Electronic and vibrational properties of defective transition metal dichalcogenide Haeckelites: new 2D semi-metallic systems

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Abstract

The electronic properties of monolayered Haeckelites constructed from transition metal dichalcogenides (TMDs) such as MoS$_2$, WS$_2$, WSe$_2$ and MoSe$_2$, have been studied by first principles calculations. It was found that monolayered Haeckelites exhibit a semi-metallic behavior, whereas the traditional monolayered TMDs show a direct band gap, which is characteristic of semiconducting TMDs. Furthermore, metallic TMD monolayers of NbS$_2$ or NbSe$_2$ transform into direct and indirect gap semiconductors, respectively when arranged into Haeckelite geometries. The vibrational properties and Raman spectra of NbS$_2$ Haeckelites were also calculated.

Keywords: layered materials, graphene, Raman spectrum

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Introduction

In recent years there has been a large number of published papers related to monolayered materials, initiated by the realization of the fascinating physicochemical properties of graphene. However, TMDs constitute other layered structures that have not been so heavily studied. In particular, these layered systems are very rich from the electronic standpoint, since these can be semiconductors, metals and even superconductors [1–7]. Although the introduction of defects has been studied extensively for graphene, defects in layered materials such as TMDs have not been widely studied or understood. Only recently have vacancies and grain boundaries been observed in MoS$_2$ and models which involve the introduction of 8-4 or 5-7 defects have been proposed [8–13]. In fact, TMDs exhibiting trigonal prismatic structures can acquire positive and negative Gaussian curvature, preserving the stoichiometry by the introduction of square-like defects and octagonal-like defects, respectively [14]. Therefore, planar sheets could be generated in TMDs when using 8-4 defects, as studied with 5-7 defects in graphene to generate the so-called pentahapetes or Haeckelites in honor of the German biologist and naturalist Ernst Haeckel [15, 16]. Graphene Haeckelites and their corresponding nanotubes possess metallic behavior [15], graphene being a semimetal, but little is known about having Haeckelites in TMD systems. In graphene, a disordered Haeckelite structure has been generated in situ in an aberration corrected high-resolution electron microscope using electron irradiation. This achievement has now opened the possibility of studying amorphous materials in two dimensional systems [17].

In this work, first principles calculations using density functional theory (DFT) were carried out in different Haeckelites constructed from TMDs such as MoS$_2$, MoSe$_2$, WSe$_2$, WS$_2$, WTe$_2$, NbS$_2$ and NbSe$_2$. Trigonal prismatic phases of monolayer semiconducting TMDs (MoS$_2$, MoSe$_2$, WSe$_2$, WS$_2$) are known to exhibit a direct band gap at the K point of the Brillouin zone; the band gap becomes indirect when adding additional layers. For this reason, monolayers of semiconducting TMDs (that do not exhibit center of inversion) could be extremely useful in the construction of novel optoelectronic devices, nonlinear optics and valleytronics [18–23]. For NbS$_2$ and NbSe$_2$, the monolayers are metallic and in bulk can be superconductors at low temperatures and even possess charge density wave behavior [6, 7, 24, 25]. As we will describe below, Haeckelite monolayers of semiconducting TMDs obtained by arranging 8-4 defects, exhibit a surprisingly small band gap which could be regarded as a semimetal resembling graphene. In addition, Haeckelites from metallic TMDs exhibit a band gap. Therefore, the electronic properties could be significantly modified if arranged in a Haeckelite structure when using TMDs, and further experimental studies are now needed in order to investigate the possibility of synthesizing these novel 2D systems.

Methods

Our calculations are based on DFT using the local density approximation (LDA) as implemented in the plane wave code CASTEP [26], considering the Ceperley–Alder–Perdew and Zunger (CA-PZ) [27, 28] functional with 9 × 9 × 3 Monkhorst–Pack K-points and a plane waves cut off of 600 eV. All the structures were relaxed, including the unit cells, until the forces became smaller than 0.01 eV Å$^{-1}$ and the energy tolerances were less than 5 × 10$^{-6}$ eV/atom. A vacuum of 20 Å between the layers was considered. Our results were compared to others
published in the literature finding agreement under the same level of theory [29, 30]. It is noteworthy that DFT-LDA underestimates the band gap in semiconductors, however, in the particular case of semiconducting TMD the direct band gap coincides with the optical gap observed in absorption or photoluminescent experiments [2–4, 31]. In order to have a deeper picture of the electronic behavior of these systems, GW calculations in combination with solving the Bethe–Salpeter (BSE) equation are required to correct the band gap considering excitonic effects [32–34]. Nevertheless, DFT-LDA could be used as the first approximation to understand the behavior of the defective systems as we have done in this account. For the phonon dispersion, the phonon density of states and the Raman calculations, density functional perturbation theory (DFPT) with the above parameters, but extending the plane waves cut off to 720 eV, and using the linear response approach for insulators [35], was implemented.

**Results and discussion**

In order to preserve the TMD stoichiometry, all Haeckelites considered in this manuscript were constructed by introducing 8-4 defects, and we have called them MX$_2$-8-4 (M = Metal, X = chalcogen; see figure 1). The Haeckelite crystals belong to the Pbam space group and the path of the Brillouin zone considered was Γ-X-S-Y-Γ (see figure 2). It is noteworthy that in all cases there is a bond linking the transition metal atoms in the square-like defect (see figure 1).

Our results are divided into two groups: Haeckelites from semiconducting TMDs and Haeckelites from metallic TMDs (see below).

*Haeckelites from semiconducting TMD: MoS$_2$, MoSe$_2$, WSe$_2$, WS$_2$, WTe$_2$*

In this case, the band structure is very similar for MoS$_2$-8-4 and MoSe$_2$-8-4, though there is a difference in their lattice parameters ‘a’ and ‘b’: for MoS$_2$-8-4 the lattice parameter ‘a’ (6.28 Å) is very close to ‘b’ (6.29 Å), but for MoSe$_2$-8-4, ‘a’ (6.56 Å) is larger than ‘b’ (6.49 Å; see table 1). This difference in lattice parameters can be regarded as a distortion that deforms the octagonal-like and the square-like defects, becoming larger for W-based Haeckelites (see figures 1(c)–(d)). On the other hand, it is noted that the direct band gap, which characterizes semiconducting trigonal prismatic phases, is reduced to 0.005 eV, an almost touching of bands for the MoSe$_2$-8-4 case, and could result in a value of 0.142 eV for MoS$_2$-8-4 (see table 1 and figure 2). Due to the small distortion (difference in lattice parameters ‘a’ and ‘b’) the small band gap shifts slightly from Γ (Γ-X) in MoSe$_2$-8-4. The tungsten based Haeckelites (WS$_2$-8-4, WSe$_2$-8-4 and WTe$_2$-8-4) reveal a larger cell distortion (difference in lattice parameters) as the chalcogen atom gets heavier, being WTe$_2$-8-4 the largest (see table 1 and figure 1). Moreover, the WTe$_2$-8-4 exhibits the lowest relative energy with respect to their corresponding trigonal prismatic monolayer (0.69 eV/formula of WTe$_2$), thus, WTe$_2$-8-4 could be a suitable candidate for introducing 8-4 defects. Surprisingly, the WTe$_2$-8-4 Haeckelite exhibits almost touching bands (0.016 eV at an intermediate point between Y-Γ) with a very symmetric density of states which resembles that of graphene (see figure 3 and table 1). Simulations of high resolution transmission electron microscopy and the diffraction pattern were carried out for WTe$_2$-8-4 Haeckelite using the multi-slice method as implemented in the code Simulatem [36] (see figure 4).
The group of Haeckelites which comes from metallic TMD exhibits larger band gaps when compared to the previous case, being direct for NbS$_2$-8-4 at the S point in the Brillouin zone (0.45 eV), and indirect (S-$\Gamma$) for NbSe$_2$ (0.35 eV; see table 1 and figure 3). In addition, these

**Figure 1.** Relaxed models of TMD Haeckelites. (a) MoS$_2$-8-4; (b) NbSe$_2$-8-4; (c) WSe$_2$-8-4; (d) WTe$_2$-8-4. Note the bonding between the transition metal atoms and the distortion (deformation of octagonal and square like defects, due to the difference in cell parameters) in W-based Haeckelites.

**Haeckelites from metallic TMD: NbS$_2$ and NbSe$_2$**

The group of Haeckelites which comes from metallic TMD exhibits larger band gaps when compared to the previous case, being direct for NbS$_2$-8-4 at the S point in the Brillouin zone (0.45 eV), and indirect (S-$\Gamma$) for NbSe$_2$ (0.35 eV; see table 1 and figure 3). In addition, these
cases reveal lower relative energies and lower lattice distortions than the Haeckelites from semiconducting TMDs (see table 1). The phonon dispersion, phonon density of states and Raman spectrum have been calculated for the NbS$_2$-8-4 using DFPT. The results indicate that the structure is stable as no imaginary frequencies in the phonon dispersion are found (see figure 5). Moreover, there are two main Raman active peaks at 224.71 cm$^{-1}$ ($B_{1g}^1$) and 315.13 cm$^{-1}$ ($A_{1g}^1$); the $B_{1g}^1$ mode corresponds to perpendicular sulfur vibrations and in plane niobium vibrations, and the $A_{1g}^1$ is mainly due to diagonal out of plane sulfur vibrations (see figure 6). The vibrational modes belong to D$_{2h}$ point group, so it is possible to use the character tables to name the modes; since there are several modes with the same symmetry we have used super indices to distinguish among them (see figure 6). It is also interesting to note that the trigonal prismatic phase of NbS$_2$ exhibits Raman signals at 304 cm$^{-1}$ for the $E_{2g}^1$ mode (in plane mode) and 379 cm$^{-1}$ for the $A_{1g}$ mode (out of plane mode which involves just the sulfurs) [37, 38]. Therefore, the NbS$_2$-8-4 Haeckelite possesses Raman modes which are not related to

Figure 2. (a) Brillouin zone of the TMD Haeckelites showing the high symmetry points $\Gamma$, $X$, $Y$ and $S$ which are used in the band structure calculations; $g_1$ and $g_2$ are the reciprocal lattice vectors (the atomic model of the unit cell is included for clarity); (b) band structure and density of states (DOS) of MoS$_2$-8-4-Haeckelite; (c) band structure and density of states (DOS) of MoSe$_2$-8-4-Haeckelite; (d) band structure and density of states (DOS) of WS$_2$-8-4-Haeckelite.
the most stable trigonal prismatic phase, thus making possible to identify isolated 8-4 defects in grain boundaries around the values shown here (224.71 \( \text{cm}^{-1} \) and 315.13 \( \text{cm}^{-1} \)).

**Conclusion**

Haeckelite structures based on TMDs containing 8-4 defects have been studied with first principles calculations. We found that the electronic properties of Haeckelites show very different electronic behavior when compared to the traditional (stable) trigonal prismatic TMD monolayers. In particular, the Haeckelites derived from semiconducting TMDs exhibit semimetallic behavior and those arising from metallic TMD phases, possess a semiconducting behavior. It is worth noting that 8-4 defects in TMD have been observed in the structure of grain boundaries in MoS\(_2\) \[12\] and should also appear in other TMDs, thus more studies need to be carried out in this direction in order to identify other defects which might be present in TMD systems. The Haeckelites studied here are an extreme case in which all the hexagonal lattice of the trigonal prismatic phase is substituted by a rectangular lattice by introducing 8-4 units. Most probably, Haeckelites in which just some regions exhibit these defects could be found in defective or irradiated TMD systems. It might be possible that some TMDs are more prone than others to admit defects: for example, according to our results, NbS\(_2\) and NdSe\(_2\) are suitable candidates to generate 8-4 defects which might be introduced by ionic bombardment followed by thermal annealing. Using HRTEM for generating defects would be another possibility, but since the displaced atoms are the chalcogen atoms, not the transition metals, more intense irradiation could be needed \[8\]. Raman spectroscopy constitutes one of the best tools to identify defects and correlate them with the systems studied here. In particular, grain boundaries

| Structure  | Gap in eV (gap in trigonal prismatic cell in eV) | Relative energy/formula \( \text{MX}_2 \) WRT trigonal prismatic phase in eV | Lattice parameters in Å (space group) |
|------------|-----------------------------------------------|-----------------------------------------------|---------------------------------------|
| MoS\(_2\)-8-4 | 0.142 (1.82) | 0.9812 | \( a = 6.28, b = 6.29 \) (Pbam) |
| MoSe\(_2\)-8-4 | 0.005 (1.61) | 0.8865 | \( a = 6.56, b = 6.49 \) (Pbam) |
| WS\(_2\)-8-4 | 0.015 (1.94) | 1.11 | \( a = 6.19, b = 6.35 \) (Pbam) |
| WSe\(_2\)-8-4 | 0.025 (1.68) | 0.9539 | \( a = 6.22, b = 6.76 \) (Pbam) |
| WTe\(_2\)-8-4 | 0.016 (1.21) | 0.6903 | \( a = 6.38, b = 7.24 \) (Pbam) |
| NbS\(_2\)-8-4 | 0.454 Direct (metal) | 0.6161 | \( a = 6.467, b = 6.469 \) (Pbam) |
| NbSe\(_2\)-8-4 | 0.354 Indirect (metal) | 0.5599 | \( a = 6.601, b = 6.603 \) (Pbam) |

*Table 1. TMD Haeckelite properties. DFT-LDA band gap in eV. In parenthesis the corresponding band gap in the trigonal prismatic phase. Relative energy in eV per formula of corresponding \( \text{MX}_2 \) (M = Metal, X = chalcogen). Lattice parameters of the relaxed unit cells and in parenthesis the corresponding space group.*
exhibiting 8-4 defects should exhibit characteristic signals as shown here for NbS$_2$-8-4. Similar to graphene, Haeckelites based on TMDs remain elusive, but it might be possible that with the right experimental conditions or the right synthetic templates, these structures could become a reality.

Figure 3. (a) Band structure and density of states (DOS) in WSe$_2$-8-4-Haeckelite; (b) band structure and density of states (DOS) in WTe$_2$-8-4-Haeckelite; (c) band structure and density of states (DOS) of NbS$_2$-8-4-Haeckelite; (d) band structure and density of states (DOS) in NbSe$_2$-8-4-Haeckelite.

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Figure 4. (a) WTe$_2$-8-4-Haeckelite simulated image of a HRTEM operating at 400 kV with $-450$ Å defocus; (b) diffraction pattern of (a); (c) NbS$_2$-8-4-Haeckelite simulated image of a HRTEM operating at 400 kV with $-450$ Å defocus; (d) diffraction pattern of (c). The darker spots in (a) and (c) correspond to the two projected chalcogen atoms (Te and S respectively). The scale bars in (a) and (c) correspond to 1 nm.
Figure 5. NbS$_2$-8-4 Haeckelite. Phonon dispersion (a) and phonon density of states (b).

Figure 6. (a) Calculated Raman spectra of NbS$_2$-8-4 Haeckelite; (b) top and side views of the $B^{1}_{1g}$ mode in the unit cell as indicated by the arrow; (c) top and side views of the $A^{1}_{g}$ mode in the unit cell as indicated by the arrow.

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