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Group theory analysis of phonons in two-dimensional transition metal dichalcogenides

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Transition metal dichalcogenides (TMDCs) have emerged as a new two-dimensional material’s field since the monolayer and few-layer limits show different properties when compared to each other and to their respective bulk materials. For example, in some cases when the bulk material is exfoliated down to a monolayer, an indirect-to-direct band gap in the visible range is observed. The number of layers $N$ ($N$ even or odd) drives changes in space-group symmetry that are reflected in the optical properties. The understanding of the space-group symmetry as a function of the number of layers is therefore important for the correct interpretation of the experimental data. Here we present a thorough group theory study of the symmetry aspects relevant to optical and spectroscopic analysis, for the most common polytypes of TMDCs, i.e., $2H_a$, $2H_c$ and $1T$, as a function of the number of layers. Real space symmetries, the group of the wave vectors, the relevance of inversion symmetry, irreducible representations of the vibrational modes, optical activity, and Raman tensors are discussed.

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I. INTRODUCTION

The interest in two-dimensional (2D) layered materials increased after the successful isolation of monolayer graphene (the 2D component of graphite) reported in 2004 [1]. The monolayer of hexagonally-linked carbon atoms made it possible to study a brand-new set of magnetic, electric, and optical phenomena related to the Dirac-like nature of graphene electrons [2]. The lack of a band gap, however, imposes some difficulties to graphene’s application in electronics, despite its high carrier mobility.

Other classes of 2D materials are now also being intensively studied for many different applications motivated mainly by the need of a band gap. Perovskite-based oxides, van der Waals solids such as Bi$_2$Se$_3$, Bi$_2$Te$_3$ [3], hexagonal boron nitride (h-BN) [4], and transition metal dichalcogenides (TMDCs), such as MoS$_2$ and WSe$_2$ [5–7], offer a wide range of compounds and combinations with potential use in the emerging field of 2D heterostructures [8] (for example, tunable optoelectronic applications [11–13]). A detailed study of these symmetry aspects for few-layers TMDCs is valuable to predict interesting characteristics and to properly interpret experimental results for these compounds, since few-layers TMDCs will belong to different space groups according to the number of layers, and their space groups will be different from those of their bulk crystal counterparts.

The dependence on the number of layers ($N$) and on the changes of the symmetry group have already been investigated in the characterization of the various TMDC optical properties, by means of Raman spectroscopy and second harmonic generation (SHG) [21,23–29]. Group theory provides a valuable theoretical tool that can be used to understand the selection rules for the optical transitions, to find the eigenvectors for the lattice vibrations, and to identify the lifting of degeneracies due to external symmetry-breaking perturbations [30,31]. A detailed study of these symmetry aspects for few-layers TMDCs is valuable to predict interesting characteristics and to properly interpret experimental results for these compounds, since few-layers TMDCs will belong to different space groups according to the number of layers, and their space groups will be different from those of their bulk crystal counterparts.

Group theory has already been used to describe the structure of TMDCs in the bulk form for different polytypes [32,33], in the few-TL $2H_c$ polytype for zone center phonons (at the $\Gamma$ BZ point) [23–25] and for the electronic structure at the

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and for a more detailed understanding of some nonlinear optical processes [26]. In this work, group theory is applied to TMDCs in both the trigonal prismatic (H) and octahedral (T) metal atom coordinations, considering the stacking order for 2Ha and 2Hc for H, and 1T for T, and the dependence on the number of layers N (even or odd), and considering the full set of wave vectors in the BZ, i.e., going beyond the zone center. In Sec. II, the symmetry analysis in real space is developed for the 2H (Sec. II A1) and 1T (Sec. II A2) polytypes, while the reciprocal space treatment is shown in Sec. II B. The relevance of inversion symmetry for the different TMDCs polytypes is discussed in Sec. II C. The irreducible representations for vibrational modes for few-TL TMDCs considering the high-symmetry points and lines in the BZ are presented in Sec. II D, and the Raman and infrared selection rules are shown in Sec. II E, while Sec. II F gives the Raman tensors. Finally, Sec. III summarizes the main conclusions and comments on the cases of lowering of symmetry induced by strain in MoS2, by engineering heterostructures, and by breaking the out-of-plane translational symmetry in WSe2.

II. SYMMETRY ANALYSIS

A. Real space symmetry

The family of layered TMDCs is composed of several polytypes with a different number of TLs, or different metal atom coordinations that form the primitive unit cell (see Table I). The main polytypes under experimental and theoretical consideration nowadays (and analyzed in the present work) are the trigonal prismatic 2H [two TLs in a trigonal prismatic coordination (H) are required to form the bulk primitive unit cell] and the octahedral 1T [one TL in an octahedral coordination (T) is required to form the bulk primitive unit cell] (see Fig. 1). Each polytype, in turn, has a monolayer (one TL) as a basic 2D building block unit. The bulk crystal is made by piling up these monolayer units, namely 1H (trigonal prismatic or AbA coordination, where upper cases represent chalcogen atoms and lower cases represent metal atoms) and 1T (octahedral or AbC coordination), as can be observed in Figs. 1(a) and 1(b), respectively. The blue spheres represent transition metal atoms, and the orange spheres represent the chalcogen atoms. For bulk versions of these layered materials, where the out-of-plane translational symmetry is present, the lateral views of the unit cells are highlighted with red rectangles in Figs. 1(c), 1(d), and 1(e).

There are several other polytypes for stacks of more than two TLs, and at least 11 polytypes were identified in TMDCs [33]. For example, the unit cell of the 3R-MoS2 (with the stacking /AbA BcB CaC/) [32,33] comprises nine atoms in three TLs. The treatment of these polytypes with a high number of TLs is beyond the scope of this work, but for the 3R case, Table I summarizes some symmetry considerations and gives representative TMDC examples.

1. 2H polytype

The 2H bulk polytype can assume two forms with different stacking symmetries: 2Ha (or /AbA CbC/ stacking) [32,33], and 2Hc (/CaC AcA/ stacking) [33]. In 2Ha stacking, one transition metal atom is always on top of another transition

| Table I. Number of structural formulas (Z), space groups and Wyckoff positions for 2H, 1T, and 3R TMDCs polytypes. One structural formula comprises one transition metal (M) and two chalcogen atoms (X). |
|---|---|---|---|---|---|---|---|
| Polytype | Number of layers | Structural formulas (Z) | Group | Wyckoff positions | Compounds |
| 2H polytype | N even | Be | P63/mmc (2a) | M(1a) | X(4f) |
| | N odd | Be | P63/mmc (2a) | M(1a) | X(4f) |
| 2H polytype | N even | Be | P63/mmc (2a) | M(1a) | X(4f) |
| | N odd | Be | P63/mmc (2a) | M(1a) | X(4f) |
| 1T polytype | N even | B | Pm3m (1a) | M(3a) | X(2d) |
| | N odd | B | Pm3m (1a) | M(3a) | X(2d) |
| 3R polytype | N even | B | Pm3m (1a) | M(3a) | X(2d) |
| | N odd | B | Pm3m (1a) | M(3a) | X(2d) |

aAccording to previous literature on TMDCs [32-33]. The fact that 3D space groups and the respective Wyckoff positions have been constructed considering translation along the out-of-plane direction does not change the conclusions that will be drawn in the present work, because we disregard the wave vector along this nonexisting direction. The Wyckoff positions for the space groups of N odd and N even layers of TMDCs are not established in the International Tables of Crystallography [35].
metal atom of the next layer, as shown in Fig. 1(c). This polytype is reported to occur in NbSe₂, NbS₂, TaS₂, and TaSe₂ crystals [32]. In 2Hc stacking, any transition metal atom is sitting on top of two chalcogenides atoms of the subsequent layer, as shown in Fig. 1(d). This polytype occurs in MoS₂, WS₂, MoSe₂, and WSe₂ crystals. Both polytypes belong to the nonsymmorphic hexagonal space group P6₃/mmc [32] (D₆h in Schönflies notation, or #194 in the International Tables for Crystallography Vol. A (ITCA) [35]). The primitive unit cell for the bulk has six atoms (Z = 2, where Z is the number of structural MₙX₂ units required to form the primitive unit cell), and three atoms in each TL, as can be seen in the red rectangles of Figs. 1(c) and 1(d). The Wyckoff positions for the 2H bulk polytypes, as well as the number of structural formulas Z are given in Table I.

The 2Hb polytype is possible and occurs for nonstoichiometric compounds with an excess of metal atoms intercalated in the van der Waals gap [33]. Table I gives symmetry information and examples for this polytype. Some differences between the definition of 2Hb and 2Hc are found in the literature [32,33], and the most recent nomenclature is used in this work [33,36].

For few-layer systems there is a reduction in symmetry due to the lack of translational symmetry along the z axis (the z axis is perpendicular to the basal plane of the TLs). The symmetry operations are reduced from 24 in the bulk to 12 for both even and odd numbers of TLs. Therefore, the few-TLs space groups are different from the bulk space groups and depend on the parity of the number of layers (even or odd number of TLs).

Figure 2 illustrates the 1TL and 2TL stacking arrangements for the 2Hc polytype. The hexagonal real space for 1TL and 2TLs are given in Figs. 2(a) and 2(d), respectively.

The 2Hc polytype symmetry operations are illustrated in Figs. 2(b) and 2(e), which are the top-views of the primitive unit cells. In Figs. 2(c) and 2(f), the lateral views of the primitive unit cells are given for 1TL and 2TLs, respectively.

The space groups of few-layer TMDCs can be renamed according to the “layered subperiodic groups”, from the International Tables for Crystallography Vol. E (ITCE) [37], but here we adopt the ITCA nomenclature [35] for comparison with related literature [38]. The 1TL of the 2H polytype belongs to the P6₃m2 (D₆h or #187) hexagonal symmorphic space group, as well as to other few-layer compounds with odd number of layers, whose point symmetry operations are E (identity), 2C₃ [clockwise and anticlockwise rotations of 120° about the axis represented as a black triangle in Fig. 2(b)], 3C₂ (two-fold axis in the σₜ plane), σₜ (the horizontal reflection plane that passes through the transition metal atom), 2S₃ (C₃ clockwise and anticlockwise rotations, followed by a σₜ reflection), and 3σₜ (vertical reflection planes).
The 2TLs of $2H$ polytype and any other even number of TLs belong to the $D_{3d}^{1}$ ($P\bar{3}m1$, #164) symmetric space group, whose symmetry operations are $E$, $2C_3$, $3C'_2$ [rotation axes placed in between two adjacent TLs, i.e., in the middle of the van der Waals gap in Fig. 2(f)], inversion $i$ [red dot in the $\sigma_h$ plane of Fig. 2(f)], $3\sigma_d$ [dihedral vertical mirror planes represented by red lines in Fig. 2(e)], and $2S_6$ (clockwise and anticlockwise rotations of 60° followed by a $\sigma_h$ reflection). For the 3TLs case, when another TL unit is added to the 2TLs shown in Figs. 2(d), 2(e), and 2(f), the symmetry operations are the same as those observed for 1TL, since the $\sigma_h$ plane is recovered as a symmetry operation. The addition of subsequent layers will always show symmetry variations depending on whether the number of layers is odd or even, and the difference between these two groups is ultimately given by the presence of the inversion symmetry in 2TLs (which is absent in 1TL) and the presence of the $\sigma_h$ plane in 1TL (which is absent in 2TLs).

2. 1T polytype

From a symmetry standpoint, the 1T polytype is constructed by piling up single 1TL units, where each subsequent layer is exactly the same as the previous one, with one transition metal atom (or chalcogen atom) on top of another transition metal atom (or chalcogen atom), in an octahedral coordination. In the bulk TMDC, the stacking is /AbC/AbC/ (see Fig. 1). The bulk form belongs to the $D_{3d}^{1}$ ($P\bar{3}m1$, #164) symmetric space group. The unit cell comprises three atoms of one TL [red rectangle in Fig. 1(e)]. The Wyckoff positions and number of structural formulas (2) for the 1T polytype TMDCs are given in Table I. Because all layers are identical, the symmetry operations do not change by increasing the number of TLs, no matter if $N$ is even or odd. Figures 3(a) and 3(d) show the 1TL and 2TLs structures, respectively, of the 1T polytype. The symmetry operations of 1TL are $E$, $2C_3$, $3C'_2$ [the $C'_2$ rotation axes are in the reflection plane, between the two chalcogen atoms, dividing in half the transition metal atom, as shown in the black lines in Fig. 3(c)], inversion $i$ (red dot in the transition metal atom), $3\sigma_d$ [dihedral vertical mirror planes represented by red lines in Fig. 3(b)], and $2S_6$ (clockwise and anticlockwise rotations of 60° followed by a $\sigma_h$ reflection). In the 2TL case, the same operations are still valid, but now the inversion and the reflection plane [Fig. 3(f)] for the $S_6$ operation are located in the van der Waals gap.

B. Group of the wave vector

The reciprocal space high-symmetry points and directions for the 2H and 1T polytypes are shown in Fig. 4. Here $a_1$ and $a_2$ are the primitive vectors of the real 2D lattice described by Eq. (1) and are shown in Fig. 2(a). Correspondingly, $b_1$ and $b_2$ [described in Eq. (2)] are the reciprocal lattice vectors shown in Fig. 4.

$$\begin{align*}
\vec{a}_1 &= \frac{a}{2}(\sqrt{3}\hat{x} + \hat{y}), \\
\vec{a}_2 &= \frac{a}{2}(−\sqrt{3}\hat{x} + \hat{y}),
\end{align*}$$

(1)

$$\begin{align*}
\vec{b}_1 &= \frac{2\pi}{a}\left(\frac{\sqrt{3}}{3}\hat{k}_x + \hat{k}_y\right), \\
\vec{b}_2 &= \frac{2\pi}{a}\left(−\frac{\sqrt{3}}{3}\hat{k}_x + \hat{k}_y\right).
\end{align*}$$

(2)

The differences between the space groups $D_{3d}^{1}$ and $D_{3d}^{3}$ when the number of TLs is odd or even define different symmetries for the group of the wave vectors (GWW) at each high-symmetry point or direction of the reciprocal space. Knowledge of the GWW is important because the invariance of the Hamiltonian under symmetry operations usually leads to degeneracies at these high-symmetry points or directions in the BZ [39–41]. The GWW for the 2H TMDCs is similar.
to the GWV found for \( N \)-layer graphene and bulk graphite [38], since the space groups for bulk, \( N \) even, and \( N \) odd \( (N \geq 3) \) TLs in the TMDC family resemble the corresponding graphene systems. However, the 1TL case in TMDCs lacks inversion symmetry and therefore belongs to the same space group \((P6m2)\) as that for other \( N \)-odd layers. Table II shows the groups that are isomorphic to the GWV for all the BZ high-symmetry points and axes occurring for bulk and for both odd or even number of TLs in the 2\( H \) polype.

The 1\( T \) polype has the same GWV regardless the number of layers in the sample. The bulk is symmorphic, so it has the same GWV. Table III shows the GWV for different high-symmetry points and axes within the BZ for this polype.

C. Relevance of inversion symmetry

The presence or absence of inversion symmetry is an important aspect of TMDCs since it opens the possibility of coupled spin and valley physics [17]. The strong spin-orbit coupling in TMDC materials is due to the \( d \) orbitals in their heavy metal atoms. The absence of inversion symmetry lifts the degeneracy of the same energy at the same \( k \) value, at the \( K \) point of the BZ, and spin splitting values on the order of 0.4 eV have been observed in WSe\(_2\) [21].

The inversion symmetry is also important for optics, e.g., the second-harmonic generation (SHG) technique, which has been routinely used to probe not only the presence of inversion symmetry, but also the crystal orientation [26,27] and, recently, the effect on SHG of two artificially stacked TMDC layers [42]. For centrosymmetric crystals, the \( \chi^{(2)} \) nonlinear susceptibility vanishes [43], and no SHG signal is observed. The 2\( H \) TMDCs polype (and in this case, also including the 1TL) belong to the noncentrosymmetric space group \( D_{6h} \) and then it is possible to observe a SHG signal [21,26–28,42–44]. The \( N \)-even TLs for 2\( H \) TMDCs do not show SHG since their space groups are centrosymmetric. For the 1\( T \) TMDCs polype, both \( N \)-even and \( N \)-odd TLs have the same centrosymmetric space group \( D_{3d}^3 \), and the SHG signal is not expected. In this sense, the SHG mapping (together with other characterization tools) could be used to detect different polypes in the same sample since the 2\( H \) polype with an odd number of layers shows SHG, while the layered 1\( T \) polype does not.

D. Irreducible representations for vibrational modes

The irreducible representations for the lattice vibrations \((\Gamma^{vib})\) are given by the direct product \( \Gamma^{vib} = \Gamma^{eq} \oplus \Gamma^{vec} \), where \( \Gamma^{eq} \) denotes the equivalence representation for the atomic sites, and \( \Gamma^{vec} \) is the representation for the \( x \), \( y \) and \( z \) real space vectors [40]. The \( \Gamma^{vec} \) representation can be written as \( \Gamma^{vec} = \Gamma_x \oplus \Gamma_y \oplus \Gamma_z \), or \( \Gamma^{vec} = \Gamma_1 \oplus \Gamma_2 \) when \( x \) and \( y \) have the same irreducible representation. The \( \Gamma^{vib} \) representations for the 2\( Ha \), 2\( Hc \), and 1\( T \) polypes are given in Tables IV, V, and VI, respectively, for all the BZ high-symmetry points and lines (shown in Fig. 4), and for odd or even numbers of TLs. It is worth noting that for the 2\( Hc \) polype, the \( \Gamma^{vib} \) for the \( K' \) point is the complex conjugated form of the \( \Gamma^{vib} \) for the \( K \) point, while for the 2\( Ha \) polype the atomic sites are different (due to different Wyckoff positions) and the \( \Gamma^{vib} \) of the \( K \) and \( K' \) points are the
TABLE III. Space group and group of the wave vector (GWV) for the high-symmetry points and directions in the BZ for 1T polytype in TMDCs, valid for N-layer (even or odd) and bulk.

| Space group | Γ | K(K') | M | T(T') | Σ | u |
|-------------|---|-------|---|-------|---|---|
| D3d (P3m1, #164) | D3d (P3m1, #164) | D3d (P321, #150) | C2/m (C2, #12) | C2 (C2, #5) | C2 (or C2, Cm, #8) | C1 (P1, #1) |

“σ” denotes the σ’s mirror plane.

same. In the 1T polytype, the Γ'''' for the K and K' points is also the same. The conversion from the space group (SG) to the point group (PG) notation for the irreducible representations is indicated in each character table of the Supplemental Material [45]. The irreducible representations for vibrations for each high-symmetry point and line of the BZ for the bulk polytypes are also given in Tables SI, SII, and SIII of the Supplemental Material [45].

E. Raman and infrared activity

For bulk 2H polytypes (1T polytype), the lattice vibration irreducible representations Γ'''' for the 19 (9) zone center phonons are reproduced in the first line of Table VII (see also Tables SI and SII from the Supplemental Material) [45]. The classification of the modes as Raman active, infrared (IR) active, acoustic, and silent are given in Table VII.

For the 2D polytypes, the Raman and IR active modes show symmetry variations depending on the number of layers since the high-symmetry Γ point has different GWV. The GWV at the Γ point is D3d for N-odd 2H polytypes, D3d for N-even 2H polytypes, and D3d for the N-even and N-odd 1T polytype. The total number of modes for N even or N odd layers in the 2H and 1T polytypes, including their classification as Raman active, IR active, acoustic, and silent modes are given in Tables VIII and IX, respectively.

In the 1T polytype, since the space group is the same in both N-even and N-odd, the representations for the few-TL films of this polytype refer to the same irreducible representations of the group of the wave vector D3d at the Γ point, which in turn are the same found for its bulk counterpart.

F. Raman tensors

To define whether or not a specific vibrational mode will be experimentally observed in a given Raman scattering geometry, we use the Porto notation [46,47], which indicates the crystal orientation with respect to the polarization and propagation directions of the laser. Four letters are used in the Porto notation to describe the scattering process in the a(bc)d form: while “a” and “d” are the propagation directions of the incident and scattered light, respectively, “b” and “c” represent the polarization directions for the incident and scattered light, respectively. One common Raman experimental geometry is the backscattering configuration, where the incident and scattered light have an opposite sense. For example, in the ℏ(xyz) configuration the “xyz” and “y” are the directions of the incident and scattered light, and “x” is the polarization direction of the incident light, and “y” is the polarization direction of the scattered light.

The Raman scattering intensity given by the Hamiltonian perturbation term is proportional to [ℏ[^2] ** ℏ[^2]]^2, where ℏ[^2] is the unit vector along the polarization direction of the scattered light, ℏ[^2] is the unit vector along the polarization direction of the incident light, and ℏ[^2] is the Raman tensor. The quadratic functions (x y, xz, yz, ...,) indicate the irreducible representations for the Raman-active modes. Following this procedure, the Raman tensors for all the Raman active modes of N-layer thin films can be found. For the 2H polytype with N-odd few layers (D3d group of the wave vector for the Γ point), the Raman tensors are [48]

```
Γ_1^+ (A_1') :
( a 0 0 )
( 0 a 0 )
( 0 0 b )

Γ_3^- (E') :
( 0 d 0 )
( d 0 0 )
( 0 0 0 )

Γ_3^- (E') :
( 0 0 c )
( c 0 0 )
( 0 0 0 )
```

For the N-even 2H polytype, and for the N even or odd for the 1T polytype, as well as for the 1T bulk crystal (D3d)

TABLE IV. Normal vibrational mode irreducible representations (Γ'''' for the N-layer TMDCs 2Ha-polytype (/AbA CbC), considering all the high-symmetry points and lines in the BZ.

| N odd | N even |
|-------|-------|
| Γ | (3N/2−1)(Γ_1^+ + Γ_1^-) | (1/2)(Γ_1^+ + Γ_3^+ + Γ_3^- + Γ_3^-) |
| K(K') | (3N/2−1)(K_1^+ + K_1^- + K_1^-) | (1/2)(K_1^+ + K_3^+ + K_3^-) |
| M | 3N(M_1 + M_3) | 3N(M_1 + M_3) |
| Σ | 3N(Σ_1 + Σ_3) | 3N(Σ_1 + Σ_3) |
| T(T') | (3N/2−1)T' + (3N/2−1)T^- | (3N/2−1)(T_1 + T_3) |
| u | (3N/2−1)u^+ + (3N/2−1)u^- | 9N_2 |

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TABLE V. Normal vibrational mode irreducible representations (Γ_vib) for the N-layer TMDCs 2Hc-polytype (/CaC AcA/), considering all the high-symmetry points and lines in the BZ.

| 2Hc-polytype (/CaC AcA/) | N odd | N even |
|--------------------------|-------|--------|
| Γ                        | (3N−1)/2)Γ_1 + Γ_3 | (3N)/2)Γ_1 + Γ_3 + Γ_2 + Γ_3 |
| K(K')                    | (3N+1)/2)(K_1 + K_2) + (3N−1)/2)K_2 | (3N+1)/2)(K_1 + K_2) + 3NK_3 |
| M                        | 3N(M_1 + M_2) + (3N−1)/2)M_2 | 3N(M_1 + M_2 + M_3) + (3N−1)/2)(M_1 + M_3) |
| Σ                        | 3N(S_1 + S_2) + (3N−1)/2)S_2 | 6NΣ_1 + 3NΣ_2 |
| T(T')                    | (3N+1)/2)T_1 + (3N−1)/2)T_2 | (3N+1)/2)(T_1 + T_2) |
| u                        | (3N−1)/2)u_1 + (3N−1)/2)u_2 | 9Nu |

TABLE VI. Normal vibrational mode irreducible representations (Γ_vib) for the N-layer TMDCs 1T-polytype (/AbB/AbC/), considering all the high-symmetry points and lines in the BZ.

| 1T-polytype (/AbB/AbC/) | N odd | N even |
|--------------------------|-------|--------|
| Γ                        | (3N−1)/2)Γ_1 + Γ_3 | (3N)/2)Γ_1 + Γ_3 + Γ_2 + Γ_3 |
| K(K')                    | (3N+1)/2)(K_1 + K_2) + (3N−1)/2)K_2 | (3N+1)/2)(K_1 + K_2) + 3NK_3 |
| M                        | (3N−1)/2)(M_1 + M_2) + (3N−1)/2)M_2 | 3N(M_1 + M_2) + (3N−1)/2)(M_1 + M_3) |
| Σ                        | 6NΣ_1 + 3NΣ_2 | 6NΣ_1 + 3NΣ_2 |
| T(T')                    | (3N−1)/2)T_1 + (3N−1)/2)T_2 | (3N−1)/2)(T_1 + T_2) |
| u                        | 9Nu | 9Nu |

TABLE VII. Normal vibrational mode irreducible representations (Γ_vib) for bulk TMDCs at the Γ point within the 2Ha, 2Hc, and 1T polytypes. The Raman active, infrared active, acoustic, and silent mode irreducible representations are identified.

| 2Ha and 2Hc polytypes | 1T polytype |
|------------------------|--------------|
| Γ_vib                  | Γ_1 + 2Γ_3 + Γ_5 + 2Γ_6 + 2Γ_7 + 2Γ_8 + 2Γ_9 + 2Γ_10 + 2Γ_12 | Γ_1 + Γ_3 + 2Γ_2 + 2Γ_4 |
| Raman                  | Γ_1 + Γ_3 + 2Γ_2 | Γ_1 + Γ_3 |
| Infrared               | Γ_7 + Γ_9 | Γ_7 + Γ_9 |
| Acoustic               | Γ_2 + Γ_5 | Γ_2 + Γ_5 |
| Silent                 | 2Γ_1 + Γ_4 + 1Γ_6 | - |

TABLE VIII. Normal vibrational mode irreducible representations (Γ_vib) for the N-layer TMDCs at the Γ point within the 2Ha and 2Hc polytypes. Raman active, infrared active, acoustic, and silent mode irreducible representations are identified.

| 2Ha and 2Hc polytypes | N odd | N even |
|------------------------|-------|--------|
| Γ_vib                  | (3N−1)/2)(Γ_1 + Γ_3) + (3N+1)/2)(Γ_5 + Γ_7) | (3N−1)/2)(Γ_1 + Γ_3 + Γ_5 + Γ_7) |
| Raman                  | (3N−1)/2)(Γ_1 + Γ_3 + Γ_5 + Γ_7) | (3N−1)/2)(Γ_1 + Γ_3 + Γ_5 + Γ_7) |
| Infrared               | (3N−1)/2)(Γ_1 + Γ_3 + Γ_5 + Γ_7) | (3N−1)/2)(Γ_1 + Γ_3 + Γ_5 + Γ_7) |
| Acoustic               | Γ_2 + Γ_5 | Γ_2 + Γ_5 |
| Silent                 | - | - |
TABLE IX. Normal vibrational mode irreducible representations (\(\Gamma^{\text{irb}}\)) for the \(N\)-layer TMDCs at the \(\Gamma\) point within the 1T-polytype. Raman active, infrared active, acoustic, and silent mode irreducible representations are identified.

| 1T polytype | \(N\) odd | \(N\) even |
|-------------|------------|------------|
| \(\Gamma^{\text{irb}}\) Raman | \((\frac{3N-1}{2}) (\Gamma_1^{+} \oplus \Gamma_2^{+}) \oplus (\frac{3N+1}{2}) (\Gamma_2^{+} \oplus \Gamma_3^{+})\) | \((\frac{3N-1}{2}) (\Gamma_1^{+} \oplus \Gamma_2^{+} \oplus \Gamma_3^{+} \oplus \Gamma_4^{+})\) |
| Infrared | \((\frac{3N-1}{2}) (\Gamma_2^{+} \oplus \Gamma_3^{+})\) | \((\frac{3N-1}{2}) (\Gamma_2^{+} \oplus \Gamma_3^{+} \oplus \Gamma_4^{+})\) |
| Acoustic | \(\Gamma_2^{+} \oplus \Gamma_3^{+}\) | \(\Gamma_2^{+} \oplus \Gamma_3^{+}\) |
| Silent | - | - |

For the nonsymmorphic space group for the bulk 2\(H\) polytype, the Raman tensors are [48]

\[
\Gamma_1^{+}(A_{1g}) : \begin{pmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & b \end{pmatrix},
\]

\[
\Gamma_3^{+}(E_{2g})_{(1)} : \begin{pmatrix} c & 0 & 0 \\ 0 & -c & d \\ 0 & d & 0 \end{pmatrix}, \quad \Gamma_3^{+}(E_{2g})_{(2)} : \begin{pmatrix} 0 & -c & -d \\ -c & 0 & 0 \\ -d & 0 & 0 \end{pmatrix}.
\]

III. SUMMARY AND DISCUSSIONS

In this work, symmetry-related aspects of bulk and \(N\)-layer \(2H\) and 1T TMDCs polytypes were discussed from a group theory perspective. The analysis of the presence of inversion symmetry gives different behaviors (in the case of odd number of TLs) for the same number of layers in a given material, with different polytypes. Therefore, it is possible to design experiments to probe, for example, the presence of different polytypes within the same sample, with the same number of layers. The breaking of inversion symmetry is crucial in materials suitable for specific applications, like the development of valleytronic devices, and group theory predictions give directions to researchers on how to design their devices to achieve their desired symmetry-related goals.

Some perturbations can lower the symmetry of these thin films and this approach has been used to tune some characteristics of these materials. In a strained MoS\(_2\) monolayer, where the doubly degenerate Raman active mode \(E'\) splits into \(E^{-}\) and \(E^{+}\) peaks (depending on the magnitude and symmetry of the strain), an optical band gap was found and its magnitude is approximately linear with strain for both monolayer and bilayer MoS\(_2\) [30,31,49]. By using different TMDCs, it is possible to engineer the optical band gap of interest to the researcher. Another possibility is the piling of different TMDCs to engineer new heterostructures, where the inversion symmetry is broken with more options made available by using multiple materials. Such heterostructures are expected, for example, to give rise to tunable band gaps from 0.79 to 1.16 eV [9].

The symmetry properties of the vibrational modes were found for the high-symmetry points and lines in the BZ, extending previous knowledge beyond the zone center phonons in TMDCs. One important aspect of this symmetry analysis is that, from symmetry variations, it is possible to predict the difference in phonon modes in these structures. \(N\) new Raman-active modes have been observed in few layers TMDCs like in WSe\(_2\) [24]. Density functional theory (DFT) combined with polarization-dependent Raman measurements and group theory were used to understand the first-order Raman spectra. For example, the appearance of the inactive mode \(B_{1g}^{\prime}\) in bulk WSe\(_2\) and only for specific laser lines is still not well understood and is usually attributed to resonance effects [24]. However, for \(N\) even and \(N\) odd few layers, \(A_{1g}\) (for \(N\) even TLs) and \(A_{1}'\) (for \(N\) odd TLs) are both observed at 310 cm\(^{-1}\). Furthermore, the \(E_{1g}\) mode at around 175 cm\(^{-1}\) in bulk WSe\(_2\) (\(2H\) \(C\) polytype) is not measurable under the backscattering along the \(c\) direction of light propagation, as well as the \(E'\) mode for 1TL of the same polytype (see the Raman tensors in Sec. II F). In films with \(N \geq 2\), the \(E'\) mode develops into \(E_{2g}\) symmetry, for \(N\)-even TLs, and into \(E'\) modes for \(N\)-odd layers, which are both detectable under \(\Sigma \xi(x \pm z)\) and \(\Sigma \xi(x)\xi(z)\) polarizations (these different behaviors are not related to substrate effects, since these modes are also detected in suspended samples) [24]. The mode at 260 cm\(^{-1}\) in bulk WSe\(_2\) was previously attributed to the Raman-active out-of-plane \(A_{1g}\) mode, but polarization measurements have shown that even for \(\Sigma \xi(x)\xi(z)\) configuration this mode is observed, in contrast with the group theoretical prediction and the previous symmetry assignment. This mode was consequently attributed to second-order Raman scattering [24]. Similar results were observed for MoTe\(_2\) [25] and are expected for other TMDCs. The extended group theory analysis described here should be used to guide researchers in making correct mode assignments using the tables and discussion given in the present work.

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