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Introductory Chapter: A Brief Mention for High-Pressure in Oxides from DFT Simulations

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1. Introduction

High pressure simulations are employed in materials because of the resistance and advanced properties. The material modifications from high pressures are essential to reach new crystalline structures. In geophysics, many high pressure processes happen inside Earth. Diamonds are a clear example on the matter transformations under high pressures. In this case, the diamond is the natural material more resistance already found; several studies were performed to understand how carbon in graphite form can be changed to diamond and the result was a synthesis procedure based on high pressure in a short time. The initial studies using pressure were performed in gas phase. The definition of the pressure is clearly connected to how a surface is modified from an applied force. All gaseous kinetic theory has the pressure as a central point to understand the atomic and molecular movement in macroscale. In solids investigations, the pressure is the property that deform or change the surface of the material. The high material resistance regarding to gas, the deformations were classified as total and partially elastic or inelastic showing a point of view on reversible and irreversible processes. Such concepts origin the idea on malleability of the solids since metals to plastic. Amorphous and crystalline solids have similar resistance; however, the cleavage of each one is dominated from the molecular ordering. The high pressure finds to investigate the phase transitions in crystalline solids without to reach the crystal's cleavage. The compression modulus theory are the scientific approaches more developed to understand solid deformations from applied external pressure. Since one-dimensional (1D) deformation denominated as Young Modulus, and, posteriorly, Shear (2D) and Bulk Modulus (3D); it is knowledge that Equation of States (EOS) are associated to the energy x volume curve to calculate Bulk Modulus.

From coming Quantum Mechanic, more specifically, the Computational Chemistry in solid state; the making of the energy x volume curve becomes a possibility to calculate the Bulk Modulus from only theoretical proceedings. In this terms, the Density Functional Theory (DFT) has been broadly applied to predict and to investigate material's compressibility from chemical substitutions or new crystalline structures. Such new approach reaches to a new level for research in Chemistry of Materials area.

2. Short points in pressure

The pressure play an important role in chemical and physical systems. It is defined as force on area (1) showing as an external force acts on substances or materials in solids, liquid, and gas states. Automatically, the pressure is a physical

property in molecular level only associated to the molecular collisions from a perception to push or to pull molecules causing molecular deformation. The association of the displacement molecular and classical physics from Newtonian mechanism created the gas kinetic theory. This essential approach allowed advances on how the pressure acts on the inside or the outside of a physical system.

$$p = \frac{F}{A} \quad (1)$$

The matter absence drives to pressure absence, there is not pressure without atoms or molecules. Explosions and vacuum are directly connected with the pressure. A recent demonstration was the explosion in the Beirut's port, the energy and gas expansion from the chemical reactions increased hugely the local pressure in a short time crushing lives and buildings. The vacuum is the concept on the absence of matter or the null pressure. This concept was already understood as a breach in the nature, the absence of matter were something unnatural. However, previous experiments revealed that the vacuum is part of nature or the nature does not refuse the vacuum. Today, the vacuum is connected to very low pressure, where same an isolated molecule in a closed vessel can create pressure from the collision with the vessel's wall. Then, the intensity of the pressure is dependent of the molecular motion and amount of molecules.

The pressure and the Gibb's energy variation (ΔG) are connected. The non-expansion work or the spontaneity of a chemical reaction involving gas phase is dependent from pressure. Such concept is expanded for the liquid phase. Raoul's and Henry's Laws investigated the ΔG deviations from perfect behavior how the influence of the long-rang molecular interactions from vapor pressure changes. In solid phase, the vapor pressure is low; however, the pressure can be applied directly on the solid structure. Crystalline and amorphous structures are susceptible to pressure creating solid deformation or crash. In particular, for crystalline structures in deformation process, an external applied pressure changes the Gibb's energy variation causing a phase transformation for other phases. The modifications in crystalline material are connected to spatial groups; it is very interesting because the applied pressure carry out work on the crystalline structure deforming the chemical bonds from "push" the atoms or molecules. This deformation process from pressure is directional, i. e., it dependent of the spatial direction from the pressure is applied. The high ordering implicit to crystalline solids is showed as the Miller indices (h, k, l) connected to crystalline spatial group. Then, the applied pressure can be performed in the three directions of space simultaneously denominated as isostatic pressure; in two directions (bi-axial deformation) or one direction (uni-axial deformation).

Thomas Young, a scientist of nineteen century, investigated the deformation in wires or uniaxial direction creating the Young's Modulus [1]. This study proposes the description of the resistance of a material against the stretch or uniaxial deformation from an external applied pressure or strain. The formalism reached by Young is used until today to measure resistance in several materials as metals, plastic, and composites in automatic devices capable to quantify an applied strength in micro- or millinewtons dimensions. The Young's Modulus, **Figure 1a**, shows in macroscopic dimension, the microscopic forces involved in the continuous resistance inside of the material. In the molecular level, the chemical bonds are on an intense strain to break them. Therefore, the greater the bond strength the greater the material resistance to strain. The bi-axial deformations are knowledge as Shear Modulus [2], **Figure 1b**. In this kind of deformation, the pressure is applied orthogonality on a surface or a bi-axial stretch in x, y-coordinates creating a bidimensional strain on the material. The applied pressure is distributed from strain gradient on all surface

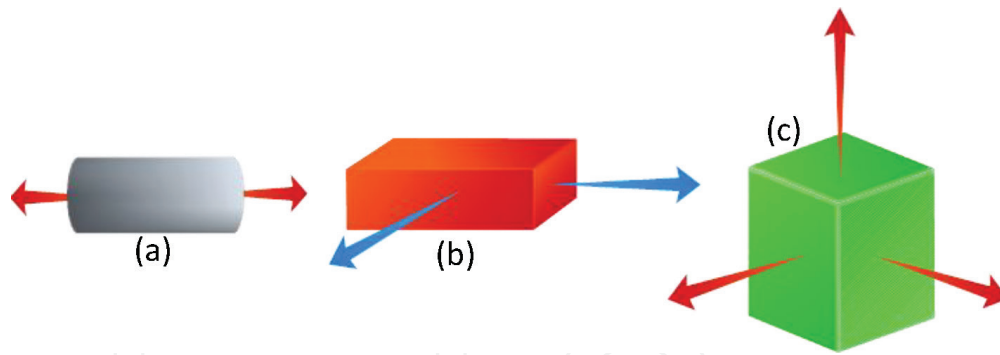


Figure 1. Schematic representation for (a) Young's modulus, (b) shear modulus, and (c) bulk modulus.

or a stress point. Applications are performed in metallic sheet, thin films, and other. The Bulk Modulus [3], **Figure 1c**, is a formalism for three dimensions or volumetric deformation. Such approach is an isostatic procedure; a general experimental procedure is reached from a hydrostatic pressure from hydraulic press. The limitations are the applied pressure by hydraulic press and the resistant container. In general, a sample is insulated from aqueous environment inside of resistant container. Posteriorly, the container is filled with distilled water and closed. The water into the resistant container is compressed applying a isostatic pressure on the sample.

The Bulk Modulus can be positive or negative. The positive value is interpreted as the increase of pressure on the solid causing the decrease of volume; while, if the solid volume increases from pressure increase, the Bulk Modulus value is negative and associated to a thermodynamic instability because of the Le Chatelier's Principle break. The volume always decrease from pressure increase. Then, the Bulk Modulus value is connected to an indication on the energetic instability of a crystalline solid. The Eq. (2) shows the connection among pressure (p), initial volume (V_i), final volume (V_f), and Bulk Modulus (B):

$$p = \frac{B(V_f - V_i)}{V_f} \quad (2)$$

It is an important comment that for all kind of deformations, the thermodynamic ways are classified as reversible or irreversible processes. In reversible process, the material has a partial or total elastic behavior to reverse the applied strain. In the irreversible process, the applied strain causes a permanent deformation or fracture of the crystalline structure.

From a microscopic point of view, the Bulk Modulus can be calculated from Equations of State (EOS). There is not a general EOS formalism to describe all modifications on crystalline structures. However, various EOS were discovered to represent the possible phase transitions under applied pressure. These EOS are applied in solids with high Bulk Modulus, such scientific theme is called as high pressure investigations. In large scale, the Birch-Murnaghan Eq. (3) is the most EOS used [4]. This formalism describes very well the Bulk Modulus from an Energy x Volume curve. The point to point variations between the internal energy (U) and unit cell volume (V) build the curve. Posteriorly, the curve is fitted by Birch-Murnaghan Equation, which is a third degree polynomial.

$$U(V) = \frac{B_0 V}{B'_0} \left[\frac{\left(\frac{V_0}{V}\right)^{B'_0}}{B'_0 - 1} + 1 \right] + U_0 \quad (3)$$

where, U_0 is the total internal energy for the ground state, $U(V)$ is the total internal energy for deformed unit cell, V_0 is the initial unit cell volume in the ground state, V is the deformed unit cell, and B_0 is the Bulk Modulus with B'_0 derivative.

All crystalline materials collapse from applied external pressure. Nevertheless, phase transitions are very essential to technological applications. In the area of the chemistry of materials, the phase transitions from applied external pressure are investigated to modify the electrical, optical, magnetic, and mechanical properties. In particular, Quantum simulations are largely applied to investigate modifications in crystalline structures under pressure. The phase transitions under pressure are simulated because of geophysics processes, piezoelectric technological devices, resistance materials, and magnetic phase transitions. The DFT increased in broad scale in the molecules and solids. DFT approaches for high pressure researches have a high level of publication and good agreement with experimental results. Recently, Quantum simulations are the source for energy (U) x unit cell volume (V) curve to be applied to EOS, for example, the Birch-Munaghan Equation. In codes based on Quantum formalism have implemented an automatic routine to calculate the *Bulk Modulus* and, posteriorly, the simulation for Gibb's x pressure curve showing phases transition analyses.

3. High pressure and density functional theory

A DFT approach to investigate the tetragonal-cubic phase transition of the PbTiO_3 was proposed to analysis the molecular connection between two crystalline structures [5]. The piezoelectric PbTiO_3 material is widely studied because of the high performance in sensors and other devices. It is knowledge that the tetragonal structure is a paraelectric phase with aggregation charges under an applied external pressure, the piezoelectric effect. The molecular structure is distorted through atomic displacement from the applied external pressure. In the PbTiO_3 , there is the spontaneous polarization effect caused by the Ti atom displacement from the octahedral center inside $[\text{TiO}_6]$ cluster. Such molecular dynamic connects the Ti atomic displacement to the electric charging of the PbTiO_3 material from an anisotropic charge distribution. Simultaneously, the crystalline structure ways to cubic structure increasing the material resistance to applied external pressure, for each change in the applied external pressure there is a change in the electric signal of the PbTiO_3 material. Then, it was proposed DFT simulations to identify crystalline transition structures between tetragonal and cubic structures. The crystalline intermediary structures were featured showing a chemical path in consistence with the most recent concepts and schemes used in the solid state theory. The association between tetragonal-cubic phase transition and chemical path is very grateful presenting a high potential to clarify many molecular mechanisms associated to piezoelectric.

Another type of DFT simulation is the phase transition among more two crystalline structures [6]. One example, it was the phase transition investigated for seven SnO_2 crystalline structures. The rutile, CaCl_2 , $\alpha\text{-PbO}_2$, pyrite, ZrO_2 , fluorite, and cotunnite symmetries were researched to demonstrate the changes in phase transition under pressure, structure, and optical properties. The calculated phase transitions showed a several phase transition points among symmetries with a high quantity of inter transitions, around seven interconversions structural, in a range of 30 GPa. A high malleability of this material was revealed and an increasing linear behavior for the band-gap in the 0 to 40 GPa range. From this expressive amount of calculations was possible to map many phase transitions and features for each crystalline structures.

The application of the external pressure on crystalline structures is intrinsically connected to density of the solid. From the increase of the applied pressure higher the density of solid; from Le Chatelier's Principle predicts that [7] "a decrease in volume accompanies first-order transitions from low pressure to high pressure"

Then, lower densities solids have lower Bulk Modulus because can be compressed to structures densest and ordered; whereas, the change in the Bulk Modulus for high densities solids is difficult because the crystalline structure does not support an increase on density or coordination number.

A DFT investigation using high pressure procedure researched a set of materials based on iron in the ABO_3 ilmenite structure [8]. Such materials are magnetics and the B cation (+4) was modified among 4A (Si, Ge, Sn) and 4B (Ti, Zr, Hf) group cations. The $FeBO_3$ materials showed an increase of density from Si to Hf; however, it was possible group it from similar densities, $FeSiO_3$ (4.72 g cm^{-3}) and $FeTiO_3$ (4.73 g cm^{-3}), $FeGeO_3$ (5.72 g cm^{-3}) and $FeZrO_3$ (5.27 g cm^{-3}); $FeSnO_3$ (6.41 g cm^{-3}) and $FeHfO_3$ (7.87 g cm^{-3}). The similarity is centered on the table periodic period showing the influence of the ionic radius on the density. The calculated Bulk Modulus showed that $FeZrO_3$, $FeGeO_3$ and $FeSiO_3$ are the most compressible materials with 12.38 GPa, 32.86 GPa, and 43.70 GPa, respectively. The $FeTiO_3$ is the most hard material for compression; while, the $FeSnO_3$ and $FeHfO_3$ materials are unstable because the calculated Bulk Modulus were -731.76 GPa and -142.94 GPa , respectively. Then, the lower materials in Bulk Modulus have possibility to change to other phases. For the $FeTiO_3$, the phase transition is hard because high Bulk Modulus; whereas, $FeSnO_3$ and $FeHfO_3$ materials have a high possibility to decompose to SnO_2 , FeO , and HfO_2 simple oxides.

4. Conclusions

High pressures theoretical approaches are very used to simulate energetic stability and structural properties in several materials. The Bulk Modulus modification from chemical substitutions or crystalline structures is a versatile tool to predict some properties of a material. In oxide semiconductors simulations, the Bulk Modulus project the material's compressibility for phase transition or piezoelectric applications. Electric, optical and magnetic properties can be associated to high pressures changes creating sensors devices.

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