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AB INITIO CALCULATION OF THE PROPERTIES OF XS2 NANOSTRUCTURES: USING DFT

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Resumo

Os Dichalcogenetos de Metais de Transição (TMDs) constituem uma classe de materiais emergentes, que podem ocorrer emdiversas fases, tais como: 1H, 1T e 1T'. Dependendo da sua forma polimorfa, esses materias exibem diferentes propriedades estruturais. Assim, utilizando a teoria do funcional da densidade (DFT) implementada no código computacional CASTEP, investigamos as propriedades estruturais, eletrônicas e vibracionais, das monocamadas do dissulfeto de cromo (CrS2), dissulfeto de molibdênio (MoS2) e dissulfeto de tungstênio (WS2). Realizamos os cálculos utilizando as abordagens baseadas nas aproximações do gradiente generalizado (GGA) e da densidade local (LDA). Nesse estudo, verificamos que a fase 1H e 1T' apresentam estabilidade na sua dinamica de fônos. Porém, a fase 1T revelou instabilidade apresentando modos imaginários na dispersão de fonos, encontrando-se em concordância com os dados da literatura. Nossas simulações demonstram que as monocamadas na fase 1H é um semicondutor de bandgap direto e na fase 1T' semimetal.
Palavras-chave: TMD, Propriedades eletrônicas, Propriedades vibracionais

Abstract

Transition Metal Dichalcogenides (TMDs) are characteristic of a class of emerging materials which can occur in several phases, such as: 1H, 1T and 1T'. Depending on their polymorphic form, these materials present different structural properties. Thus, using the density functional theory (DFT) invented in the CASTEP computational code, we investigated the structural, electronic and vibrational properties of the monolayers of chromium disulfide (CrS2), molybdenum disulfide (MoS2) and tungsten disulfide (WS2). We performed the calculations using the approaches based on the generalized gradient approximation (GGA) and local density approximation (LDA). In this study, we verified that the 1H and 1T' phase presents stability in its phonon dynamics. However, the 1T phase revealed instability presenting imaginary modes in the phonon dispersion, in agreement with the literature data. Our simulations demonstrate that monolayers in the 1H phase are a direct bandgap semiconductor and in the 1T' phase a semimetal.
Keywords: TMD, Electronic properties, Vibrational properties

1 Introduction

Synthesizing the most resistant material in the world earned researchers Andre Geim and Konstantin Novoselov the Nobel Prize in 2010 (Macieira, 2013) and from then on we were interested in discovering and finding new materials that could be used in new applications. we were interested in a network of materials that, after the discovery of graphene (NOVOSELOV, et al., 2004, 2005a, 2005b, 2007, 2012; GEORGAKILAS, et al., 2012, SANTOS et al., 2023a), we had the emergence of a range of possibilities in which we had our eyes focused on new dimensional materials (2D) that have good electronic and mechanical properties but do not perform well in electronics, so we had a new class of dimensional material, the transition metal dichalcogenides (TMD) that their structure chemistry is of the XY2 type in which X represents a transition metal and Y for chalcogens. (KOLOBOV, 2016.). Someone noticed that TMDs have a thin structure of atomic thickness, with great nano-technological potential. Until now, this material shows properties originating from insulators, semimetals, metals and semiconductors. Subsequently, TMD semiconductors have outstanding properties in optoelectronics. (COUTINHO, et al., 2017; MOUCHEREK, et al., 2022).

Investigation into two-dimensional semiconductor materials, particularly transition metal dichalcogenides (TMDs), has surged in response to graphene's electrical properties. This growth stems from two primary factors. Firstly, it enables the creation of an appropriate band gap, vital in the development of electronic devices. Secondly, these materials, when in a single-layer state, offer direct gaps that prove valuable in optoelectronic devices. In this way, the interest of the scientific community in the possibilities of this material that can be the solution to develop new and better devices, the use of these materials can be used in various physical applications, as well as being a material of interest and curiosity since it is promising, as it presents new possibilities for developing electronic, optoelectronic and photonic devices. (CASTRO, 2023)

One of the particularities of TMDs is their van der Waals interactions between the chalcogenide layers, allowing the creation of single-layer structures. (KADANTSEV, HAWRYLAK 2012.). In a single layer, the bandgap is generally straightforward, and this aspect is crucial when considering its application in more robust electronic devices. Single TMD layers have several possible polymorphic

structures, each offering distinct optical and electronic properties. These structures can assume different phases, such as 2H semiconductor (hexagonal), 1T metallic (trigonal) and 1T' semimetallic (monoclinic), in general. (SANTOS et al., 2023b; SANTOS et al., 2023c)

In this study, we carried out an analysis of the structural, electronic and vibrational properties of Transition Metal Dichalcogenides of type XS2 (X= Cr, Mo and W) in three different crystalline structures: hexagonal (2H), trigonal (1T) and monoclinic (1T '). Our objective is to investigate the influence of the crystalline structure on the nature of these materials and make a comparison between them, aiming to refine them for technological application.

2 Materials and methods

The techniques used to investigate the properties of TMD nanostructures are based on quantum calculations carried out at the Laboratory of Computational Simulation and Modeling of Nanomaterials (LABMOL). The code used was CASTEP (CLARK, et al., 2005) which is based on quantum many-body theory. The initial network parameters for XY2 TMDs (where X = Cr, Mo and W, and Y = S) were accessed from the C2DB database (HAASTRUP, et al. 2018). All calculations were performed within the Density Functional Theory (DFT) formalism proposed by Hohenberg and Kohn (1964) and Kohn and Sham (1965), using the plane wave code CSTEP. For the LDA exchange-correlation functional, the standard parameterization of Perdew and Cerpeley (Cerpeley-Alder-Perdew-Zunger-CAPZ) (CEPERLEY, ALDER, 1980; PERDEW, ZUNGER, 1981) was chosen. For the GGA exchange-correlation functional, we chose the Perdew-Burke-Ernzerhof (PBE) formula (PERDEW et al., 1992; PERDEW et al, 1996).

Integration across the Brillouin zone was performed employing k-point sampling in a 5 x 5 x 2 configuration, ensuring convergence of the electronic structure. The convergence criteria for all geometric optimizations of the unit cell were as follows: total energy variation less than 2.0 × 10^-5 eV, maximum force less than 0.05 eV/Å, maximum stress component less than 0.1 GPa, and maximum displacement less than 2.0 × 10^-2 Å."

3 Results

3.1 Geometry Optimization

The convergence criteria for the unit cell geometry optimizations are: energy fluctuation below 2.0 × 10–5 eV, maximum force below 0.05 eV/Å, maximum strain component below 0.1 GPA, and maximum displacement less than 2.0 × 10–2Å. We use a three-level convergence tolerance with the BFGS minimizer optimization method (PFROMMER, et al., 1997) aiming to find the minimum energy. Despite changes in unit cell volume, the quality of the base assembly remains stable. We analyze the band structures and density of states of various combinations of XS2 (X = Cr, Mo, W) after unit cell optimization. Specifically, we study molybdenum, chromium and tungsten disulfides (XS2) in their hexagonal (H), trigonal (T) and monoclinic (T') phases, observing how the structural properties change according to each phase.

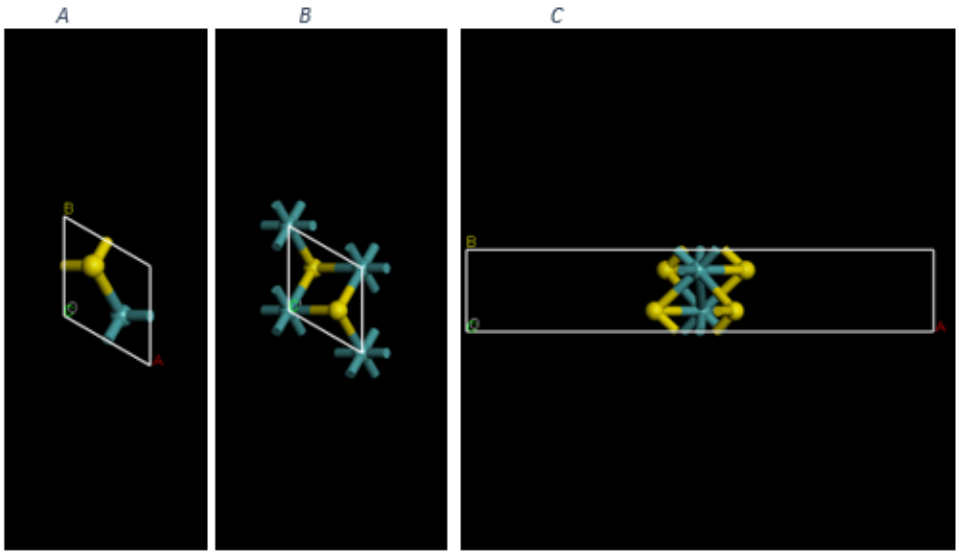

Figure 04: representation of the geometry of TMD (CrS2) in the respective hexagonal (A), trigonal (B), and monoclinic (C) phases

Source: Own work

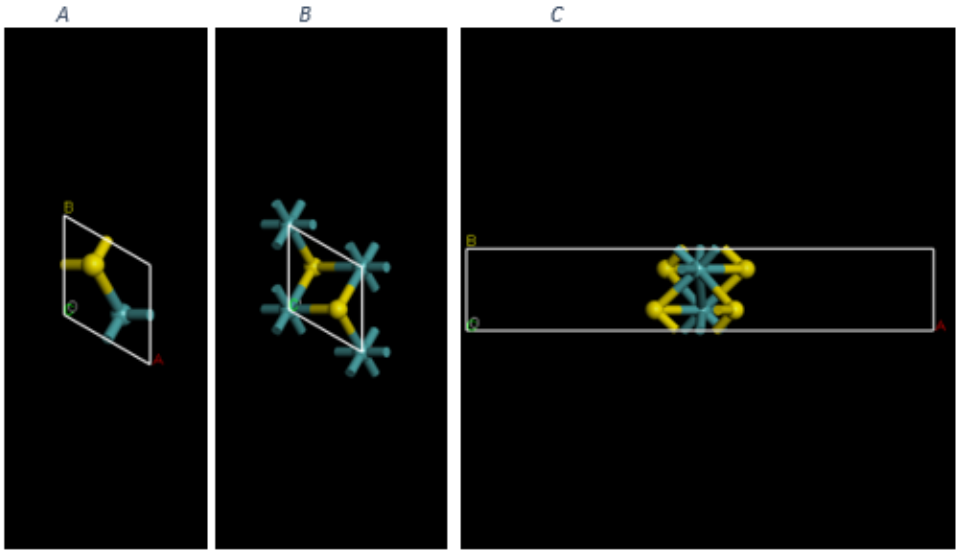

Figure 05: representation of the geometry of TMD (MoS2) in the respective hexagonal (A), trigonal (B), and monoclinic (C) phases.

Source: Own work

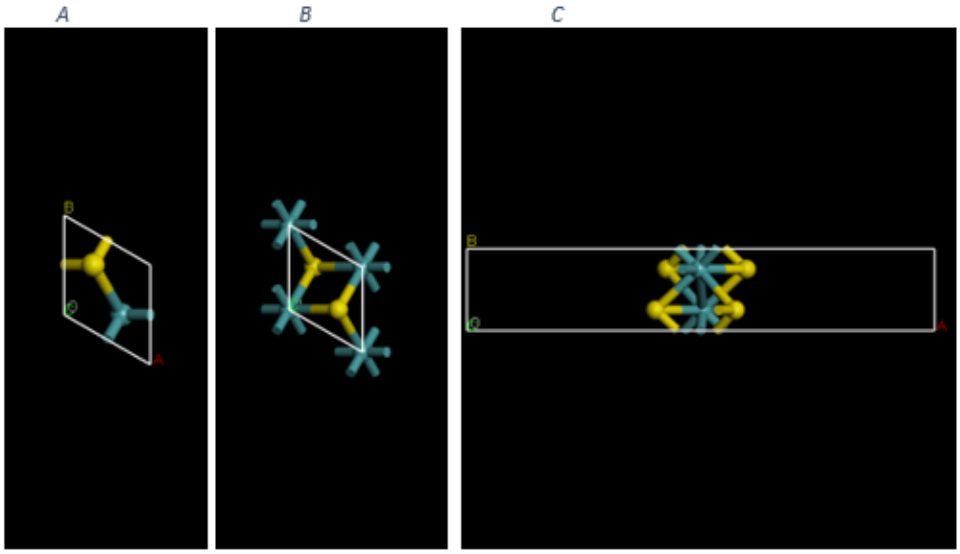

Figure 06: representation of the geometry of TMD (WS2) in the respective hexagonal (A), trigonal (B), and monoclinic (C) phases.

Source: Own work

3.2 Energy bands and density of states (DOS) of TMD structures

In this part, we show results on how certain materials from the transition metal group act as semiconductors or insulators. Semiconductors are solids where, at very low temperatures, electrons occupy all available spaces in the valence band, which generates conductivity when excited to the conduction band. The energy

required to lift an electron determines whether a material is a conductor, semiconductor or insulator.

Band theory in solid physics offers models to understand the behavior of materials by describing electronic states. The interaction between particles in a solid influences the behavior of electrons. The allowed energy range for electrons is called the bandgap. Furthermore, there is an energy level that electrons cannot accept, the bandgap. To understand electronic behavior, we calculate the band structure and density of states. The band structure describes the energy levels occupied by electrons by looking at the energy paths in the Brillouin zone.

The sequence of high symmetry points used is as follows: Γ (0.000, 0.000, 0.000), K (-0.333, 0.667, 0.000), M (0.500, 0.500, 0.000), Γ (0.000, 0.000, 0.000). This path was used for the structures XY2 (X=Cr, Mo and W), in the respective phases (Hexagonal H and Trigonal T). For the Monoclinic phase (T') the following sequence of points was used: Γ (0.000, 0.000, 0.000), Z (0.000, 0.000, 0.500), C (0.000, 0.500, 0.500), Y (0.000, 0.500, 0.000), Γ (0.000, 0.000, 0.000). We can see in the figures below the illustration of the high-symmetry points along the ZB.

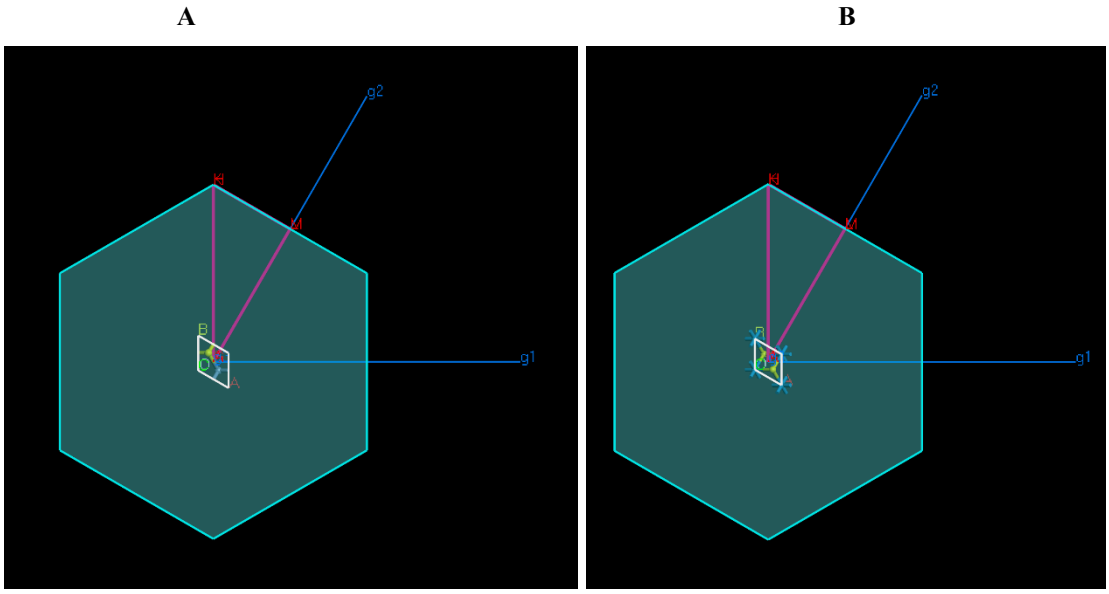

Figure 07: Representation of the Brillouin Zone generated for the crystalline structures XY2 (Y = Cr, Mo, and W), where the pink lines display the chosen path between the high-symmetry points of the systems in their respective H(A) and T(B) e T'(C) phases.

Source: Research production

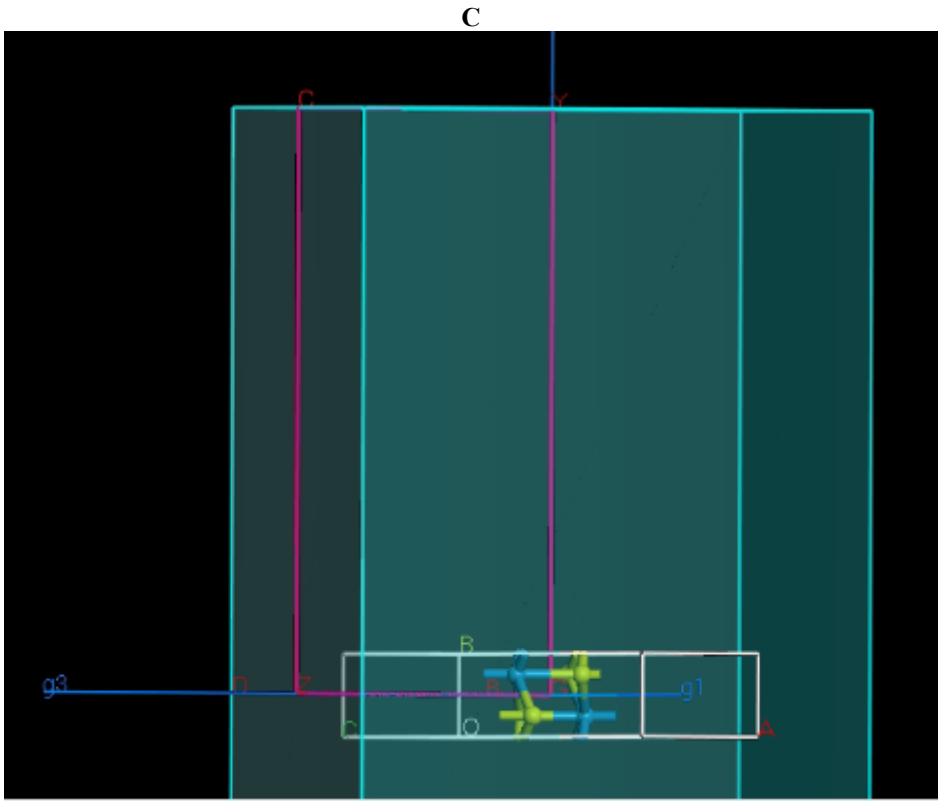

Figure 08: Representation of the Brillouin Zone generated for the crystalline structures XY2 (Y = Cr, Mo, and W), where the pink lines display the chosen path between the high-symmetry points of the systems in their respective T'(C) phases.

Source: Research production

Analyzing the figs. 9, 10 and 11 of the Band structures, we see similarities between the TMDs in the Hexagonal and Monoclinic phases, behaving like semiconductors and semimental, which is in accordance with the literature (MATHIAS, et al., 2023; YANG, et al., 2019). In the Trigonal phase, they act as conductors. In the Hexagonal and Trigonal phases, the LDA eigenenergies are lower for conduction compared to GGA, resulting in smaller bandgaps. The differences in gaps between LDA and GGA influence the energy required for electronic transitions, varying in each phase of the TMDs. The Density of States (DOS) describes the number of states per energy interval, complementing the band structure results (LIU, et al. 2024; TANG et al. 2023; XU, et al. 2020).

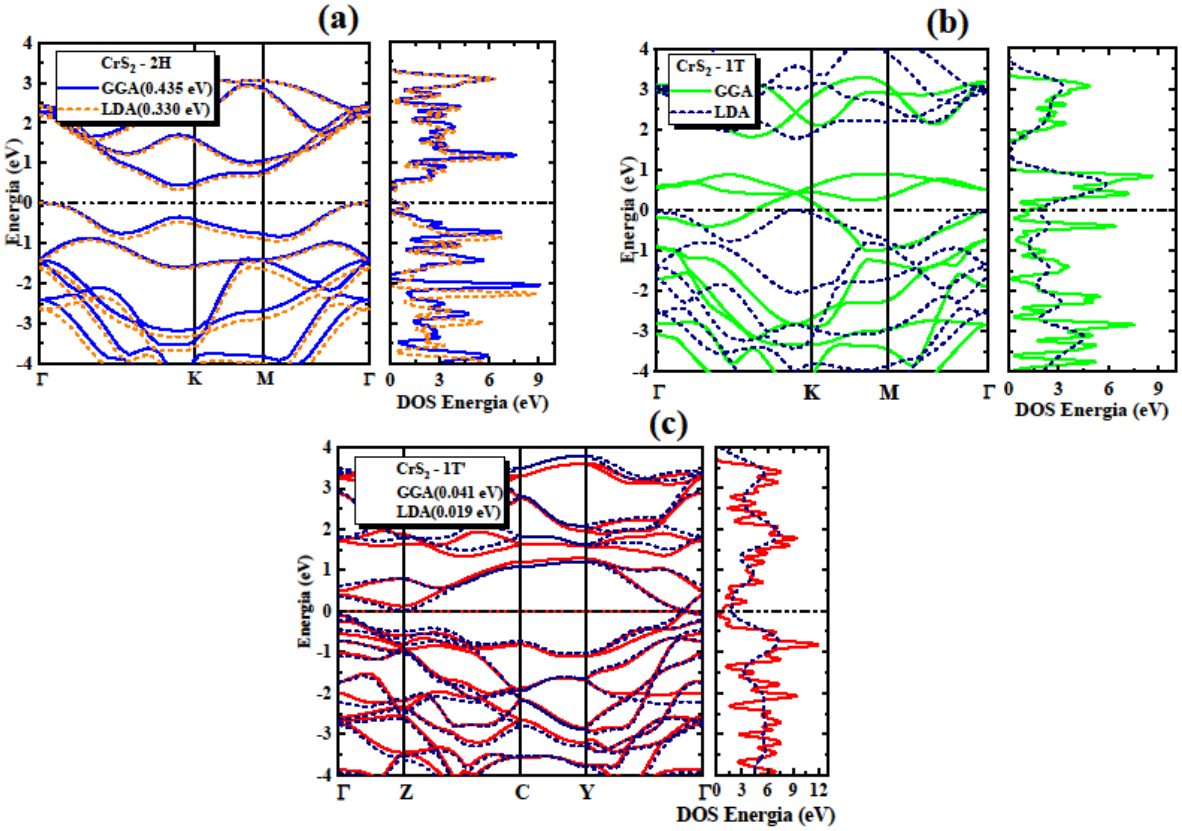

Figure 09: Comprehensive representation of the Kohn-Sham band structure and density of states (DOS) for (CrS2) in the respective H (a), T (b), and T' (c) phases using the approximations: LDA-CAPZ (dashed) and GGA-PBE+TS (solid).

Source: Own work

In direct band gap semiconductors, the valence band maximum and conduction band minimum occur at the same crystal momentum vector. In other words, the points between the layers are aligned, allowing efficient radiative electronic transitions with the absorption or emission of photons. For this reason, direct band gap materials are highly effective in optoelectronic devices such as LEDs, lasers, photodetectors, and solar cells. In indirect band gap semiconductors, the valence band maximum and conduction band minimum are located at different points. In other words, they are not vertically aligned, but in different positions, implying that electronic transitions require the assistance of a phonon to conserve momentum. This condition reduces the probability of photon emission, making these materials less suitable for emissive applications, although they are still valuable in conventional electronic devices such as transistors.

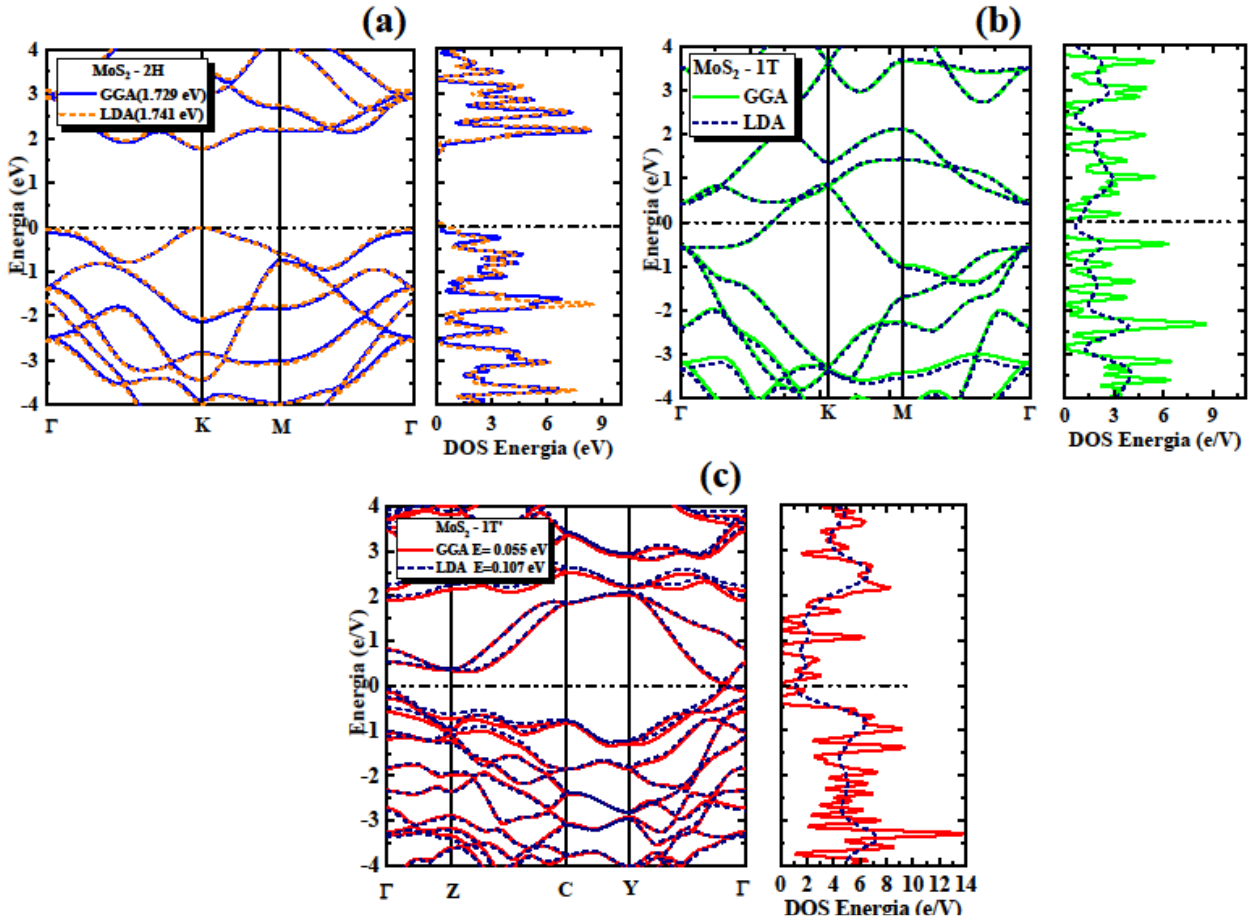

Figure 10: Comprehensive representation of the Kohn-Sham band structure and density of states (DOS) for (MoS2) in the respective H (a), T (b), and T' (c) phases using the approximations: LDA-CAPZ (dashed) and GGA-PBE+TS (solid).

Source: Own work

To further clarify the effect of exchange-correlation functionals, a quantitative comparison of the bandgap values was performed. The analysis reveals that although LDA generally underestimates the bandgap compared to GGA — as seen in the 2H phases of WS_2 (0.741 vs. 0.706 eV) and CrS_2 (0.438 vs. 0.330 eV) — this trend is not universal. In the 1T' phases of MoS_2 and WS_2, LDA yields slightly higher bandgap values than GGA, suggesting that structural reconstructions in these phases significantly affect the functional's response. For all materials in the 1T phase, both functionals predict metallic behavior, with no gap opening.

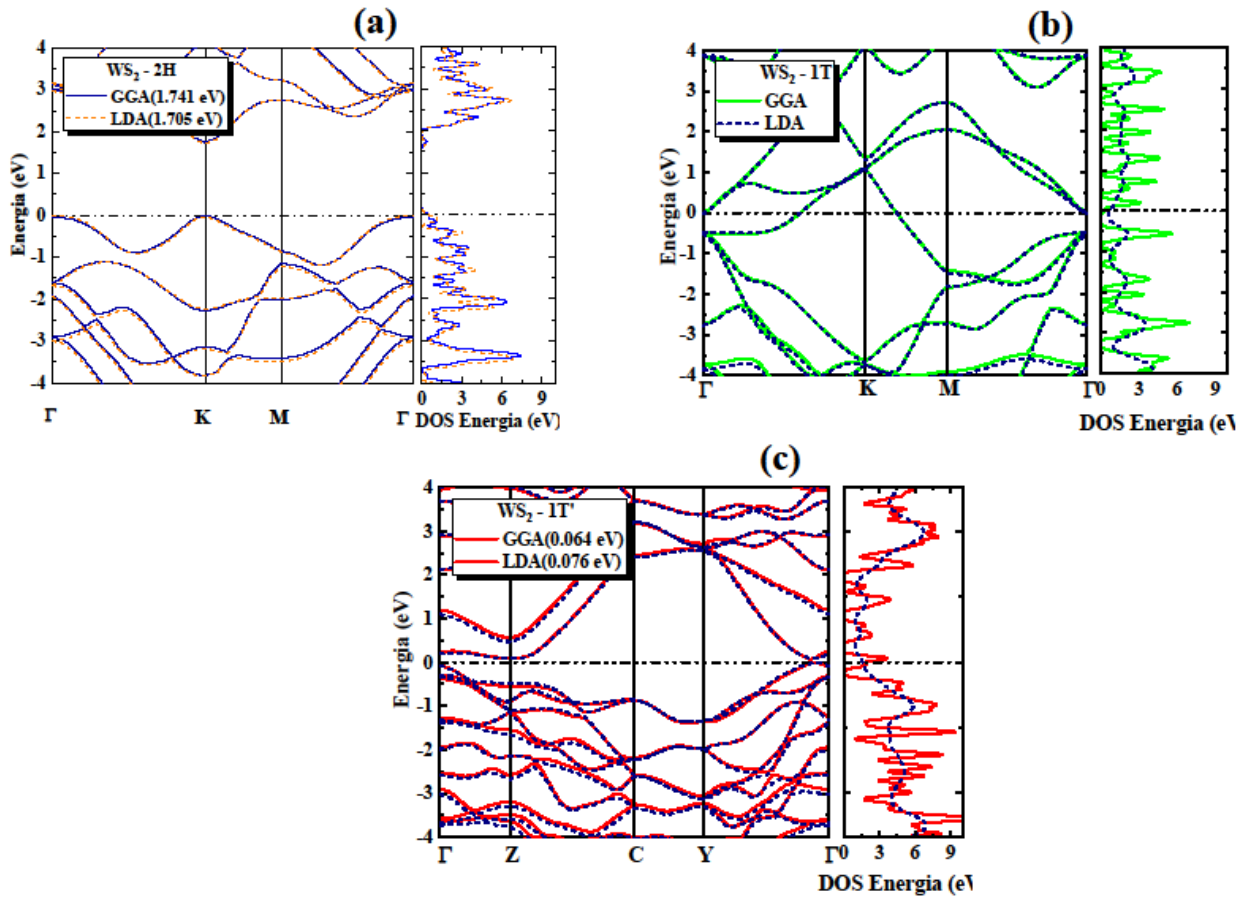

Figure 11: Complete representation of the Kohn-Sham band and the density of states (DOS) of (WS2) in the respective H (a), T (b) and T' (c) phases using the approximations: LDA-CAPZ (dotted) and GGA-PBE+TS (solid).

Source: Own work

3.3 Vibrational properties of phono TMDs

After the structural optimization process, we performed calculations of the lattice vibrations using density functional perturbation theory (DFPT), to understand the mechanical stability of the XS2 nanostructures with (X = Cr, Mo and W). We use norm-conserved pseudopotentials, which are necessary for calculations based on linear responses (SANTOS, et al. 2020, SANTOS, et al. 2023d, BITTENCOURT, et al., 2024).

The vibrational properties of TMDs are linked to the symmetry of their crystal structures. This is evident in the presence or absence of degenerate modes in the phonon dispersions. Among the TMDs analyzed, it was possible to observe that the symmetric phase presents degenerate optical modes. This degeneracy occurs due to the high symmetry of the trigonal spatial group, which imposes restrictions on how atoms can vibrate together. When the symmetry is reduced,

this degeneracy breaks, leading to the separation of frequencies that were previously equal and the distinction between longitudinal and transverse modes, both acoustic and optical. Furthermore, symmetry breaking can activate modes that were previously forbidden, increasing the number of Raman and infrared modes that can be detected. These findings are in line with experimental results and group theory.

LDA-CAPZ, despite having a lower computational cost, presents some difficulties compared to GGA-PBE when it comes to vibrational modes. This is because, due to its calculation method, LDA-CAPZ tends to overestimate the bonds and rigidity of structures, which can compromise the results of vibrational calculations. GGA-PBE, on the other hand, is more suitable in this case, as it offers a more accurate description of the structure and vibrational modes. In this way, the vibrational properties were studied with the GGA-PBE.

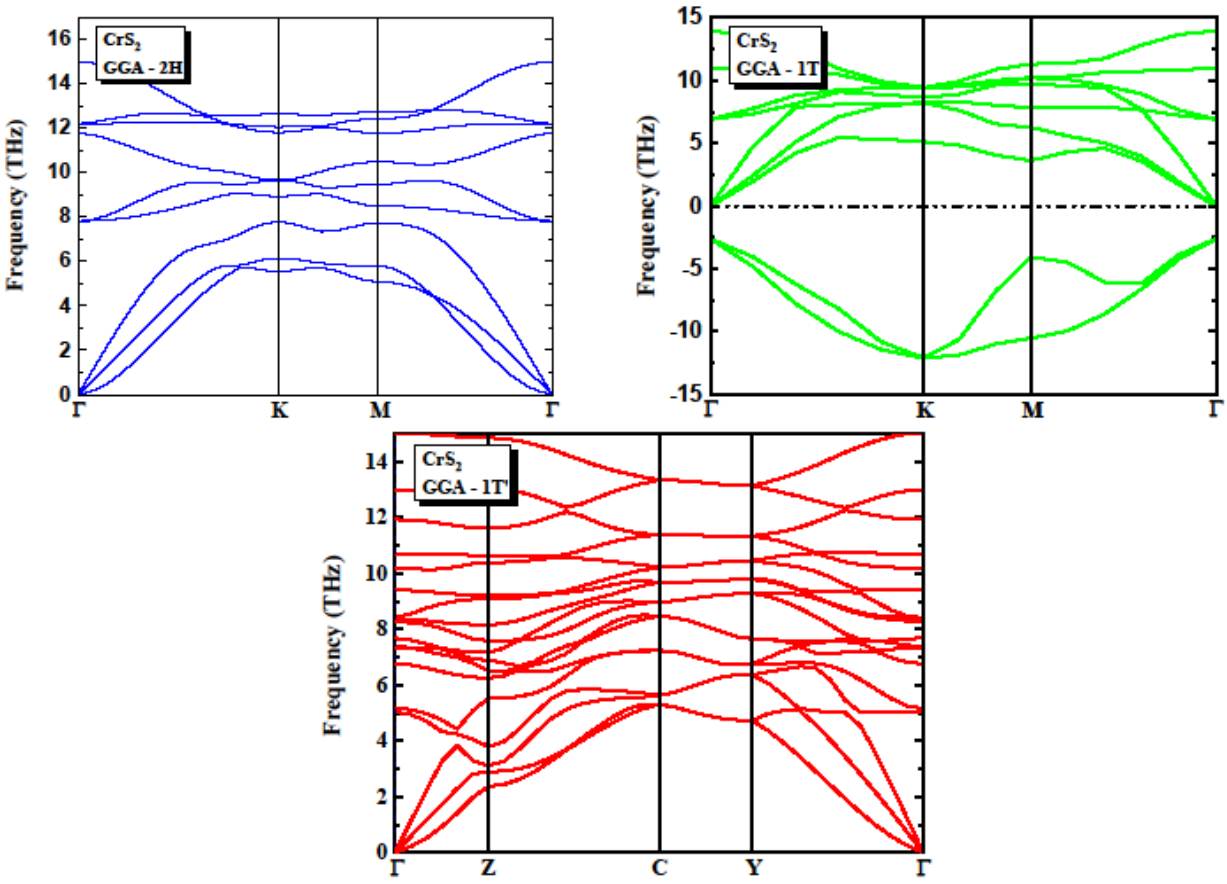

Figure 12: Representation of the phonon dispersion of the TMD (CrS2) in the respective H, T, and T' phases.

Source: Own work

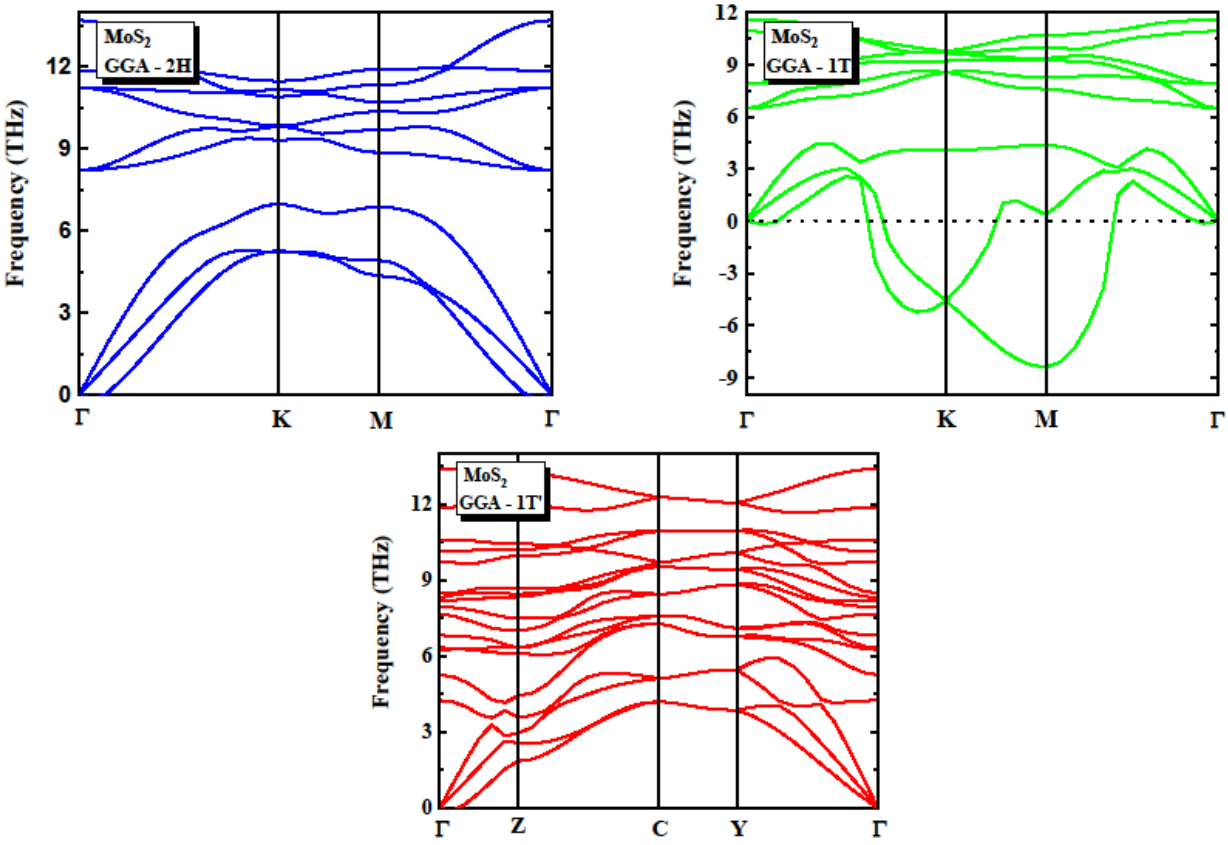

Figure 13: Phonon dispersion representation of the TMD (MoS2) in the respective H, T, and T' phases.

Source: Own work

After analyzing figures 12, 13, and 14, a compelling observation arises in this study of XS2 type Transition Metal Dichalcogenides (TMDs): regarding the T phase, both XY2 nanostructures (where X = Cr, Mo, and W) exhibit instability. The phonon dispersion graphs show negative frequencies, indicating that these materials are virtual, meaning non-existent in this phase. In the H and T' phases, however, all vibration modes show positive values, suggesting the possibility of synthesizing both TMDs. The results presented here align with data from the literature (MATHIAS, et al., 2023).

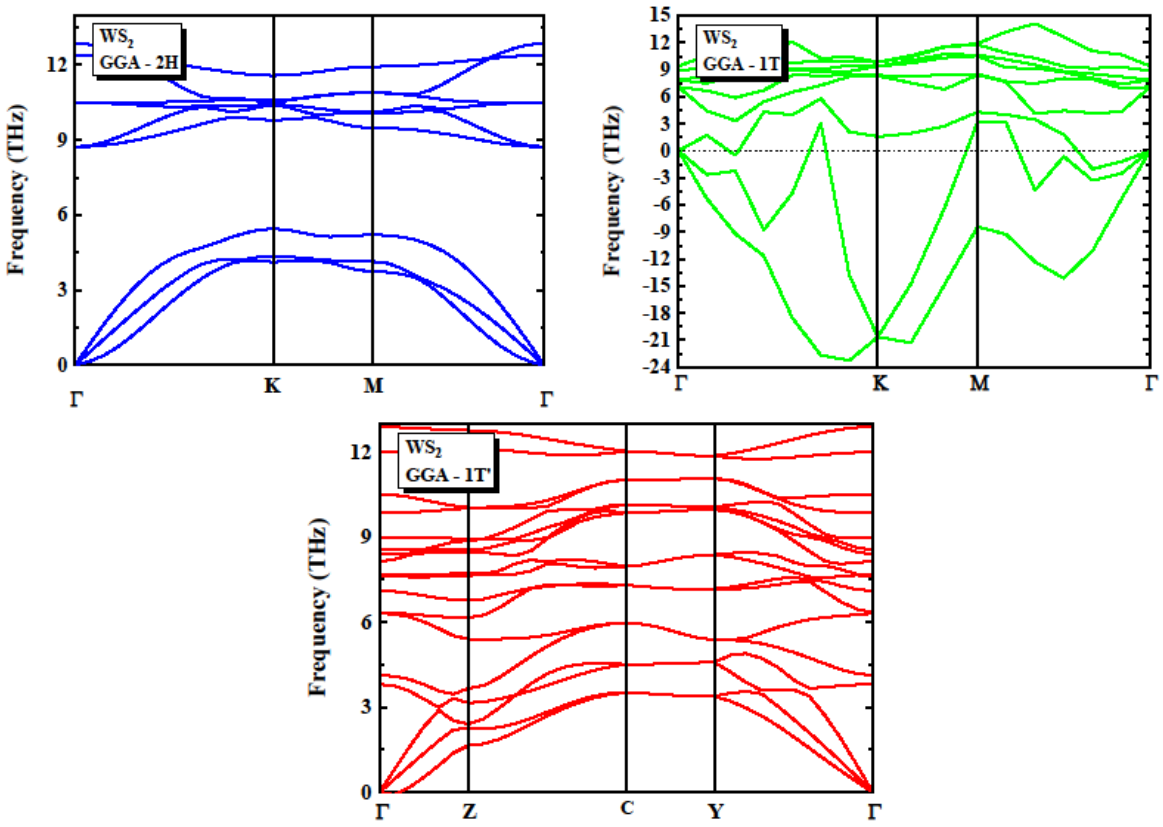

Figure 14: Phonon dispersion representation of the TMD (WS2) in the respective H, T, and T' phases.

Source: Own work

4 Conclusion

In this section, we will present our conclusions drawn from the calculations performed in this study, employing first-principles calculations based on Density Functional Theory (DFT), utilizing the LDA-CAPZ and GGA-PBE approximations to compute electronic properties, in the only GGA-PBE vibrational properties of XY2 monolayers (where X = Cr, Mo, and W).

It is evident that the properties of Transition Metal Dichalcogenides (TMDs) depend on the structural configuration of how atoms organize within the 2H, 1T, and 1T' unit cells. It is noticeable that the stable phases were 2H and 1T'. In the phonon dispersion, positive frequencies were observed in the 2H phase, while phase 1T exhibited instability for both nanostructures.

Regarding electronic properties, the Band Structure (BS) and Density of States (DOS) for the monolayers reveal that materials exhibiting semiconductor characteristics present an indirect band gap for CrS2 in the 2H phase and a direct

gap for MoS2 and WS2. However, for phase 1T', all TMDs exhibit semimetal characteristics.

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