# EFFECTS OF HIGH PRESSURE ON MATTER

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Summary: When materials are under high pressure (in the range of 0-hundreds of gigapascals (GPa), 1 GPa=10000 bars) new properties, function and behavior appear. In these conditions, the nature ofthe chemical bonds changes dramatically, producing important variations in the chemical and physical properties of the molecules or the crystalline structures. Present results highlight that applied pressure can be an effective tool to tune electronic landscapes and access novel properties in materials, which would otherwise be unachievable at ambient conditions. In addition, some of these materials have unique properties that will be explained throughout the text, as well as it will be introduced some of the experimental and theoretical methods that are used actually in order to predict the structures and properties of this new materials under pressure.
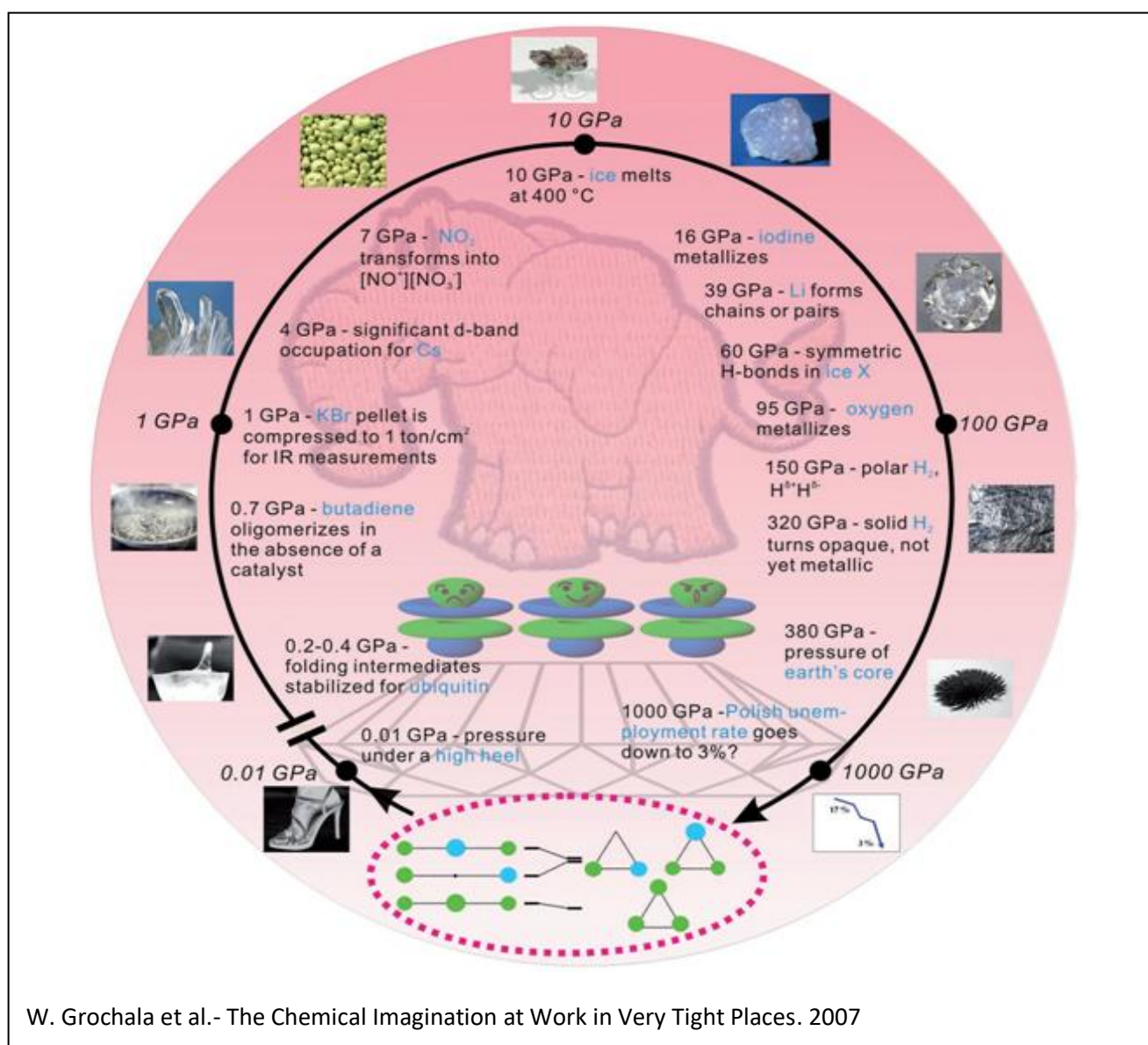
W. Grochala et al.- The Chemical Imagination at Work in Very Tight Places. 2007

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1. Introduction

Pressure is a thermodynamic variable and physical magnitude that measures the force projection in a perpendicular direction per unit of surface, and serves to characterize how a determined force is applied on a line.

Pressure serves as a fundamental thermodynamic variable that has been used to create novel structure, accelerate chemical reaction, and control the properties of materials (Grochala, Hoffmann, Feng, & Ashcroft, 2007)(Zhao, Xu, & Tian, 2016). As one efficient tuning knob, it provides a driving force not only to reduce interatomic distances but also to modify electronic orbitals and bonding structures. Accordingly, the pressure is emerging as a convenient and versatile tool to make quick discovery and fabrication of new materials, which can not be accessible at ambient conditions. Through this manuscript, we want to overview of how the study of materials under high pressure offers completely different and new ways not onlyin scientific investigation of fundamental phenomena but also in technological elaboration of new materials with enhanced or completely new properties.

The pressure changes of the order of atmospheres have some importance in the equilibrium of some reactions whose reactants are gaseous, however, if we increase the pressures to levels of tens or hundreds of Gigapascals (1 Gigapascal = 9869.23 atm), the pressure starts to play a fundamental role in the characteristics and nature of the chemical bonds of the matter.

The application of hydrostatic pressure has emerged as an effective means of tuning the structural phases and properties of materials (Zhang, Wang, Lv, & Ma, 2017)(Zhao et al., 2016). Under pressure, the crystal structure of these materials evolves through several structural phases that are inaccessible by temperature variation. In addition, applied pressure reveals novel properties by influencing their energetic landscapes and charge-carrier dynamics. Then, by increasing the pressure, the interatomic distances are reduced, which causes a distortion of the electronic orbitals and changes in the bonding patterns of the atoms. This opens the door to the synthesis of new materials that are not viable under normal conditions.

The pressure effects have been usually understood in the frameworks of the chemical thermodynamics and kinetics. Gibbs free energy is a extensive state function with units of energy that gives the condition of balance and spontaneity for a chemical reaction. This is referred by the following equation:

$$G = H - TS \quad (1)$$

Therefore, we define the Gibbs free energy according to the enthalpy, temperature and entropy of the system. Enthalpy can also be decomposed and replaced in the Gibbs free energy equation

$$H = U + PV \quad (2)$$

$$G = U + PV - TS \quad (3)$$

Then, we can decompose the G, which now depends on the internal energy, pressure, volume, temperature and entropy.

Under conditions of atmospheric pressure, the term "PV" has a low contribution to the Gibbs free energy, but when the pressure exceeds 100 GPa, the energy change of the system reaches 10 eV for every two atoms, which exceeds the energy of any chemical bond under normal pressure conditions (Hemley, 2002).

From kinetic point of view, according to the classical crystallization theory, crystallization proceeds though addition of molecular monomers or ions into acrystal lattice, which is governed by the minimization of system energy or the Gibb's free energy $G = E + PV - TS$ due to crystallization. (Science & Science, 1987). While current material syntheses are largely developed through the solution chemistry at ambient conditions,the externally applied pressure through mechanical compression stresses, instead of solution chemistry, provides an additional processing parameter to change material structuresvia altering the term of PV in the system energy. This term enables the formation of new material phases and configurations that impart innovative chemical and physical properties that have not been possible using current solution-based chemical methods (Yu et al., 2017)(Q. Li et al., 2017).

2. How to obtain high pressures

High pressure can be applied by using two types of equipment: systems that generate static pressure, including diamond anvil cells and large-volume presses (Such as piston-cylinder devices, opposite-anvil and multiple-anvil systems); and large-scale shock-wave facilities that generate dynamic compression.

The diamond anvil cell (Figure 1) is the most widely used laboratory device for generating static, multi-megabar pressures. Pressures of up to 770 GPa have been attained by using nanodiamonds as seconf-stage anvils in double-stage diamond anvil cells. (Dubrovinsky, Dubrovinskaia, Prakapenka, & Abakumov, 2012)

Figure 1
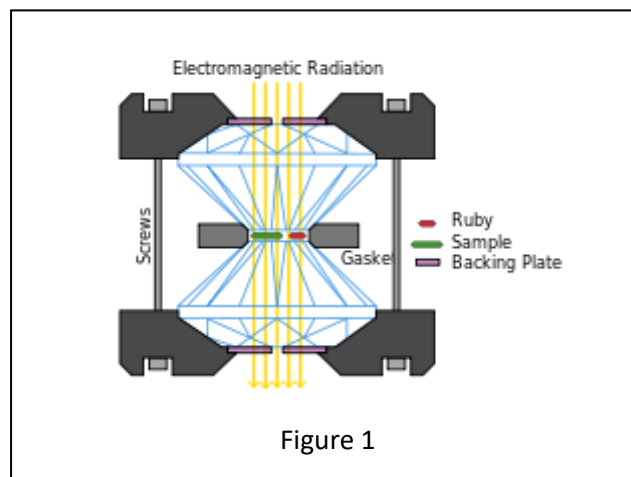
In addition to the extremely high generated pressures, diamond anvil cells have the advantage of being compatible with a vast range of in situ measurement techniques. Indeed, diamond's excellent transmittance of almost the entire electromagnetic spectrum allows the use of various radiation detection approaches, including X-ray and neutrón diffreaction, as well as various spectroscopy, Brillouin scattering, visible light and X-ray emission/absorption spectroscopy.

By fabricating diamond anvils with embedded electrodes and other measurement circuits, measurements of electric and magnetic properties can be performed in situ. The disadvantage of diamond anvil cells is that the volumen of simple that can be accommodated in the anvil is very small.

This sometimes, results in a signal that is too weak to be measured when using techniques that require a large amount of simple, such as neutrón diffraction. Another drawback of the small simple size is the inability to use diamond cells to synthetize comercial quantities of new materials.

Large-volume presses and dynamic-compression facilites these problems disappear, and can be used to produce many usefull materials with interesting technological

applications. However, a large volume static pressure apparatus can only reach pressures of several tens of gigapascals, much lower tan those achievable in a diamond anvil cell. Improvements in the design of the apparatus and the replacement of tungsten carbide by aintered diamond allowed a máximum pressure of more than 90 GPa to be reached in a multiple anvil device that used a 14 mm sintered diamond cube (Grochala et al., 2007, Recent advantages of high pressure diamond cells)

Dynamic compression facilities use shoch waves to generate pressures well into the terapascal range. Various techniques can be used to produce the shocks, ancluding gas guns, laser-driven compression and hemispherically converging explosives.

However, the transient nature of the shock wave means that it is generally difficult for samples to reach thermodynamic equilibrium. Thus, there are usually large uncertainties in the measured properties of the investigated materials.

3. Case studies

Pressure as a conventional thermodynamic parameter is a clean and useful tool to tune the atomic/molecular distance and consequently is capable of affecting the physical properties., Then, pressure affects the nature of the chemical bonds, and modifying the chemical bonding patterns and generating new structures with breathtaking physicochemical properties at high pressure has been widely validated in experiments. In different materials, pressure induces electronic and structural transformations such as crystalline-to-crystalline (polymorphism), amorphous-to-crystal (crystallization), and crystalline-to-amorphous (amorphization) transitions.We have selected some examples of different complexity in order to show what and how the corresponding changes take place when applied pressure is very high. We highlight previous researches on how an externally applied pressure changes chemical and crystal structures and thus drives phase transformation and how these changes accordingly influence their structural and electronic optical properties as well as their mechanical stability.

3.1. Cases

3.1.1 H_2

In figure 2 the variation of the H…H distance between adjacent H_2 molecule vs. pressure is represented and an analysis of the results renders that this distance drops considerably when pressure is increased.

Figure 2 (W. Grochala et al.- The Chemical Imagination at Work in Very Tight Places. 2007)
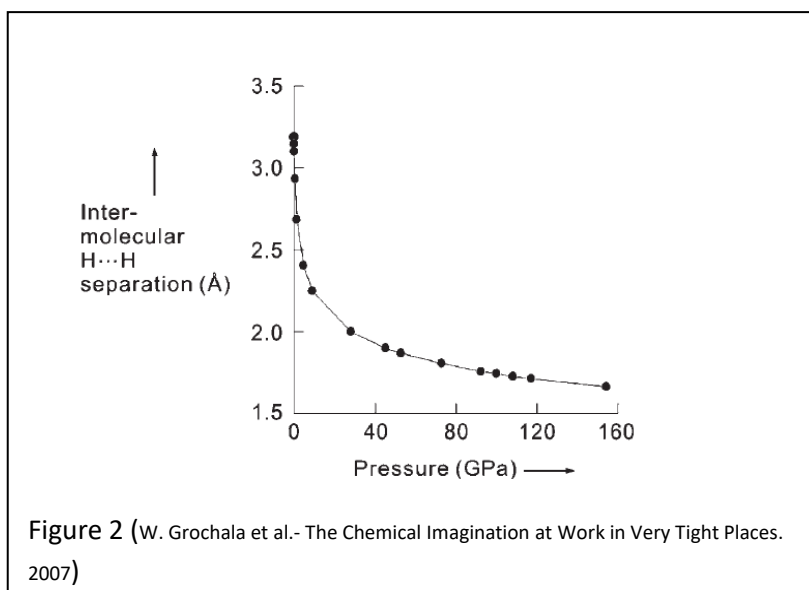
As it is observed there is a great decrease at low pressures followed by a slower decrease as the pressure increases more, since when we approach certain distances it is very difficult to compress more the intermolecular distances.

What are the consequences of this decrease in intermolecular distances? The increase in pressure causes the electronic density to be substantially reordered, which causes an increase in the coordination index of the atoms, since it is no longer prohibited by a high energy barrier, which at high pressures is compensated by the contribution of "PV" in the Gibbs free energy. This ends up causing a polymerization in one, two or three dimensions, forming an extensive polymeric non-molecular phase (Pruzan et al., 1990).

3.1.2 CO_2

CO_2 is a linear molecule, but at pressures greater than 35 GPa and 1800K it polymerizes in a structure that is currently unknown, but there are some evidences that the estructure is very similar to the estructure of SiO_2, which can be observed in figure 3 (Kerridge & Matthews, 1999).

Figure 3
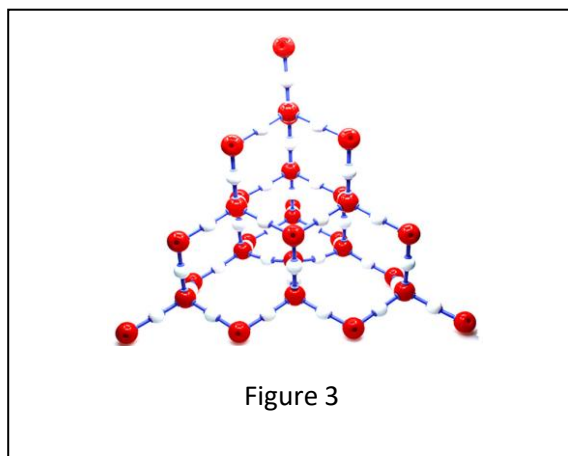
3.1.3.-H_2O

A polymerization process also takes places for a water system at high pressures. At normal pressures, the presenece of hydrogen bonds between the O and the H of the different molecules give the water very defined characteristics as its high melting point despite its low molecular weight, but when when the pressure values are larger than 60 GPa, the distances of the hydrogen bonds are reduced untila pint that it is impossible to differentiate one molecules from anothers. This state of H_2O is called ice X in which a polymeric network is fomed and the integrity of each water molecule disappears, since all the distance O-H are the same as shown in Figure 4 (Grochala et al., 2007)

Figure 4 (W. Grochala et al.- The Chemical Imagination at Work in Very Tight Places. 2007)
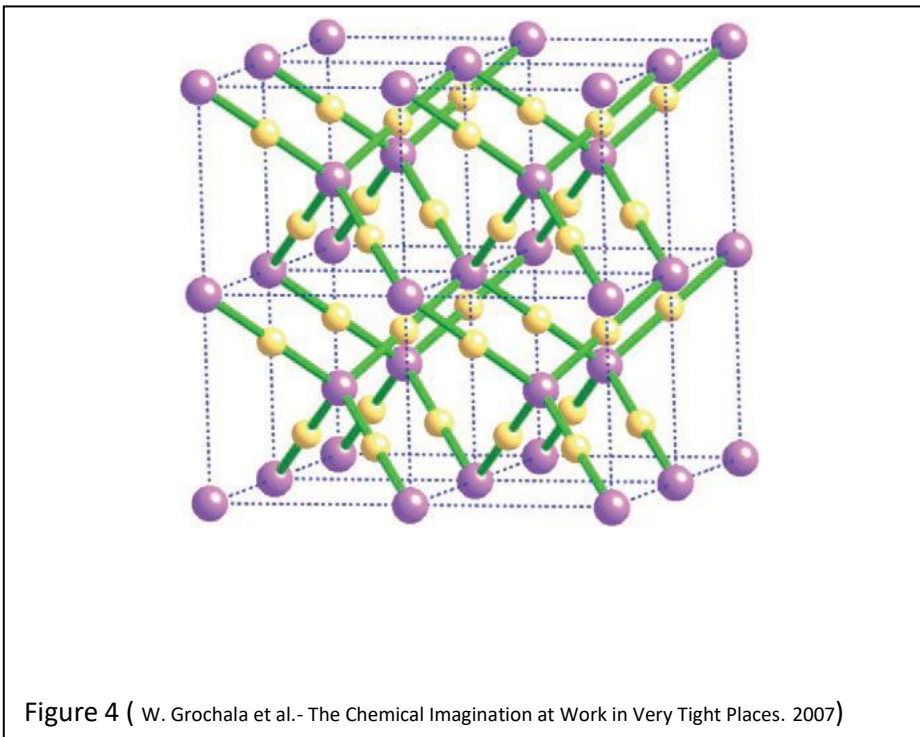
3.1.4. N_2

Despite of having the strongest homonuclear bond, the N_2 forms a polymer when sufficient pressure is applied, since at pressures higher than 110 GPa and 2000K forms a polymer coordinated with a pyramidal geometry shown in Figure 6.

Some studies in nitrogen show how the molecules behave under high pressures. In this case, the nitrogen, as we menctioned some pages before, we obtain a polimer.

But the studies have shown something that at first, should not be able to happen.

In an study made with computer calculations basen on a $(N_2)_3$ polimer (Grochala et al., 2007) we can see how a polimer can be formed, and what intermolecular distances get deformed (Figure 5).
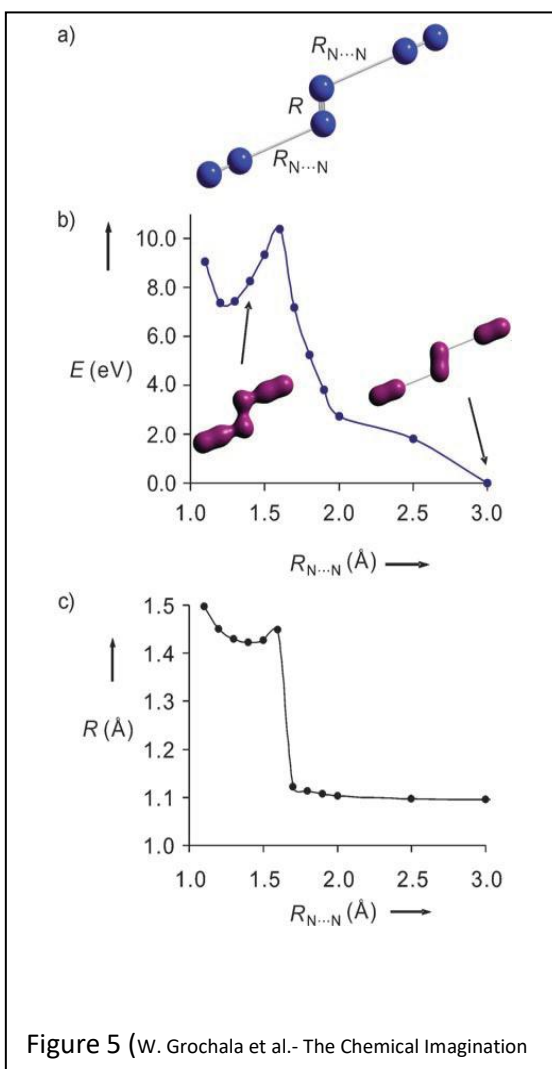
Figure 5 (W. Grochala et al.- The Chemical Imagination

As the intermolecular distance decreases, the electronic estructure gets reorganizated. The total energy of the system at first rises very slow, until 2 Å is reached. This is because this región corresponds to the Van der waals compression.

But there are also attractive interactions at work here, because the lone pairs of the outer N_2 and the π* orbitals of the N_2 central. Between 1.7 Å and 2 Å, these interactions lengthen the central bond somewhat. Then, until it reaches 1.6 Å, the energie rises very steeply, and then, the energy decreases again.

Along this path, the molecular distance between nitrogen has changed from 1.1 Å to 1.45 Å! That means that que distance becomes near of a single N-N bond. Therefore, we can see the signature of a squeezed covalent bond in a molecule of a low-Z element, at large distances.

Here it is exemplified by the region of N-N<1.2 Å. At such short N···N separations, two newly formed ("intermolecular") s bonds, as well as the original ("intramolecular") s bond of the central N_2 unit, are collectively squeezed. The calculations just begin to explore this region; we do not go further in because a model in which the distances in the external N_2 units are frozen is not realistic in this pressure regime.

Overall, as the two external N_2 molecules approach the central N_2 molecule upon squeezing, the electron density at the central N-N bond is significantly decreased, while new electron density builds up in the N···N regions.
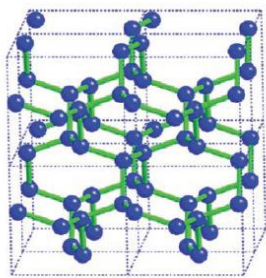
Figure 6 (W. Grochala et al.- The Chemical Imagination at Work in Very Tight Places. 2007)

3.1.5. Halogens: Iodine

The iodine is the most expensively studied halogen at high pressure (Hemley, 2002). It undergoes induced insulator-metal transition near 16 GPa. It have a secuence of transitions that is not seen very often.
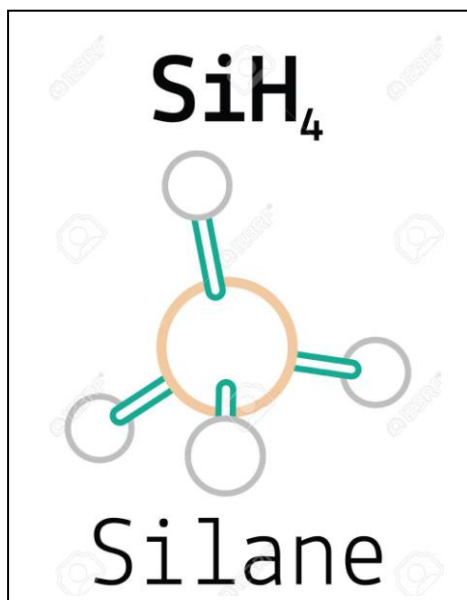
A low-pressure Cmca phase persists through the 16 GPa transition, and tha material become a body-centered orthothombic phase (Immm) at 21 GPa, followed by a transition to a body-centered tetragonal structure (I4/mmm) before reaching a closed-packed atomic structure fcc (Fm3m) at 55 Gpa. But this is not the last phase. At 276 GPa the material exhibits a metallic hexagonal closed-packed phase according to computational that is yet to be seen (Zhang et al., 2017).

Since 30 GPa the materials also have superconductivity when low temperatures are reached (1K)(Shimizu et al., 1994)
.
As we can see a system can have very different phases and caracterystics according to the pressure applied as we can see resumed in figure 7.

Figure 7 (Effects of high pressure on molecules. Annu Rev Phys Chem)
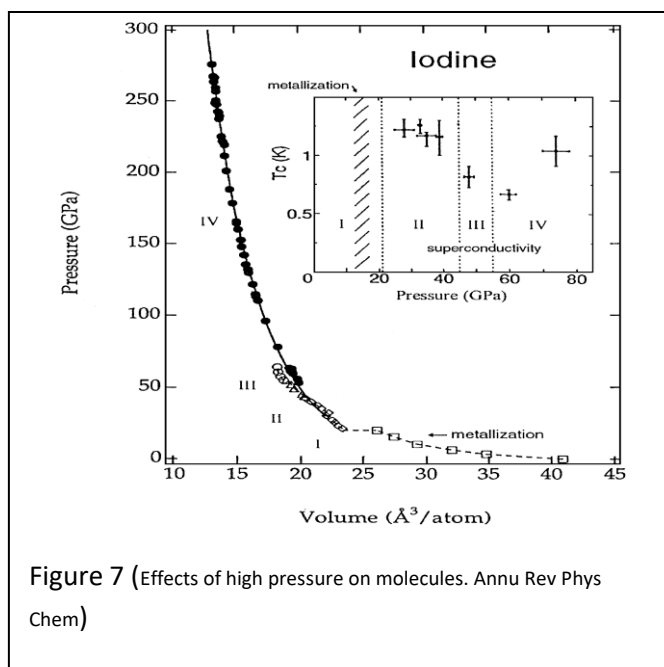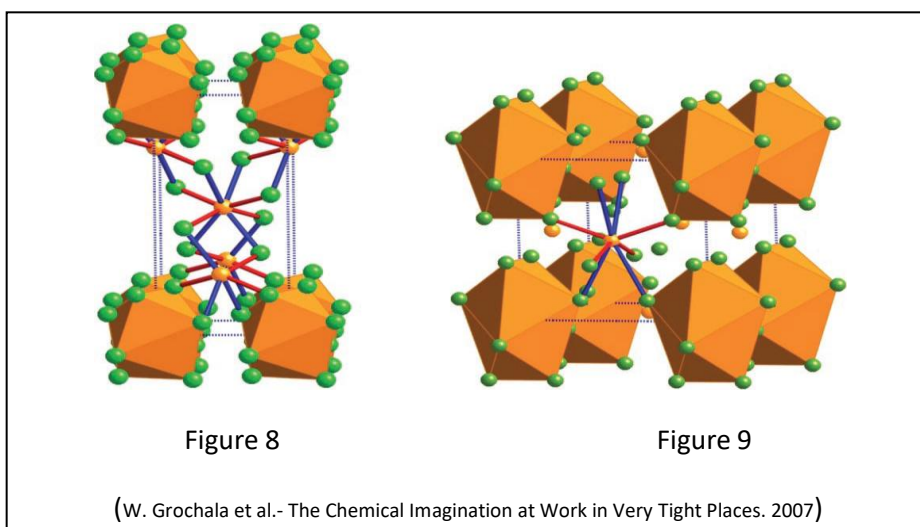
3.1.6. SiH_4

One of the structures that have been exhaustive studied at high pressure is the SiH_4. The electron-deficient bonding schemes can be used in order to describe the Si-H bond behaviour.

If we consider a low-enthalpy estructure at high pressure of the SiH_4 (space group $I4_1/a$) shown in Figure 8, each silicon atom has eight hydrogen atoms arround, pairs of which bridge to four neighboring silicon atoms (Grochala et al., 2007). Each Si---H_2---Si uses four electrons (One from each atom).

The problem is that, on the face of it, this bonding scheme requires eight participating orbitals from each silicon atom, but it has only four.

We can resolve this situation by using just the s and p orbitals of the central atom for delocalized bonding. The structure, similarly, has eight three-center electron-deficient Si---H---Si bonds around any given silicon atom, as we show at figure 9.

Figure 8   Figure 9

(W. Grochala et al.- The Chemical Imagination at Work in Very Tight Places. 2007)

This two structures are reached at 160 and 144 Gpa respectively (Pickard & Needs, 2006). To sum up, if one is starting with a saturated molecule, a methane analogue, and one subjects it to high pressure, the only way that one can move to higher coordination is through electron-deficient multicenter bonding.

Also, in other experiments, the effects of pressure have been studied on an electron-rich three-center system, and they arrived to the conclusión that the symmetrization is favored as the presure is increased, so the coordination increases too.

In summary, we can formulate an important rule according to the information that was obtained in this experiments; Increased coordination is achieved relatively easy through donor-acceptor bonding, wich shades over into multicenter bonding. That multicenter bonding, electron-rich or electron-poor, is a mechanism for compactification (so, a response to elevated pressure) for elements across the Periodic Table.

3.1.7. Metallization under high pressure: Kr

The calculations on SiH_4, predicted that hidrides of the group 14 elements should be metallized at moderated pressure, but this is not new.

In 1935, investigations of Bernal (Wigner & Seitz, 1933) noted something that we might call a rough rule: All materials become metallic under sufficiently high pressure.

Why this happens? Compression leads to greater overlap, so greater interaction among both filled and unfilled molecular orbitals.

Consider for example a hypothetical cubic lattice of Kr atoms. It's electronic configuration is $[Ar]4s^2\ 3d^{10}\ 4p^6$. His valence electrons are well separated from the unoccuped 5s orbitals (arround 8 eV, as we can see in figure 10), so at ambient temperature krypton atoms interact with other Kr atoms very weakly, due to his octec configuration. This high separation of 4p and 5s assures that the polarizability of Kr is quite small.

Figure 10

(W. Grochala et al.- The Chemical Imagination at Work in Very Tight Places. 2007)
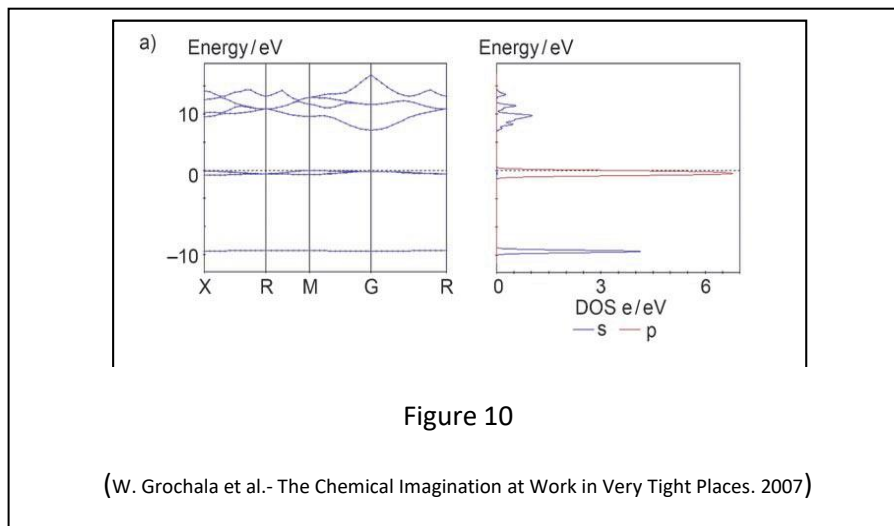
At a Kr---Kr separation of 4.04 Å (The van der Waals separation at 1 atm, in figure 14) the electronic bands formed from 4p orbitals are quite narrow, with a dispersión of 2 eV, with a 5s and 5p much more dispersed.

When we apply pressure to a model cristal, the the atoms are closer to each other, their occupied and unoccupied atomic orbitals start interacting more strongly. The corresponding bands spread progressively, and the band width grows.

The widht of the 5s/5p band increases to 20 eV at 100 Gpa, and the 4p band reaches 10 ev, as we can see in figure 11.

Figure 11 (100 Gpa)

(W. Grochala et al.- The Chemical Imagination at Work in Very Tight Places. 2007)
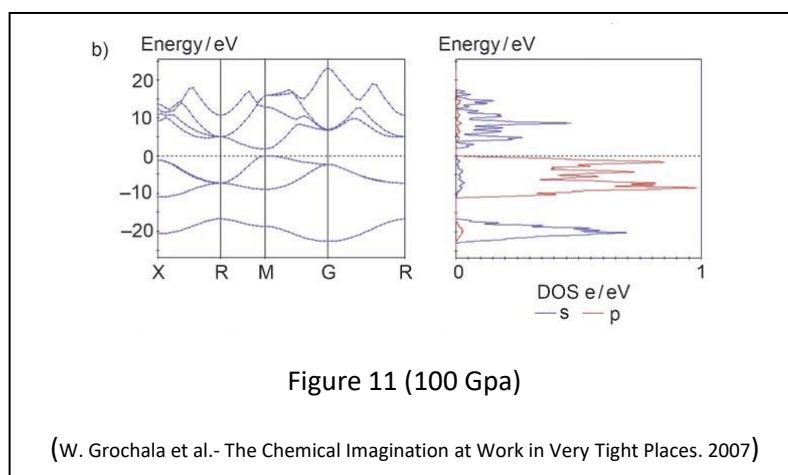
If we continue increasing the pressure, as we can see in figure 12, the gap between the two bands will be closed through band crossing. Thus, in theory at least, the localized valence electrons of every noble gas should become delocalized at some point. (Grochala et al., 2007).

Figure 12 (145 Gpa)

(W. Grochala et al.- The Chemical Imagination at Work in Very Tight Places. 2007)
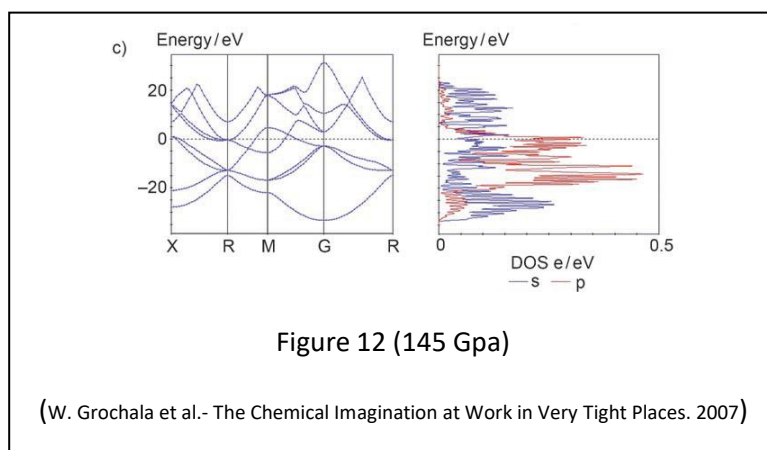
At the moment, for Kr, there are only computational calculations, but the heavier and more polarizable Xenon has been forced to surrender its nobility, by forming a hexagonal hcp lattice at 70-90 GPa, and then at 130-150 GPa it became metallic (Begemann & Boers, 1972).

Other compounds like CsI and BaTe have also been metallized at 115 and 200 GPa respectively. In CsI, the polarizable lone pairs of I^- ions achieve metallization through band overlap with diffuse Cs^+ states (Eremets, 1998).

We can see that over a range of intermediate pressures band-gap reduction is not universal. For classic semiconductors, the direct band gap often increases with pressure over a substantial pressure range.

There are also some studies that indicate that in certain metallic structures as Li or Ca, bands may narrow with pressure instead of getting wider (Nixon, L. W., Papaconstantopoulos, D. A., & Mehl, M. J. (2007). Calculations of the superconducting properties of scandium under high pressure. Physical Review B - Condensed Matter and Materials Physics, 76(13), 6–8. https://doi.org/10.1103/PhysRevB.76.13, Papaconstantopoulos, & Mehl, 2007).

3.1.8. PbS

The structures of the compounds undergo changes with high pressure, so that their spatial groups and structures undergo changes with high pressure. This produce changes in structure and different polymorphous with the same stechiometry.

Bulk PbS has a cubic rock-Salt structure (B1) with a lattice constant of 5.936 Å at ambient conditions. At a pressure of 2.2-2.5 GPa, PbS undergoes the first-order structural transformation and transforms into an orthorhombic structure (B16/B33, black pfosphorus type).

When pressure increases, the second phase transition to a CsCl type structure (B2) occurs abpve 22 GPa.

Upon release of structure, the starting rock-salt phase is completely recovered (*The effect of pressure on PbS and PbTe*, H.Kobayashi)

3.1.9.TiO$_2$

TiO$_2$ is one of the model systems in which the size/morphology not only affects the pressure where the phasetransition takes place but also substantially changes the pathway of phase transition.

In nature, TiO$_2$ crystallizes mostly in three structural polymorphs: anatase (tetragonal, I4$_1$/amd), rutile (tetragonal, P4$_2$/mnm) and brookite (orthorhombic, Pbca).

Among these structural phases, anatase has been widely explored to understand the nanoscale/morphological effects on phase transition and compressibility. Bulk anatase TiO2 undergoes a phase transition from the anatase structure to a columbite α- PbO$_2$-type structure (orthorhombic, Pbcn, referred as TiO$_2$-II in references) at 2−5 GPa, and then to baddeleyite structure (monoclinic, P21/c) at 12−15 GPa (Bai, Bian, Huang, Wang, & Fan, 2019)

During decompression, it transforms into a columbite structure at ~7 GPa, which remains stable to ambient conditions.120 When particle reduces in size down to nanoscale (below 50 nm), anatase TiO2 displays a dramatically different behavior of phase transformation.

Raman peaks of the anatase phase shift to higher wavenumber and remain to a much higher pressure of 24 GPa than that in bulk. Upon continuous compression, the Raman peaks disappear, showing a featureless profile of Raman, anatase TiO$_2$ nanoparticles become amorphous at 24 GPa (Franco et al., 2015).

Also was recorded a very different behaviour with presence of dopants in the nanocrystals of TiO$_2$ as we can see in figure 13, where some of the Raman's spectrums are presented.
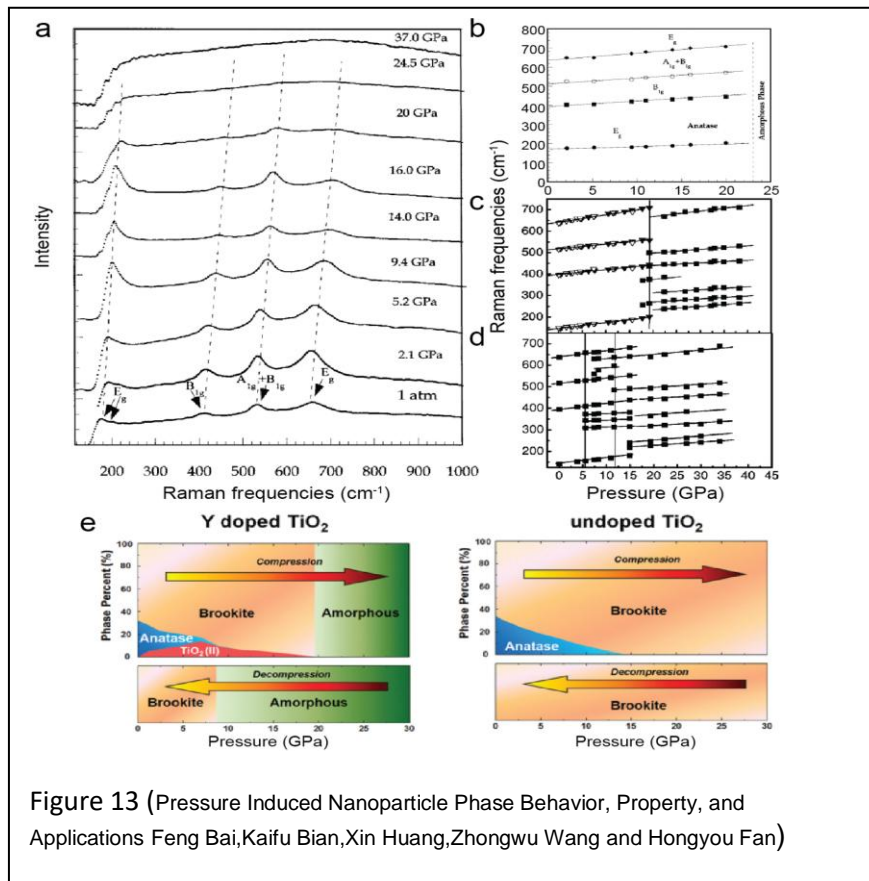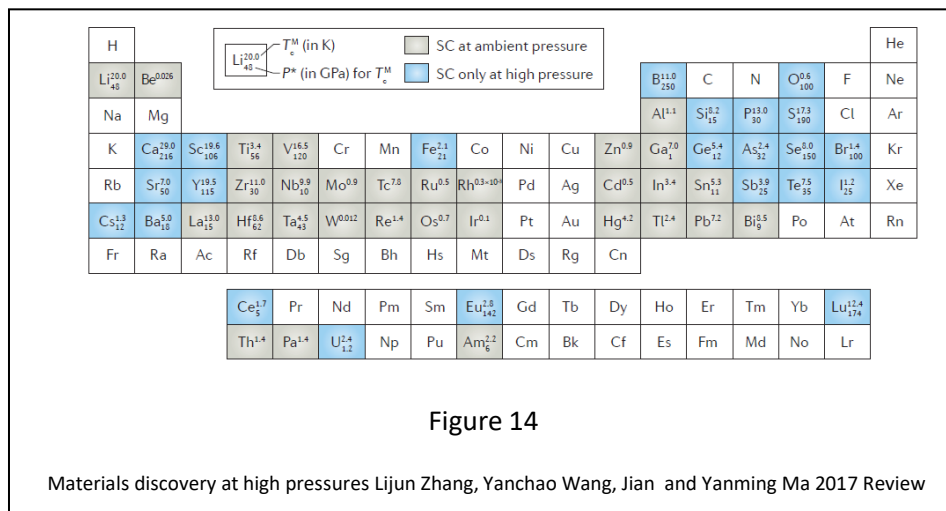
Figure 13 (Pressure Induced Nanoparticle Phase Behavior, Property, and Applications Feng Bai,Kaifu Bian,Xin Huang,Zhongwu Wang and Hongyou Fan)

3.2. Superconductors

The superconductivity is a phenomenom of exactly zero electrical resistance and expulsión of magnetic flux fields occuring in certain materials, called superconductors, when cooled below a characteristic critical temperature, wich is usually near of 0K.

Superconductors can be divided into two categories: conventional and unconventional. Conventional superconductors are described by the BCS theory; theyr superconductivity is due to the electron pairing mediated by the Exchange of phonons, which results in a superfluid-like behaviour.

High pressure had an inportant role in the discovery of conventional superconductors: of the 53 known elemental superconductors, only 30 are superconductive at an ambient pressure, the others become superconductive only at high pressure (Figure 14) (Zhang et al., 2017).

Legend: T_c^M (in K); P^* (in GPa) for T_c^M; SC at ambient pressure; SC only at high pressure. Example: $Li_{48}^{20.0}$.

Figure 14

Materials discovery at high pressures Lijun Zhang, Yanchao Wang, Jian and Yanming Ma 2017 Review

Unconventional superconductors are not described by the BCS theory, and their superconducting mechanism is yet a mystery.

Pressure strongly influences the properties of unconventional superconductors. Depending on the doping levels of the investigated materia, the critical temperature (T_c) for some cuprates and Fe superconductors can increase or decrease under high pressure.

The underlying mechanism might be associated with changes in the interplay among varius factors affecting superconductivity, such as charge, orbital or spin excitations. For example, an anormal high temperature for a cuprate superconductor (164 K) was reached at 31 Gpa (Bussmann-holder, Köhler, Simon, Whangbo, & Perali, 2017).

In Fe chalcogenide superconductor, high pressure has benn reported to destroy the original superconducting state, inducing an intriguing alternative superconducting state

with a higher T_c (Sun et al., 2012). Pressure can also efficiently suppress the magnetic orders that compete with superconductivity, as demonstrated in heavy-fermion systems and undoped Fe-based superconductors (Zhang et al., 2017).

Searching for new superconductors at high pressures is promising mainly because of two effects that pressure has on materials. In metals, pressure-induced structural phase transitions can generate new structures that can be superconductive (For example Ca, Cs, Y, Fe, Sc, Sr and Ba). In insulators and semiconductors, pressure induces electronic phase transitions from the insulating or semiconducting state to a metallic state through the closure of the band gap. Once metallized, these materials have the potential to become superconductive (Buzea & Robbie, 2005).

Thus, there is a significant number of high pressure superconductors derived from nan-metallic elements, including B, O_2, Si, P, S, Se Br_2 and I_2 are obtained (Zhang et al., 2017). Pressure also induces the generation of free carriers for superconductivity in an effect that to some extent resembles the superconductivity induced by impurity doping in insulating materials.

Among insulating materials that become superoconductive under pressure, S shows a relatively high T_c of 17K at 100 GPa. This high critical temperature is attributed to the pressure-induced suppression of charge-density-wave instabilities. Hydrogen-rich materials that are insulating at ambient pressure can be metallized and become good superconductors at high pressure (Degtyareva et al., 2007).

According to the BCS theory (Bardeen-Cooper-Schrieffer), Hydrogen, the lightest element, with one unscreened electron, under pressure would form a metallic solid with a very high T_c. For example, some theoretical studies predict that compressed H-rich material would show the spectacular T_c of 264K for a YH_6 (Y. Li et al., 2015) material under pressures of 400-500 GPa, and 166K for SiH_4. But sometimes we have the problem that this theoretical predictions are not good, because in the real life we cant synthetize this compounds. However, the compound with the highest T_c known, was also studies before of trying to get it in experimentals procedures.

The solid H_2S was not initially consideres as a high pressure superconductor, because it was believed to dissociate into its constituents elements before metalllizing under pressure; but theoretical calculations showed that dissociation would not happen, and the material could even be superconductor at 160 GPa with a T_c of 80K.

However, experiments give some incredible results. Above 160 GPa T_c increment was quite big, and arrived to 150K. A second superconductive state with a T_c of 203K is obtained in samples annealed at room temperature and can be described to a stoichiometric change from H_2S to H_3S, that con only be obtained at high pressure (Degtyareva et al., 2007).

Room temperature superconductivity is the focus of intensive research. The experimental work on H_2S has disproved the conventional wisdom that 40K is the máximum T_c that can be obtained in phonon-mediated superconductivity and demonstrated the potential of H-rich materials for high temperature superconductivity.

4.Applications

In the following some important applications of the high pressure field are summarized.

4.1. Elaboration of superconductor materials

As we explained before, actually, the high pressure is the only way of obtaining a superconductor that can operate at ambient temperature. The actual superconductors need a huge amount of energy in order to mantain the temperatures below the T_c. This also difficults working with this kind of matterials.

These superconductors could be used to make super powerful magnets that can be used in generators in order to get electricity from mechanical energy. Also it could be used to make a kind of trains that "fly" due to the megnetic repulsion and use thom to move electricity without energy loose.

4.2. Superhard materials

Superhard materials (With Vickers hardness $H_v > 40$ GPa) are of great industrial importance and find application as, for example, cutting and polishing tolos, coatings and abrasives.

Diamond and c-BN are two traditional super hard materials. Diamond is the hardest known (60-100 GPa of H_v), but it has some limitations; it is brittle, oxidizes to CO_2 at 800ºC in air and reacts with Fe during cutting.

Although c-BN (figure 15) is chemically and thermally more stable than diamond, its hardness is much lower (40-60 GPa H_v) and the synthesis of large crystals is difficult, which hinders its industrial application (Zhao et al., 2016).

Figure 15
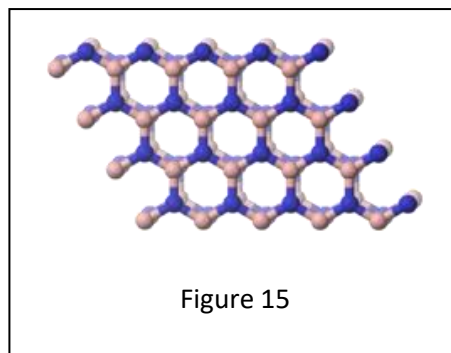
Therefore, finding alternative superhard materials that are chemically and thermally stable is an important goal for materials scientists, and high pressure is such a good field in order to get it.

For a meterial to be superhard, its structure must consist of densely packed, 3D, strongly covalent bonding networks. Pressure has become an important technique for synthetizing such materials, because it induces volumen decreases that stabilize densely packed structures. Materials formed from light elements such as B, C and N with high electronegativity have attracted considerable attention, as they can form the necessary strong and short covalent bonds, as in C diamond and c-BN

Nowadays the main fields of investigation are centred in getting new structures of this compounds that are more hard that diamond.

Some structures like fullerenes C_{60} and new carbón structures similar than diamond are the ones that could probably be the future hardest materials (Meng, Liu, Zeng, & Mao, 2012).

Theoretical calculations are capable to predict these new structures that could be stronger and facilitate the work to the experimental scientists.

4.3. High energy density materials

High energy density materials (HEDM) for propellants and explosives synthesized at high pressures also attract considerable research interest. Polymeric solids consisting of molecular units made of low atomic nomber elements are promising HEDMs, because a large amount of energy can be released during the transformation from the high energy polymeric phase to the energetically favoured molecular phase (Christe, Wilson, Sheehy, & Boatz, 2004).

For example, polymerical nitrogen would be a clear HEDM due to the high difference between the single, souble and triple bond of the nitrogen in nitrogen atoms (160-418-954 KJ/mol).

High pressure can break these bonds, and then polymeric phases can be formed. This materials could have 5 times as high as the most powerful energetic material in use actually (Zhang et al., 2017).

4.4. Materials for hydrogen storage

Materials for hydrogen storage are another class of energy materials that has been extensively studied under high pressures. They are base on H_2-containing molecular complexes that are formed by compressing together high-density H_2 molecules and other simple molecules.

The synthesis of these H_2-containing molecular complexes through high-pressure routes has been attempted by placing H_2 molecules into matrices of rare gases, silane, germano, hydrogen sulfide, methane and water ice.

All of them are being studied nowadays, but the most promising of them seems to be the H_2O-H_2 systems. This systems, when the pressure increases, the proportion of H_2/H_2O increases even up uf a 1-1 relatien avobe 2.3 GPa (Strobel, Somayazulu, & Hemley, 2011).

There are also materials based on metal hydrides with high hydrogen content. At ambient pressure, most known late-transition metal hydrides exhibit a close-packed host lattice with H atoms occupying the octahedral or tetrahedral interstitial sites. In this type of materials, the relation H/Metal is lower than 1, but with high pressure, this number can be icreased (Zhang et al., 2017).

4.5. Exotic chemical materials

High pressure can fundamentally modify the chemical identity of elements, ant thus it can lead to materials with unprecedented stoichiometries and chemical properties.

Pressure can enable some chemical reactions by altering the reaction kinetic barriers. This can lead in some materials with unprecedented stoichiometries and properties. For example, at ambient pressure CaH_2 is the only hydride of Ca known, but at high pressure we are able to synthetize CaH_6 or even CaH_{12} (Wang, Tse, Tanaka, Iitaka, & Ma, 2012).

High pressure can induce significant charge redistribution and even give rise to unusual chemical bonding. A clear example is the N_2O. When high pressure in applied emerge an ionic phase of $NO^+NO_3^-$ (Somayazulu et al., 2001).

Finally, high pressure can be used in order to synthetize electrides. These materials belong to an exotic family of materials that is based on ionic solids that consist of a cationic framework with excess electrons trapped in the lattice voids act as anions (Zhang et al., 2017).

The modification of the electron distribution by high pressure can lead to electron trapping in the interstitial voids and even to the deformation of electrides.

5.Applying Theoretical and Computational chemistry to study polymorphs and their transformation induced by pressure: the case of AgClO$_4$

Experimental techniqes are not the only way of study the high pressure, as we have seen previously in some of the cases that we presented before. First-principles density functional theory (DFT) calculations have had a substantial impact in materials discovery at high pressure. These calculations allow to predict a wide range of preperties like electronic, vibrational, magnetic and even superconductive properties like the ones that are commented at page 16.

DFT is a computational quantum modelling method used in this field of chemistry to investigate the electronic structure. It is a variational alternative method of the Schrödinger ecuation solution, where the electronic energy functional is minimized respect the electronic density. Pressure-induced phase transitions from one structures to another can be readily investigated using total energy minimization for different structures as a function of pressure.

We will investigated the possible polymorphs of AgClO$_4$ by using DFT calculations in a wide range of pressure in order to obtain the phase transitions and provide new insight and help in undestanding experimental observations. It's important to recognize that these methods can be used before the experimental procedures in order to predict what will be the new structures that experiments are able to obtain and if they will have interesting properties, so this field of the chemistry is a very important way of discover new materials and ways of getting them.

Structure-searching methods combined with reliable DFT calculations can explore complicated high-dimensional free-energy surfaces to seek the global energy mínimum corresponding to the most stable ground-state structure. With only the chemical composition, these methods can identify the thermodynamically stable structures of materials under pressure, so this give a high predictive power that can be used to guide the experimentals procedures.

Hybrid functionals are approximations to the exchange-correlation energy in DFT. These methods incorporate a portion of exact exchange from HF theory with the rest of the exchange-correlation energy from other sources like ab initio or empirical sources. The three most popular hybrid functionals that have been used in this theoretical procedure are B3LYP, PBE and HSE. They are usually constructed as a linear combination of the Hartree–Fock exact exchange functional and any number of exchange and correlation explicit density functionals. In this type of calculations, a set of basis is used to describe the orbitals of the atoms involved. This basis can have a higher or lower complexity. When higher it is, more accurate will be the calculations, but also more expensive.

5.1. Types of structures

Here will be exposed the five structures that have been studied with computational methods. This structures are:

a) A tetragonal structure, space group **I-42m** with Z=2 that is the $AgClO_4$ structure at ambient pressure.
b) A cubic structure, space group **F-43m** with Z=4. This structure appears at high temperature and ambient pressure.
c) A orthorhombic barite structure, space group **Pnma** that appears at high pressure.
d) A monoclinic distorsion of barite structure, **P2₁/n** space group that appears in the $AgMnO_4$.
e) A tetragonal $NaClO_4$ structure, with space group **Cmcm,** note that the Na^+ is bigger than the Ag^+ catión.

I-42m
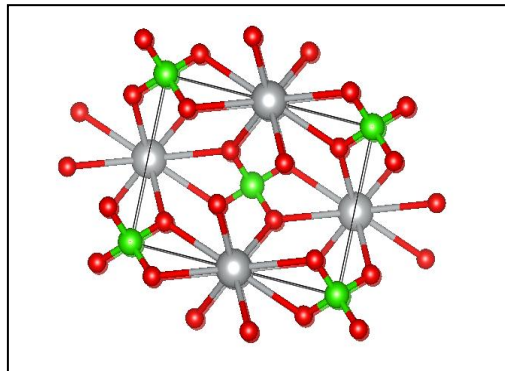
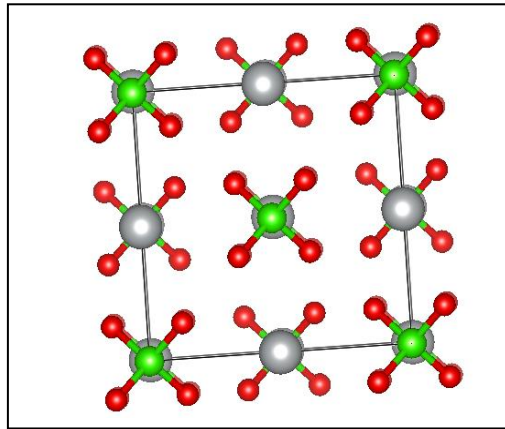A tetragonal structure with a experimental values of:
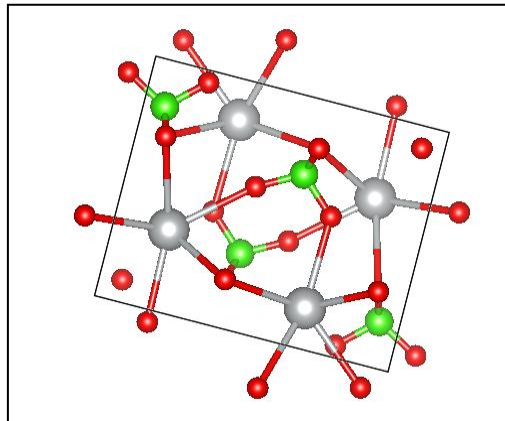
a=4.97 Å

b=4.97 Å

c=6.75 Å

alpha = betta = gamma = 90⁰

F-43m

A cubic with a experimental values of:

a = b = c = 6.94 Å

alpha = betta = gamma = 90⁰

Pnma

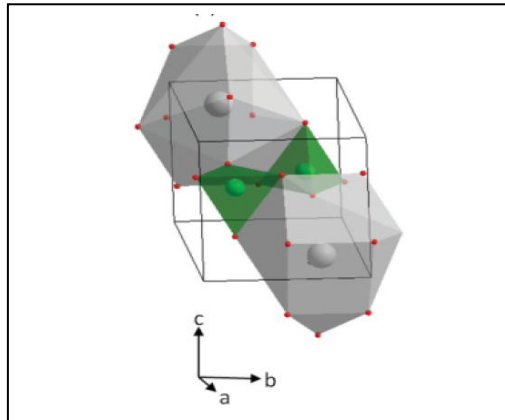A orthorhombic barite structure with a experimental values of:

a=8.21 Å

b=5.16 Å

c=6.65 Å

alpha = betta = gamma = 90⁰

Monoclinic

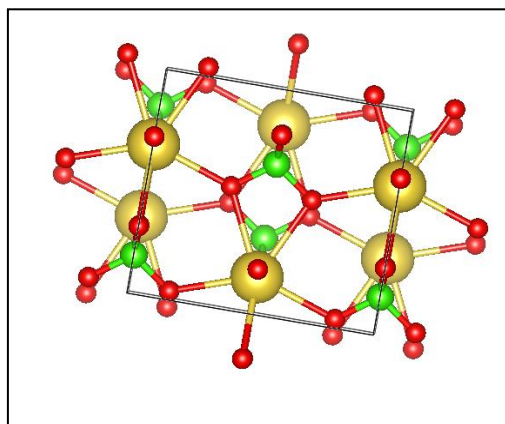A monoclinic distorsion of barite structure with a experimental values of:

a=6.20 Å

b=4.95 Å

c=4.53 Å

alpha = gamma = 90⁰

betta = 111.02⁰

Cmcm

A tetragonal $NaClO_4$ structure with a experimental values of:

a=7.08 Å

b=6.53 Å

c=7.05 Å

alpha = betta = gamma = 90⁰

5.2. Methods and computational level

Density functional theory calculations were performed with the CRYSTAL17 program.

Clorine habe been described by Cl_pob_TZVP_2012 basis set, silver by the Ag_POB_TZVP_2018 basis set, and oxigen with the O_8411(d11)_Heifets_2013 basis set (www.crystal.unito.it/Basis_Sets/).

The hybrid functionals that have been used in this theorethycal procedure are B3LYP, PBE and HSE06.

Specifically, calculations have been made with B3LYP. First an optimization have been performed. Later a frecuency calculations in order to confirm the minimun position in PES with the absence of negative frecuencies.

Finally, an EOS calculation have been performed. This calculation is made from -5 to 30 GPa, and and then a is used the X correlation in order to obtain a trend line of the pressure in this range.

Once we get it, the five possible structures are compared and the possible theoretical possible structures are performed in PBE in HSE06 in order to get other results with this two hybrid functionals.

Finally, present results are compared with the experimental results and previous calculations (Errandonea, Gracia, Beltrán, Vegas, & Meng, 2011).

5.3.Results and discussion

Full optimizations with different hybrid functionals have been carried out to obtain the geometry, and in table 1 the corresponding geometric values of I-42m structure are presented as well the experimental values reported in the literature (Errandonea et al., 2011).

|	a=b (Å)	c (Å)	c/a	Cell Volume (Å^3)	Energy (Hartrees)
Experimental	4.97	6.75	1.358	167.035	-
B3LYP	5.09	7.17	1.408	187.542	-907.503
PBE	4.95	7.27	1.468	177.885	-907.283
HSE06	5.04	6.99	1.387	177.596	-907.232

Table 1

An analysis of the results render that good agreement between experimental and theoretical values. The highest difference is of 0.5 Å in the c parameter. However, we can see that the B3LYP tends to everstimate the cell volumen (Curtiss, Raghavachari, Redfern, & Pople, 2000). In the other side, we have the PBE, that gives a better cell volumen, but the c/a relation is different than the B3LYP value. HSE06 seems to be the hybrid functional that is more similar to the experimental values.

In spite of this, B3LYP will be the principal hybrid functianal for the first calculations of this study due to the good reputation of this functional, that have been used widely around the world (Sousa, Fernandes, & Ramos, 2007) and is the principal hybrid functional used in this area in the Uji physical theorethicall calculations.

In addition, multiple problems have been noticed with HSE06 and PBE hybrid functionals. HSE06 showed some problems with the calculations due to first some problems with the optimizations of some structures, that finally were solved and second a due to a too high calculation time for a pressure calculation (A Pnma pressure calculation was above 2 weeks working).

PBE even was unable to optimize the Pnma structure in a minimum energie, something that made impossible to make a phase-transition calculation with the structures.

First calculations made with B3LYP and with the lanzacrystal17 gave the next ressults (Figure 16):

Figure 16
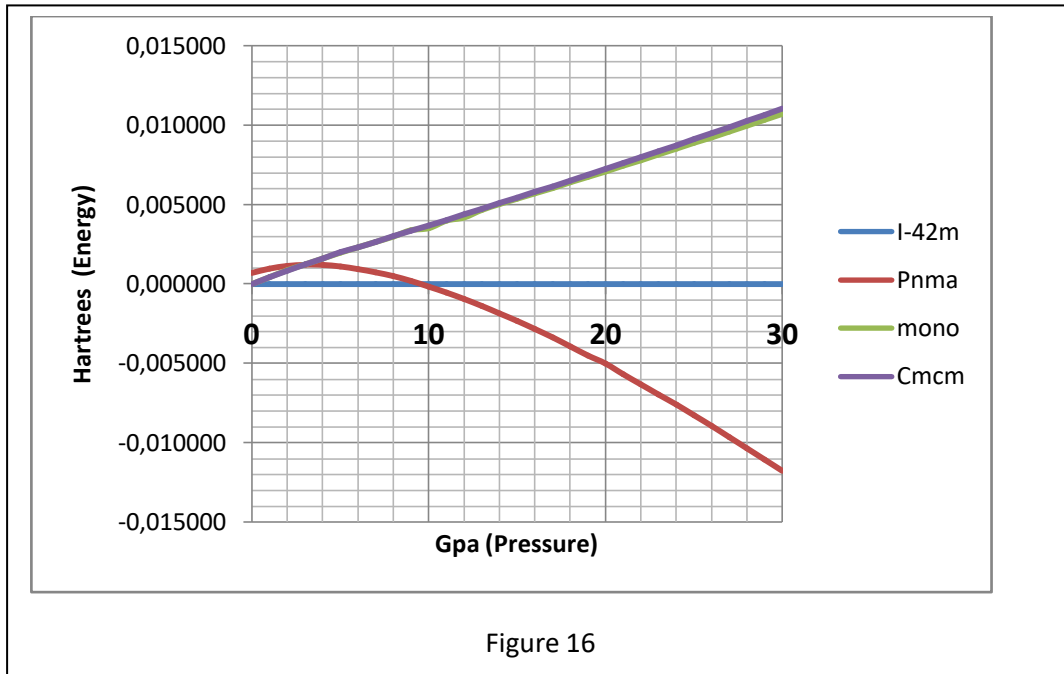
An analysis of the results renders that I-42m were the most stable structure at ambient conditions with the Cmcm and Monoclinic structures very near (Only separated by aproximately 20J/mol at 0 GPa).

Despite the Pnma structure start far from the I-42m energy, at **9.5 GPa** the energies cross and we have a phase transition from I-42m to Pnma. No other crossing was observed from 9.5 GPa to 30 GPa. Also no other cross seems to be near, as the energy values for all energies tends to be farer when pressure increases.

F-43m structure was unable to get a stable structure in the optimization step and its energie was much more higher (80KJ/mol higher). This structure also seems to be only stable at high temperatures and its the one that have negative pressures lower energies. (Some negative frequencies were obtained in the optimization).

PBE was unable to get some results due to a optimization probles (Pnma structure was unable to get optimized) and the thirth calculations made with HSE06 shown an atypical cross of the energies of I-42m and Pnma at less than 0.2 Gpa (Figure 17).

Figure 17
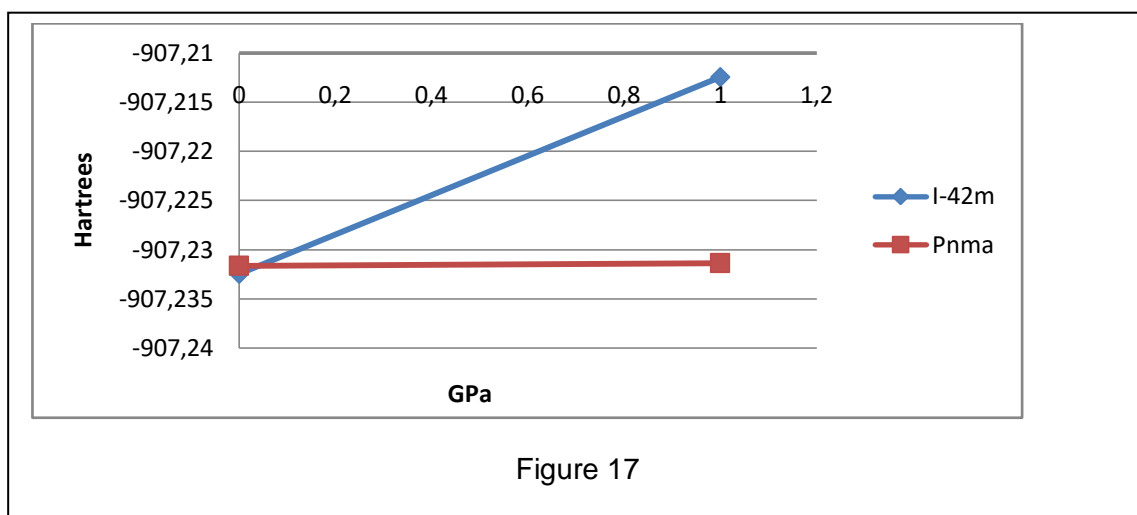
The conclusion obtained is that the more reliable result was obtained with the B3LYP hybrid functional, and showed that the structure uf the $AgClO_4$ was I-42m until the pressure is 9.5 GPa, were a transition to Pnma structure occurs.

5.4. Calculations vs experimental results

According to experimental results, the ambient conditions structure is a tetragonal structure space group I-42m. This structure remains util 5.1 GPa, where the x-ray diffraction shows a phase transtion to a orthorhombic barite structure space group Pnma. No other changes were noticed in the range of 5.1 GPa to 20.5 GPa where the experiment ended. Higher pressures were not reached due to a distorsion of the diffraction patters beyond 20.5 GPa (Errandonea et al., 2011).

Also is interesting to compare the results of the calculations made with other calculations. $AgClO_4$ is a widely studied compound. In 2011 the Physical and Analytical Chemistry Department of the Uji made an computational analisys of the same compound and structures with a B3LYP hybrid functional and a older version of lanzacrystal (lanzacrystal09) (Errandonea et al., 2011).

According to his results, the phase transition from I-42m to Pnma takes place at 2 GPa and later, at 17.2 GPa, a Pnma to a monoclinic structure transition was predicted too, but in the same way that the first transition occurs later than predicted, they affirm that if the experimental had made higher pressures experiments, this monoclinic phase should appear (Errandonea et al., 2011).

A summary of this results are presented at table 2.

	Transition from I-42m to Pnma	Transition from Pnma to monoclinic	Method used
Peirats, 2019	9.5 GPa	No	B3LYP
Errandonea, 2011	2.0 GPa	17.2	B3LYP
Experimental	5.1 GPa	No noticed in the range of 20.5 GPa	X-ray diffraction

Table 2

5.5. Conclusions

As a final conclusión, the calculations performed in this publication predict firstly that the transition to Pnma is at a higher pressure that experimental and other calculations (Errandonea et al., 2011); and secondly, no other phase transition is predicted at short term above 30 GPa, confronting the results of "Errandonea,2011" publications. In a future, new experimental experiments are necessary to confirm the theoretical results. In bibliography are found some publications where other methodologies like moller-plesset perturbation theories (MP2, MP3 and higher orders) that add dynamic electronic correlation obtain better results that DFT methods (Curtiss et al., 2000). However, this methods require a computational cost that increase exponentially and actually are still difficult to implement (Sousa et al., 2007).

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