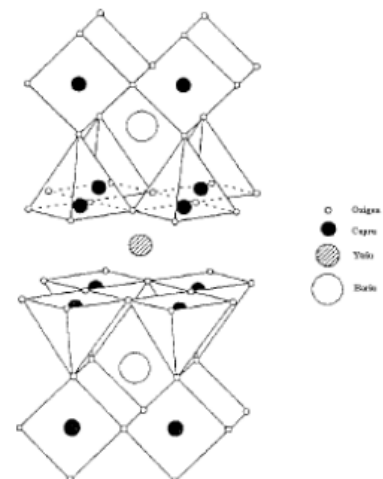
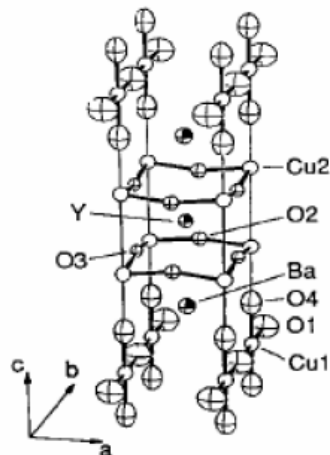


Figure 11. Preferred coordination geometry of transition metal ions. These slides are a courtesy of Prof. S. Natarajan

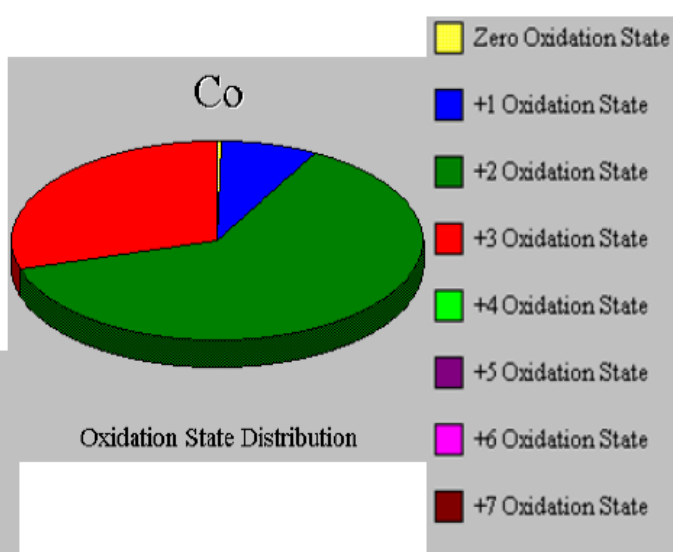
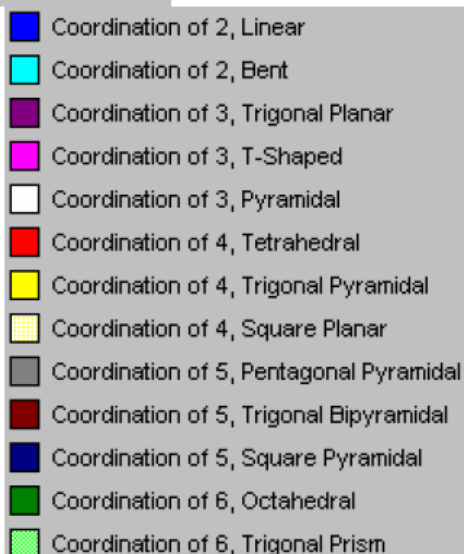
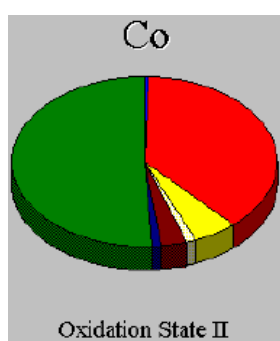
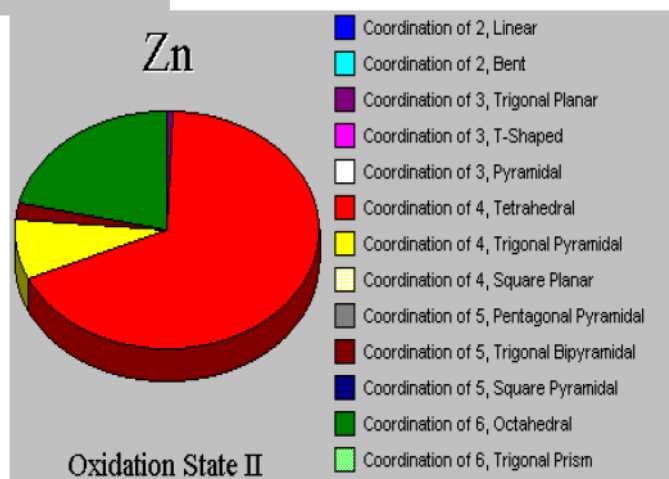
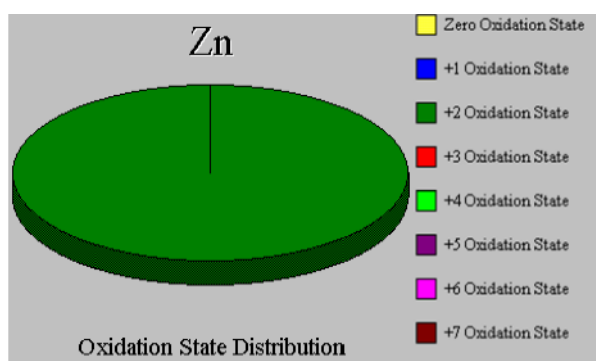
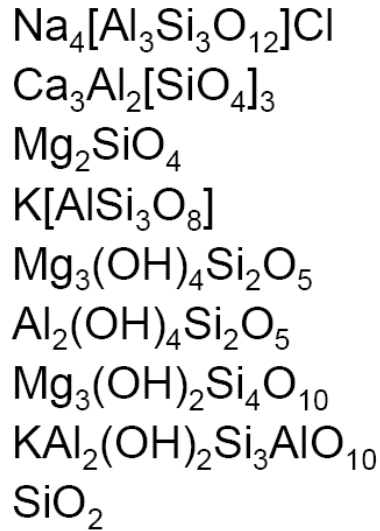
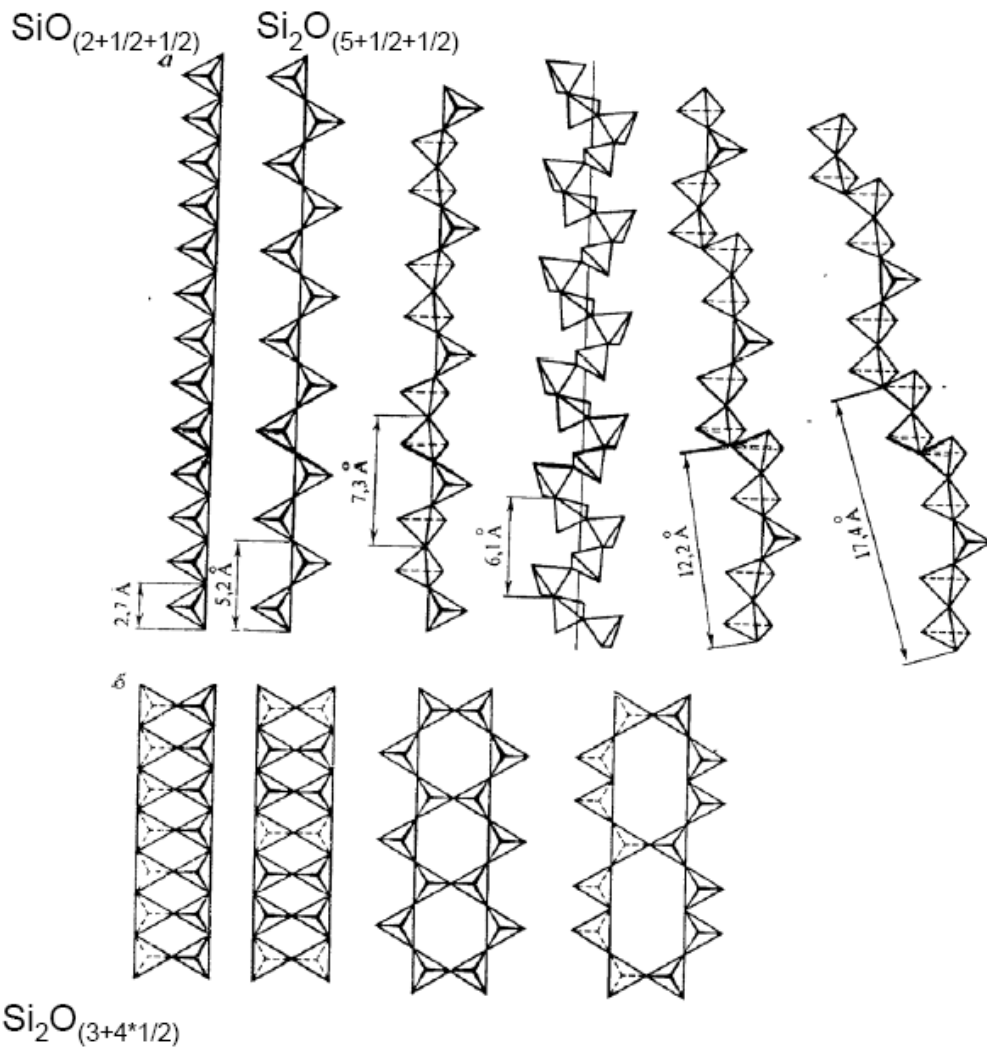


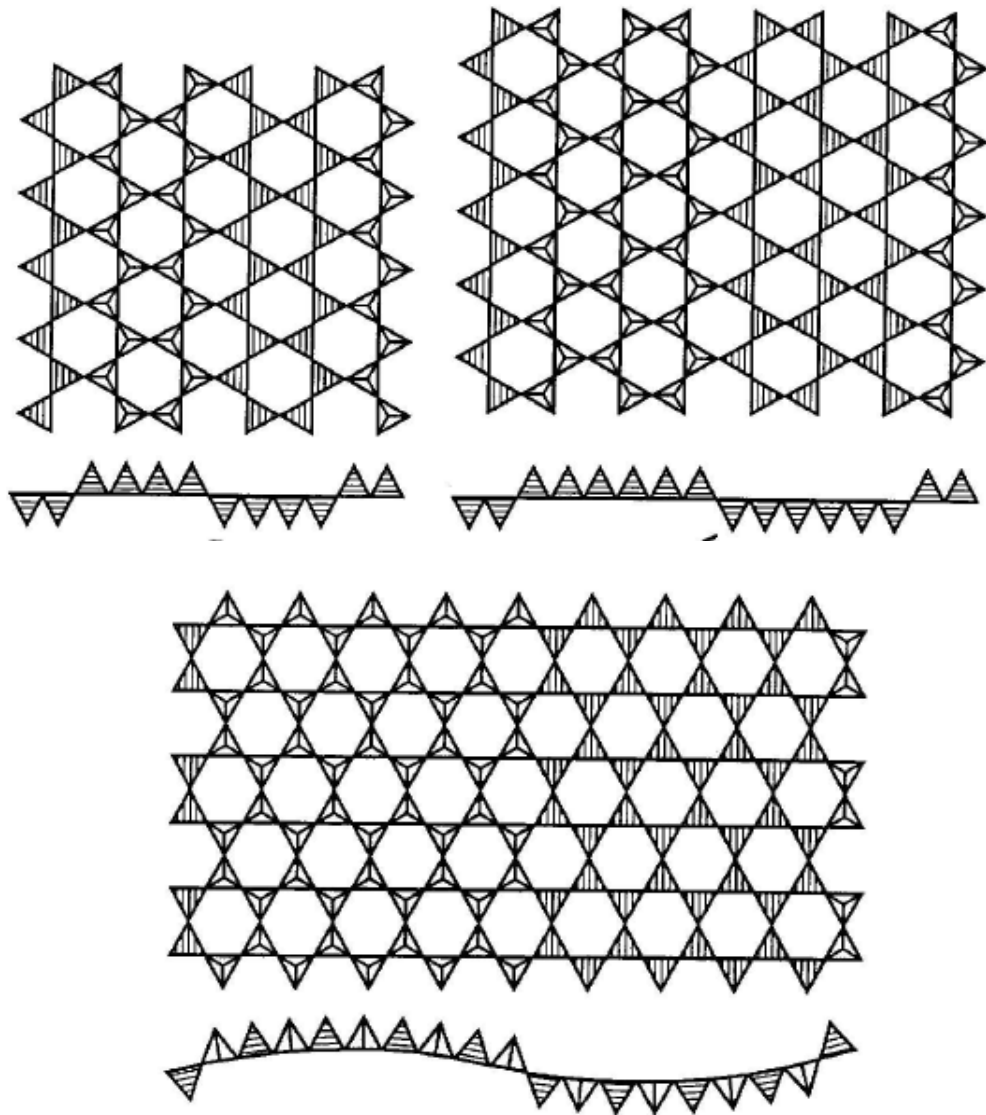
Figure 12. Silicates and SiO₂. Pearson symbols and space groups are discussed at later lectures. The slides are based on Liebau, 1985; Pushcharovsky, 1986 (Appendix C); a stishovite plot is from Wikipedia

Silicates and SiO₂

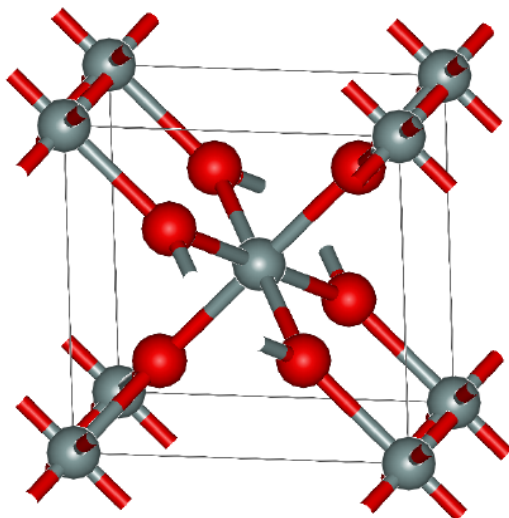


A universal structural unit:
tetrahedron (SiO₄)⁴⁻





SiO₂ with coordination number higher than 4

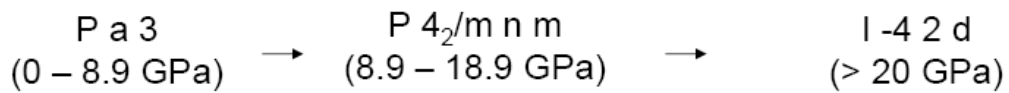
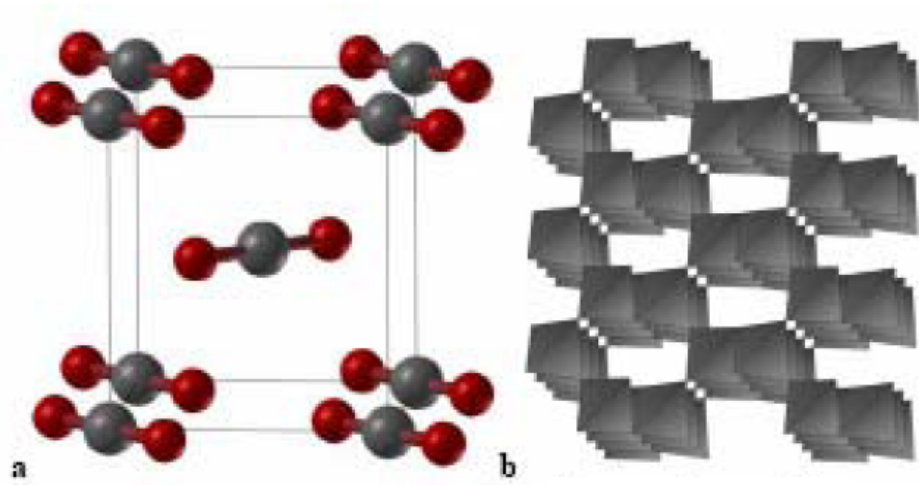
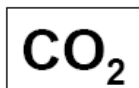


Stishovite is formed at very high shock pressures (>100 kbar or 10 GPa) and temperatures (> 1200 °C)

With a mass density of 4.287 g/cm³, stishovite is the heaviest polymorph of silica.

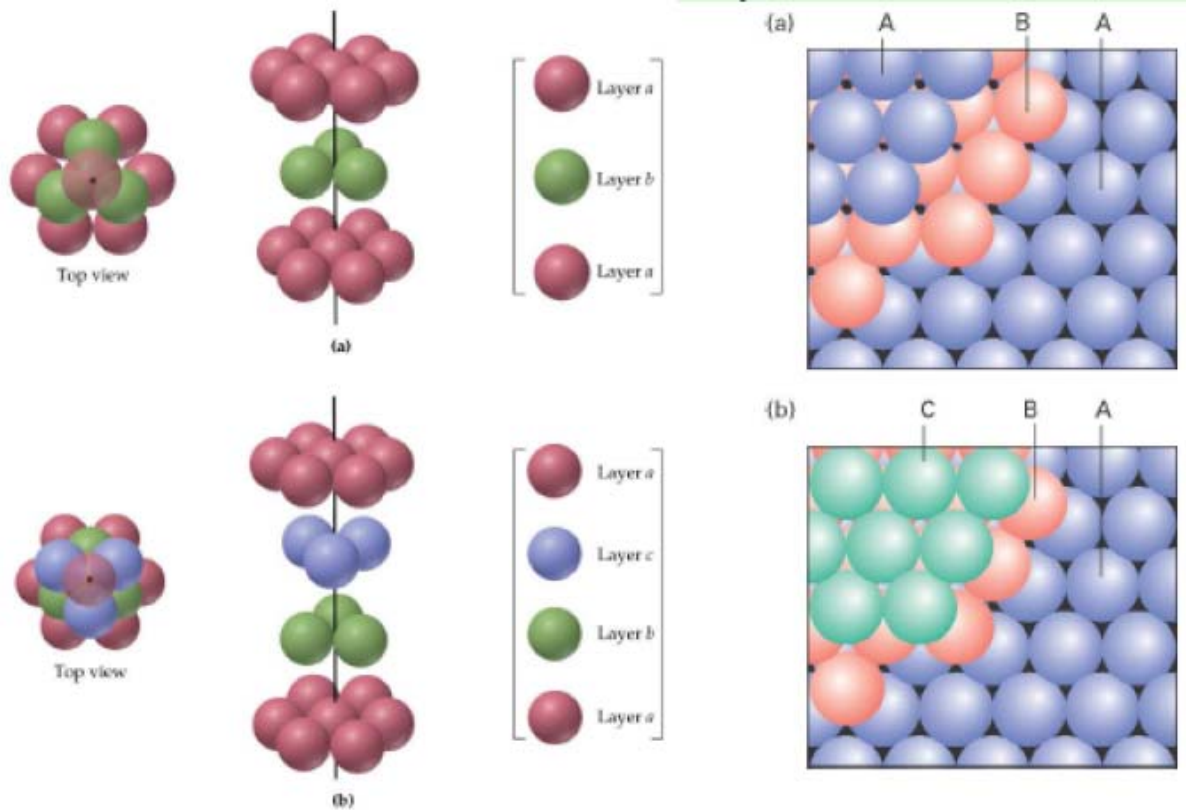
It has tetragonal crystal symmetry, P42/mnm, No.136, Pearson symbol tP6.

Figure 13. A comparison of the ambient-pressure and high-pressure polymorphs of CO₂. The slide is based on plots kindly provided by Prof. A. Oganov.



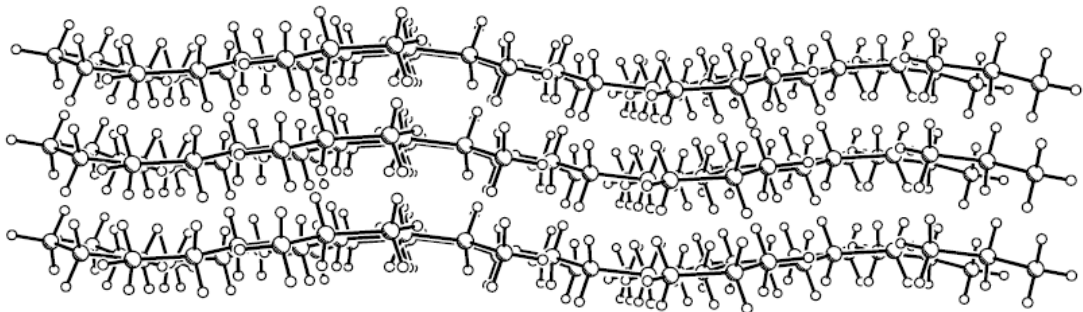
With increasing pressure, molecular crystals of CO₂ first lose the symmetry elements remaining molecular crystals, and after that carbon atoms become tetrahedrally coordinated, what is typical for SiO₂ at ambient conditions

Figure 14. A comparison of the close packing of spherical atoms and long alkane chains. The Figures are from http://en.wikipedia.org/wiki/Sphere_packing#Regular_packing (packing of spheres) and kindly provided by Prof. R. Boese (packing of alkanes and dioles)



Alkane

van der Waals interactions



Dioles

van der Waals interactions + hydrogen bonds

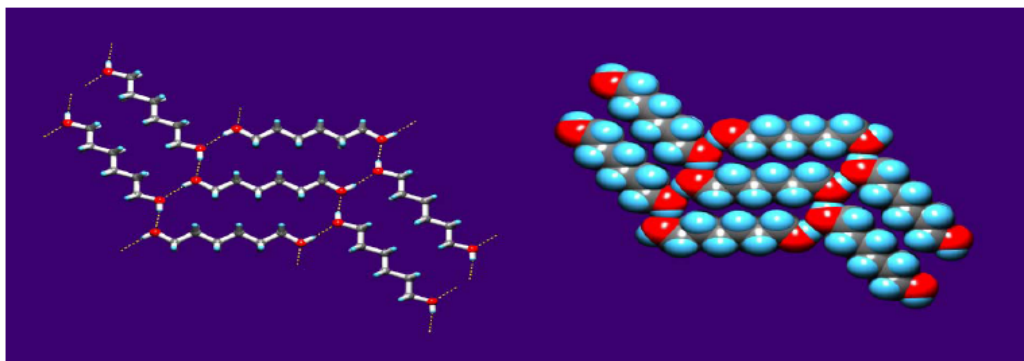


Figure 15. Nanoporous dipeptides.

Figures prepared using Mercury [http://www.ccdc.cam.ac.uk/free_services/mercury/] (Bruno *et al.*, 2002; Macrae *et al.*, 2006) based on data from Görbitz, 2002, 2003, 2007 (Appendix C)

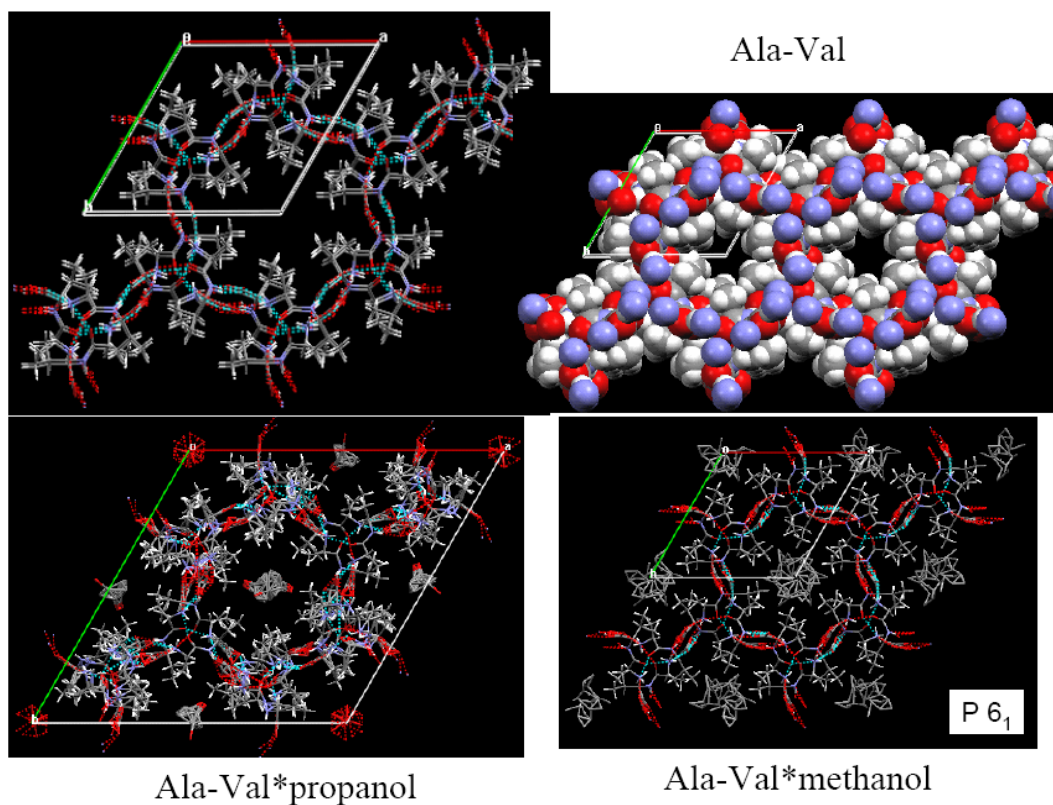


Figure 16. Dimers of acetic acid in the gas phase (a) and chains in the low-temperature (b) and high-pressure structures (c).

Figures prepared using Mercury [http://www.ccdc.cam.ac.uk/free_services/mercury/] (Bruno *et al.*, 2002; Macrae *et al.*, 2006) based on data from Allan *et al.*, 1999 & Nahrungbauer, 1970 (Appendix C)

