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Strain engineering of electronic properties of transition metal dichalcogenide monolayers

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ABSTRACT

We present Density Functional Theory (DFT) results for the electronic and dielectric properties of single-layer (2D) semiconducting transition metal dichalcogenides MX_2 (M=Mo, W; X=S, Se, Te) under isotropic, uniaxial (along the zigzag and armchair directions), and shear strain. Electronic band gaps decrease while dielectric constants increase for heavier chalcogens X. The direct gaps of equilibrium structures often become indirect under certain types of strain, depending on the material. The effects of strain and of broken symmetry on the band structure are discussed. Gaps reach maximum values at small compressive strains or in equilibrium, and decrease with larger strains. In-plane dielectric constants generally increase with strain, reaching a minimum value at small compressive strains. The out-of-plane constants exhibit a similar behavior under shear strain but under isotropic and uniaxial strain they increase with compression and decrease with tension, thus exhibiting a monotonic behavior. These DFT results are theoretically explained using only structural parameters and equilibrium dielectric constants. Our findings are consistent with available experimental data.

The isolation of atomically thin sheets from layered materials has generated enormous interest in two-dimensional (2D) crystals [1]. During the last decade, single atomic layers cleaved from materials such as boron nitride, graphite, and molybdenum disulfide exhibit novel electronic and optoelectronic properties, different from their bulk, three-dimensional (3D) counterparts [2,3]. Layered materials such as molybdenum disulfide and other Transition Metal Dichalcogenides (TMDs) had been extensively studied over the past few decades as catalysts [4–6], lubricants [7] and materials for solar cells [8–10]. Semiconducting TMDs consist of weakly coupled MX_2 hexagonal atomic layers (M=Mo, W and X=S, Se, Te), the M atom being sandwiched between X atoms. Similar to graphite, their layered 3D structure allows for the extraction of single or few layers. Unlike gapless, semimetallic graphene though [11], these new 2D materials possess a band gap and their unique electronic and optical properties are currently under intensive investigation. These properties depend on dimensionality and nanostructuring so that TMDs may be tailored for specific applications. When combined in layered 2D structures, with graphene and other materials, they are expected to revolutionize nanoscale devices [12]. It has been shown relatively recently that the indirect band gap of bulk MX_2 increases when they are reduced to a few layers and becomes direct for the monolayer, resulting in a dramatic increase in photoluminescence and in novel excitonic effects [13–23]. Breaking of inversion symmetry and strong spin–orbit coupling gives rise to valley selective circular dichroism [24]. Quasi-one-dimensional (1D) and zero-dimensional (0D) structures such as nanoribbons and flakes (dots), respectively, exhibit robust metallic edge states [25–29]. It was predicted [30] and verified experimentally [31] that single-layer TMDs exhibit piezoelectric behavior [32]. Thus, TMD 2D semiconductors of atomic thickness show great promise for optoelectronic applications and devices have already been fabricated, e.g., transistors [33,34], solar cells [35–37], and light-emitting diodes [38].

Tunability of optoelectronic properties, which is essential for applications, can be achieved by controlling dimensionality, number of layers, size and shape of nanostructures, chemical substitutions, and strain. Strain is often intentionally or unintentionally present in TMDs monolayers, depending on synthesis method, substrate, stacking, and several other conditions. These materials are flexible and large strains can be applied without damage [39], allowing for electronic structure engineering applications without any other physical or chemical modification [40]. A number of theoretical and experimental works have examined the role of strain on the electronic properties of several TMDs [41-

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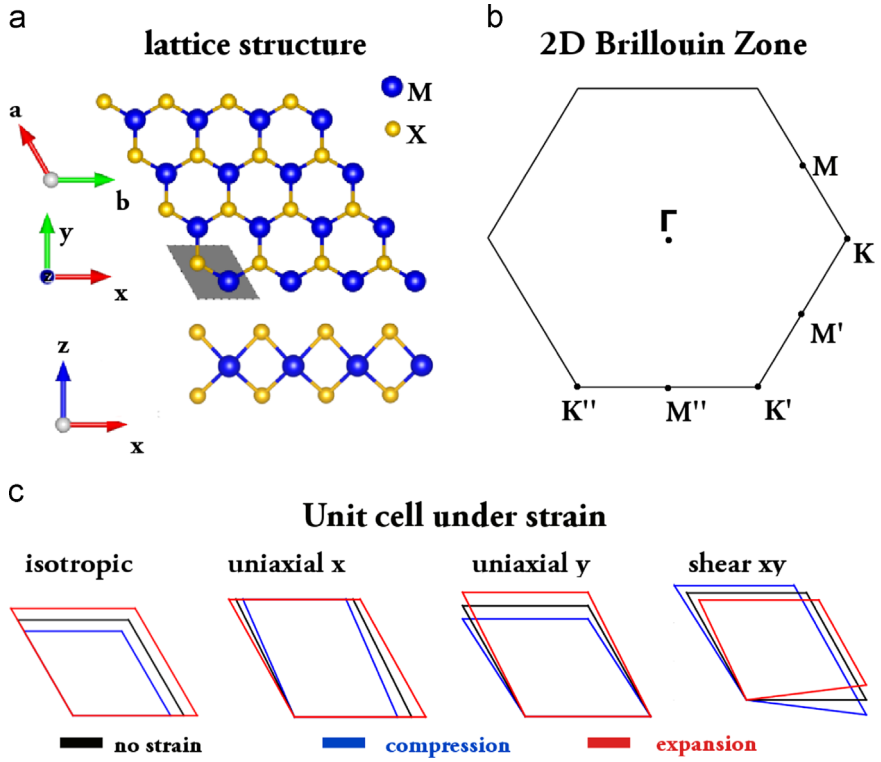

Fig. 1. (Color online) (a)Top and side view of the hexagonal lattice structure of MX_2. M and X atoms are represented by blue and yellow spheres, respectively. The shaded area corresponds to a unit cell. (b) The corresponding Brillouin Zone. (c) Schematic representation of the different types of strain applied on the unit cell.

46]. Different types of strain on different TMDs have several interesting effects. In many cases, the direct gap becomes indirect and reduced in value, to the point that the material becomes metallic under extreme strain. Detailed knowledge of the variation of electronic band structure under strain is important. Moreover, screening effects determine electron and exciton dynamics, as well as optoelectronic properties in 2D TMD semiconductors. The effects of strain on the dielectric constant are crucial in this aspect and relevant studies are limited [45]. In this work, we systematically investigate the MX_2 band structure and dielectric constant variations under principal types of strain with Density Functional Theory (DFT). The rich behavior of these systems is summarized and general trends are established. We show that our results are consistent with available experiments and in some cases we provide theoretical explanations which validate our DFT results.

The equilibrium atomic structure of an MX_2 monolayer (with M=Mo, W and X=S, Se, Te) is shown in Fig. 1(a). The 2D lattice has hexagonal symmetry (top view) and consists of an M atomic layer sandwiched between two X atomic layers (side view). It is characterized by the distance between neighboring M atoms, a, and an internal parameter, u, which describes the relative distance between M and X atoms. The x- and y-directions coincide with the zigzag and armchair directions, respectively. The corresponding Brillouin Zone (BZ) is shown in Fig. 1(b). The 3D lattice consists of stacked MX_2 monolayers which are weakly bonded with van der Waals interactions. The vector in the z-direction perpendicular to the monolayer is c, so that the distance between M and X layers is $(\frac{3}{4}-u)c$. Fig. 1(c) shows the effect of the different types of strain we apply on the unit cell, i.e., isotropic, uniaxial-x, uniaxial-y, and shear-xy. We perform DFT total energy calculations for all strain-free (equilibrium) MX_2 with full atom relaxation. Then, for all strained structures, we only allow for u-parameter relaxation.

We perform DFT calculations with the Grid-based Projected Augmented Wave (GPAW) open-source implementation [47-49]. GPAW uses a real space grid to describe electron densities and wave functions. We use the Generalized Gradient Approximation (GGA) Perdew–Burke–Ernzerhof exchange-correlation functional (PBE) [50] and, for atomic relaxation, a conjugate-gradient minimization algorithm as implemented in the open-source Atomic Simulation Environment (ASE) simulation suite [51]. The dielectric function is calculated using linear-response theory optimized for the GPAW code [52]. Electron–electron interactions are taken into account using the random phase approximation (RPA). For the in-plane polarization the electric field is parallel to the MX_2 layer ($\mathbf{E} \perp \mathbf{c}$) and for the out-of-plane polarization it is perpendicular ($\mathbf{E} \parallel \mathbf{c}$). The dielectric constant is obtained in the limit $\omega \to 0$ of $\varepsilon(\omega)$. For 2D systems, we found that a vacuum of 12 Å between monolayers gives ε values in reasonable agreement with available experimental data. We are interested in the variation of ε with strain and exact values are beyond the scope of this work. Standard DFT calculations, such as the ones we perform here, agree with photoluminescence experiments for the lowest excitation energy of single-layer TMDs. However, DFT is well known to underestimate electronic band gaps, with actual values approximately one and a half times the DFT values. Dielectric screening effects and excitons should be included. Interestingly, for MX_2, these two contributions appear to almost cancel each other. For instance, for MoS_2 the DFT band gaps are found between 1.5 and 2 eV. Inclusion of screening employing a GW scheme opens the band gap up to about 3 eV. Adding excitons by means of the Bethe–Salpeter equation brings the minimum excitation below 2 eV [18–20,36], in agreement with experiments and close to the values found in standard DFT. Apart from this fortuitous agreement between DFT and many-body calculations or experiments, standard DFT can be trusted for band structures and the calculation of the static relative permittivity, ε_r. As an average over the whole band structure, it is rather insensitive to details of the computational method and the simple DFT-RPA method employed here gives values that are within 10% off values of much more detailed calculations and experiments [52,53].