Structure, friction, and Raman spectroscopy of Re-doped bulk MoS$_2$ from first principles

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Abstract

Doping MoS$_2$ with Re is known to alter the electronic, structural, and tribological properties. Re-doped MoS$_2$ has been mainly studied in monolayer or few-layer form, but can also be relevant for applications in many-layer or bulk form. In this work, we use density functional theory to explore the phase stability, Raman spectra, and atomic force microscopy (AFM) sliding interactions of bulk Re-doped MoS$_2$. We consider the possibility of the Re dopant existing at different locations and provide experimentally distinguishable characteristics of the most likely sites—Mo-substitution and tetrahedral (t-) intercalation. We demonstrate and benchmark an approach to calculate Raman spectra of doped materials with metallic densities of states by using atomic Raman tensors from the pristine material. Applying this method to the metallic Re-doped structures, we find consistent shifts in the Raman-active peaks depending on Re dopant position: redshifts in both $A_{1g}$ and $E_{2g}^1$ peaks in the t-intercalated case versus a redshift for $A_{1g}$ and blueshift for $E_{2g}^1$ peaks in the Mo-substituted case. AFM friction forces, if the MoS$_2$ surface remains flat and unpuckered, are increased by Re dopants, similar for Mo-substitution and t-intercalation, and would decrease with the number of layers.

I. INTRODUCTION

MoS$_2$ is a versatile semiconductor having an anisotropic, two-dimensional structure, with interesting electronic,[1] optical, tribological,[2, 3] catalytic,[4] and spintronic properties.[5] Doping has been used as a strategy to tune these properties for applications of interest. Re is one of the most studied MoS$_2$ dopants[6, 7] which can be incorporated by various synthesis methods[7–11] and occurs as a natural impurity in MoS$_2$.

Most of the recent interest in Re-doped MoS$_2$ system has been in single- or few-layer structures.[7, 12–14] The bulk can also be interesting in sharing some of the opto-electronic properties and is the limit of trends in increasing layers. It is also important in macroscale applications such as solid lubrication.[2, 15] In this work, we study both bulk and few-layer systems of Re-doped MoS$_2$ with particular focus on implications for friction and atomic force microscopy (AFM).

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MoS$_2$ is an effective solid lubricant owing to the ease of shearing along the basal planes.\cite{2} Doping MoS$_2$ can result in altered material growth\cite{16} and enhanced tribological properties\cite{17}. Frictional forces on MoS$_2$, like other 2D materials, have been measured by AFM, and generally friction decreases with more layers.\cite{18} Surprising opposite trends in friction have been measured for Re-doped MoS$_2$ however.\cite{15}

The consensus in the literature is that Re in monolayer MoS$_2$ substitutes for Mo, based on annular dark-field imaging,\cite{9, 10} scanning atomic tomography,\cite{13} formation energy calculations,\cite{6} and a general chemical similarity between Mo and Re. In bulk, neighboring layers allow for the possibility of intercalation, and so the favored site is unclear and has not been established by experiments, which are not necessarily able to distinguish between the sites in a multi-layer structures. In particular, there is some experimental evidence of intercalation,\cite{15, 19} as well as DFT studies indicating the stability of other transition metals in tetrahedral intercalation,\cite{20, 21} making this and other possibilities worth investigating.

Raman spectroscopy is a key characterization method for 2D materials, and can be used to probe differences in microstructure—particularly local bonding configurations.\cite{20} Doping MoS$_2$ with Re (as with other dopants) can shift the pristine Raman-active $E_{2g}^{1}$ and $A_{1g}$ peaks. The experimental literature has found different magnitudes and directions of these shifts in Re-doped MoS$_2$,\cite{9, 14} and the interpretation in terms of Re sites has been unclear and not investigated in detail. Calculation of Raman spectra in such systems poses a problem, because of new states at the Fermi level compared to the pristine system, resulting in a metallic density of states which cannot be handled by the typical DFT methods in a static approximation.\cite{22} used in density-functional theory, despite it being physically observable. To overcome this, we develop an method to approximate the Raman tensor and thus obtain a Raman spectrum.

In this work, we investigate the structure and bonding of bulk Re-doped MoS$_2$, showing the phase stability that leads us to two structures of interest—the t-intercalated and Mo-substituted sites. We calculate sliding friction forces for a model atomic force microscopy (AFM) tip model and study the effects of the dopant site and number of layers. Our Raman calculations find clear differences between intercalated and Mo-substituted Re-doped MoS$_2$, with redshifts of both peaks in the intercalated case and a blue- and red-shift of the $E_{2g}^{1}$ and $A_{1g}$ respectively in the Mo-substituted case. To accomplish these Raman computations, we propose a method to estimate the Raman tensor for a metallic doped system, and benchmark
its accuracy. The paper is organized as follows. In Section II, we describe our computational approach. In Section III we show the stable structures found for Re-doped MoS$_2$ and their structural features. In Section IV, we compute the phase stability of the different structures. In Section V, we show results of AFM friction simulations. In section VI, we compute the Raman spectra using atomic Raman tensors derived from the pristine structure, and determine experimentally identifiable features. Finally we conclude with future prospects in Section VII.

II. METHODS

We use plane-wave density functional theory (DFT) and density functional perturbation theory\cite{23} (DFPT) implemented in Quantum ESPRESSO\cite{24, 25} version 6.6. Calculations were performed using either the Perdew-Burke-Ernzerhof\cite{26} (PBE) generalized gradient approximation with the Grimme-D2 (GD2)\cite{27} van der Waals correction, or the Perdew-Wang\cite{28} local density approximation (LDA). We use ONCV pseudopotentials\cite{29} parametrized by PseudoDojo\cite{30}.

60 Ry was used as the kinetic energy cutoff for PBE while 80 Ry was used for LDA—a higher cutoff was required for more accurate phonon modes in DFPT but not required for reasonable structural optimization. PBE+GD2 yields better structural results than PBE without van der Waals and better elastic parameters than LDA.\cite{31} Unlike PBE, LDA is compatible with Quantum ESPRESSO’s implementation of Raman intensities, so LDA was used for vibrational spectra (including initial structure optimization) while PBE+GD2 was used otherwise. A 0.001 Ry Gaussian smearing was applied to the electronic occupations to be able to handle metallic structures. Electronic energy, force, and pressure thresholds of $10^{-6}$ Ry, $10^{-4}$ Ry/Bohr, and 0.005 GPa were used respectively.

Spin-polarized calculations were used for relaxations since Re doping introduces an odd number of electrons and so there is the possibility of magnetization. Magnetization has been observed\cite{32} in 1T Re-doped MoS$_2$ and computed in monolayers.\cite{12} Using spin-polarized calculations in the AFM simulations yields irregular force results due to sporadic changing between different states with small magnetizations (from 0 to 0.04 $\mu_B$ per cell). Energy differences between spin-polarized and spin-unpolarized state are roughly $10^{-5}$ eV per atom (Table I) and so we conclude that magnetism is not significant in this system. Moreover,
TABLE I: Computed magnetization (in $\mu_B$ per cell) of structures in $\mu_B$/cell for PBE+GD2 doped structures. Energy differences (in eV per Re atom) between the spin-polarized and spin-unpolarized computations are shown as well.

| s.c. | Mo subst. | S subst. | o-intercal. | t-intercal. | Re-Mo interst. |
|------|-----------|----------|-------------|-------------|----------------|
|      | $\mu$    | $\Delta E$ | $\mu$    | $\Delta E$ | $\mu$    | $\Delta E$ | $\mu$    | $\Delta E$ | $\mu$    | $\Delta E$ |
| $2 \times 2 \times 1$ | 0.00 | 0 | 0.67 | 0.0055 | 0.00 | 0 | 0.33 | 0.0044 |
| $2 \times 2 \times 2$ | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 |
| $3 \times 3 \times 1$ | 0.33 | 0.0031 | 3.00 | 0.0842 | 1.00 | 0.0041 | 0.00 | 0 | 1.00 | 0.0459 |
| $4 \times 4 \times 1$ | 0.00 | 0 | 3.00 | 0.1160 | 0.00 | 0 | 1.00 | 0.0180 | 1.00 | 0.0180 |

our treatment of Re-doped MoS$_2$ as a periodic supercell for computational tractability likely overestimates the magnetic effects compared to the probable disordered Re distributions in a real sample. Because of this, we included magnetization when it was feasible (relaxations and total energy for phase diagrams) but used spin-unpolarized calculations for studies which are sensitive to small energy differences (AFM forces, elasticity, and Raman spectra). Adding dipole corrections to similar MoS$_2$ systems has been shown not to be necessary, so they are not included.\[33\]

Formation energy comparisons can be used to eliminate unreasonable structures and compute the required chemical potential required to obtain non-equilibrium structures. We focused on three structures: undoped 2H-MoS$_2$, Mo-substituted, and tetrahedral-intercalation (t-intercalated). All structures retained a 2H structure and we found no evidence of shifting to, for example, the 1T phase as has been obtained experimentally\[32, 34\] There is one exception – the t-intercalated $3 \times 3 \times 1$ (with PBE+GD2) relaxed to a structure\[35\] with the Mo atoms aligned above one another, in which the atom now has octahedral bonds. This corresponds to a stacking aBa cBc using the convention in Song et al.\[36\], similar to the “Min 2” structure in Levita et al.\[37\]). This structure is lower in energy than the typical stacking by 0.02 eV per atom. Mo-substituted monolayers have been found in DFT\[6\] but the tetrahedral case could be interesting as it has previously been experimentally found\[19\].
FIG. 1: Re-doped MoS$_2$ structures found to be stable or metastable.

by energy dispersive x-ray analysis on chemical vapor transport generated samples (albeit the authors posit that the 3R phase is generated and not 2H) and may be responsible for an inverted layer-dependence of AFM friction observed in experiment.[15]

We model Re-doped MoS$_2$ with periodic supercells, using increasing supercell sizes to test the dependence on Re concentration and approach the low-doping limit. Calculations used $2 \times 2 \times 1$, $2 \times 2 \times 2$, $3 \times 3 \times 1$, and $4 \times 4 \times 1$ supercells with respective Monkhorst-Pack $k$-grids of $3 \times 3 \times 2$, $3 \times 3 \times 1$, $3 \times 3 \times 2$, and $2 \times 2 \times 2$. These supercells correspond to concentrations of 4.17 at-%, 2.08 at-%, 1.85 at-%, and 1.04 at-%. We tested the out-of-plane dependence of some properties using a $2 \times 2 \times 2$ supercell.

III. STRUCTURE AND BONDING

We consider as possible Re dopant sites: Mo substitution, S substitution, t-intercalation, o-intercalation, Mo-Re split interstitial (similar to the Mo-Mo split interstitial from Komsa and Krasheninnikov [38]), bridge-site intercalation, and hollow-site intercalation. The bridge and hollow sites are unstable and relaxed to o-intercalation. These structures are commonly considered in computational studies of MoS$_2$ systems.[21, 38] The relaxed structures are pictured in Fig. [1]
FIG. 2: Electronic densities of MoS$_2$: a) pristine, b) Mo-substituted, c) t-intercalated, d) o-intercalated, e) S-substituted, and f) split-interstitial, in cross-sections of the 2×2 supercell in an Mo-S plane close to the dopant. Intercalated and S-substituted show strong out-of-layer bonding. All structures besides S-substitution show densities in the Re-S bonding region to be as strong as Mo-S bonds.

The pristine structure has $a = b = 3.190$ Å, $c = 12.420$ Å, $\alpha = \beta = 90^\circ$ and $\gamma = 120^\circ$. For most of the computed structures, the lattice parameters match the pristine to within 0.5%. There is a 1-2% increase in $c$ in t-intercalation, consistent with a previous calculation [14] and similar to results for Ni [33] but considerably less than the increase in layer spacing for Li [39]; the anomalous 3×3×1 structure [35] shows a lesser increase in $c$. The split interstitial shows a 0.5-2.5% increase in $a$ and $b$. The 2×2×1 S-substituted structure shows a significant 6.2% drop in $c$ due to the S-substituted Re forming an interlayer bond—this structure is better described as a S vacancy structure with a Mo-atop Re dopant. This is visible in the charge densities in Fig. 2. 3×3×1 and 4×4×1 show a 2% and 1% lower value in $c$ respectively. Angles are within 0.05% of the pristine with few exceptions. The t-intercalated $\alpha$ and $\beta$ are 0.4%, 0.2%, and 8.2% larger (smaller) than the pristine $\alpha$ ($\beta$) for 2×2×1, 2×2×2, and
3×3×1 respectively.

In the Mo-substituted case, there is a local symmetry-breaking around the Re atom, leading to Re-S bonds in two groups measuring about 2.38 Å and 2.41 Å respectively at a 3×3×1 supercell. O-intercalation’s 6 bonds, due to the symmetry of the site, occur in two or three groups with differences of around 0.005 Å in bond length. Re in the 2×2×1 and 2×2×2 S-substituted structures binds to the opposite layer than its starting point, as in Fig. [1].

Re is able to form interlayer covalent bonds as shown in the electronic densities in Fig. 2. This happens in o- and t-intercalation (like Ni [20]), and S substitution. While Mo-substitution is nearly indistinguishable from pristine, there is a slight increase in the density in the S-bonding region in both layers of the Mo-substitution. Re’s presence in other cases reduces the charge density in the region between two S atoms in the same layer.

IV. THERMODYNAMIC STABILITY

Using the same method as we have previously used in Ni,[20] we compute the phase diagram, marking the most stable structure at a given chemical potential. The relative stability of structures with different stoichiometries can be analyzed using the formation energy:[20]

\[ E_{\text{formation}} = E_{\text{mixed}} - \sum_i N_i E_{i,\text{bulk}} - \sum_i N_i \mu_i \]  

(1)

The energies are referenced against stable bulk elemental phases of Mo, S, and Re similar to what we have previously done for Ni.[20]

These computations require the energies and composition of different phases of Re, Mo, and S compounds. We used the set of stable and metastable structures we found: Mo substitution, S substitution, t-intercalation, o-intercalation, and the Mo-Re split interstitial. O-intercalation, t-intercalation, and Mo-Re split interstitial have the same chemical composition and thus their energies are directly comparable. Of these, t-intercalated consistently has a lower energy by 0.01-0.02 eV/atom. There is one exception: the 4×4×1 split-interstitial is energetically favorable over either intercalated structure by 0.001 eV/atom.

At 0 K, we predict only the Mo-substitution to be stable, but other phases are accessible at higher temperatures and out-of-equilibrium processes. Phase stability above \( T = 0 \) K is difficult to compute directly, but can be estimated in the harmonic approximation by
calculating the lattice vibrations’ contributions to the free energy.\[38\] \( F = E - TS \) and the entropy \( S(T) = k_B \sum_{\lambda} n_B(\hbar \omega_\lambda, T) \ln(n_B(\hbar \omega_\lambda, T)) \) where the Bose-Einstein populations \( n_B \) of phonon mode frequencies \( \omega_\lambda \) contribute to \( S \). The lowest-frequency modes contribute most to this term, namely the shearing \( E_{2g}^2 \) (35.2 cm\(^{-1}\) in pristine) and layer-breathing \( B_{2g}^2 \) (55.7 cm\(^{-1}\) in pristine) modes. Compared to Mo substitution, t-intercalation has a 6-10 cm\(^{-1}\) lower frequency in the \( E_{2g}^2 \)-like mode but a 5-20 cm\(^{-1}\) higher frequency \((i.e.\) stronger interactions) in the \( B_{2g}^2 \)-like mode. Through most of the Brillouin Zone, the \( E_{2g}^2 \)-like modes is the lowest in frequency, and will be significantly populated at room temperature. Therefore this mode can contribute considerably to the free energy. This lower t-intercalation mode suggests that as temperature rises, t-intercalation can become more favorable vs. Mo substitution, and could therefore become accessible at high temperatures even within the pristine stability triangle in Fig. 3.

The \( T=0 \) K phase diagram (Fig. 3) shows that the Mo-substituted structure is the most stable, consistent with experimental observation of monolayers.\[10\] Mo-substitution is comparable to bulk, but the monolayer adatom and bulk intercalation are not,\[33\] so observation of t-intercalation is still possible out-of-equilibrium or at higher temperatures.\[15\]

V. AFM SLIDING

We model t-intercalated, Mo-substituted, or undoped layers beneath an AFM probe tip. The tip cluster shown in Fig. 4 consists of a geometry used previously in the literature to simulate an AFM tip generated by cleaving 10 atoms perpendicular to the (111) corner of the Si unit cell then passivating all dangling bonds with H except for the tip Si atom.\[40\] The top Si layer of 6 atoms was frozen to crystalline positions, but other Si and H atoms were allowed to relax. This structure was placed 5 Å above the topmost Mo layer of Re-doped MoS\(_2\) (about 3.5 Å above the S plane). We studied the variation in energy for different distances of the tip from the MoS\(_2\) surface (Fig. 5) and chose a working distance for force calculations which was close enough to measure friction forces above numerical noise but far enough that the Si tip and MoS\(_2\) are not bonding. We used the atomic coordinates of a 4 × 4 bulk supercell with variable layers (and did not relax at the beginning, or during sliding). This lateral size of the structure provides sufficient vacuum for the AFM probe to be sufficiently separated from its periodic images in-plane. A vacuum of 12.4 Å between the
FIG. 3: The $T = 0$ K phase diagram for Re-doped MoS$_2$ in a $4 \times 4$ supercell. Only the Mo-substituted Re-doped MoS$_2$ falls within the reasonable stability region below $\mu_i = 0$ and above the pristine MoS$_2$ instability line. The black triangle is the stability region for MoS$_2$ (as in [20]). The labeled dots show the location of the intersection point for other supercell sizes. The pristine MoS$_2$ line meets the axes at $\mu_S = -1.308$ eV and $\mu_{Mo} = -2.615$ eV. Structures considered include Mo-substituted, S-substituted, tetrahedral intercalation, octahedral intercalation, and Mo-Re split interstitial.

top Si layer and the S layer was used, as shown in Fig. [4]. We varied the number of layers from 1 to 5 and varied the dopant site within each of those structures.

The small energy differences throughout sliding mean we need well-converged computational parameters. The distance between the top of the probe and the bottom of the periodic image of the lowest sulfur atom was set to be 12.4 Å. Increasing this vacuum by 5 Å led to changes in energy differences below $10^{-4}$ eV—meaning our vacuum distance is sufficient to remove spurious interactions between periodic images in the $z$ direction. Using a $3 \times 3 \times 1$ $k$-grid yields nearly identical energy curves (like Fig. [7]) to $2 \times 2 \times 1$, with differences $\lesssim 10^{-4}$ eV. Increasing $k_z$ to 2 yields even smaller changes to the energy curve as expected given the
FIG. 4: Example structure for AFM sliding: model H-passivated Si tip apex above 2-layer (2L) Mo-substituted MoS$_2$.

FIG. 5: Energy dependence of the distance between the AFM probe and the surface of 3-layer t-intercalated MoS$_2$. The distance is measured between the Mo atom and the tip Si atom of the probe. Beyond 7 Å, the sliding dependence of the energy is lost to noise. Below 4 Å the interactions are strong and the tip bonds to the surface. Therefore 5 Å was used for our friction simulations.

The probe was placed above an Mo atom two rows away from the Mo-substitution site, as far as possible laterally. This is the best option as we do not expect a single-atom tip to be perfectly aligned with the dopant in experiment. Placing the tip directly above the Re
site leads to larger variations in the forces while sliding as shown in Fig. 6. The probe was displaced in the \(x\)-direction in steps of \(1/40\)th the cell’s width \((\Delta x = 0.319 \text{ Å})\) until the probe had moved by exactly one lattice vector. At each step, we calculated the DFT total energy. By differentiating with respect to the displacement, we compute the force along the path, \(F_x = -\frac{\partial E}{\partial x} \approx -\frac{\Delta E}{\Delta x}\), which corresponds to friction forces. It is worth noting that the AFM structure does not have \(xz\)-mirror symmetry although \(\text{MoS}_2\) does (see Fig. 4), and thus the sliding forces in Fig. 6 do not have that symmetry. The Hellmann-Feynman forces are computed by ESPRESSO, but we found the forces incorrectly did not obey periodicity, i.e. \(\int_{\text{cell}} F_x dx \sim 10^{-4}\text{Ry/Bohr} \neq 0\) incorrectly. This imbalance can be improved by increasing the plane-wave cutoff, but we found that the effect was simply a constant shift [35], and that the high-cutoff Hellman-Feynman forces agreed with lower-cutoff numerical derivatives forces (which correctly integrated to zero). Therefore we used the latter approach for lower computational expense.

The forces from each displacement are then collapsed into a distribution as shown in Fig. 7 based on how frequently the AFM experienced a given force throughout sliding. If \(n_i\) is the distribution of the forces while sliding an \(i\)-layer system, then the cumulative distribution is \(n_{\text{cumul}, i} = \frac{1}{N} \sum_{j \leq i} n_j\). We use distributions rather than raw sliding forces since our single-atom tip is more fine than an experimental tip. In theory, we would have to compute an \(N\)-layer (\(NL\)) system with the dopant in different locations, rather than just using fewer layers, but we found that adding undoped layers away from the dopant and AFM do not alter the energies. The distribution is accumulated with smaller-layered distributions to average them and generate Fig. 8. We are assuming the dopant may be in any layer with equal probability, in the absence of clear evidence of the true distribution. There may be preferential locations however: placing the atom in different layers does lead to some changes in the energy, as we estimate by comparing energies for unrelaxed doped systems (i.e. the structure is that of pristine, with substitution or intercalation). In a 3-layer system, Mo substitution in the middle layer vs. surface is favored by 0.31 eV, while t-intercalation favors being bonded to a surface layer by about 0.15 eV in a 4-layer system.

The force distributions for doped systems with many layers would be expected to converge to the pristine distribution as the Re atom’s influence wanes with increasing distance from the AFM tip. However, we find convergence to a different distribution than pristine (Fig. 8). We tried to test whether this might be due to localization at the surface of electronic charge
FIG. 6: The sliding force calculated at different in-plane distances from the Re atom. A, C, and E are computed for a 3-layer Mo-substituted structure while B and D are computed for a 2-layer Mo-substituted MoS$_2$. In A, the tip passes directly above the Re atom, thus the forces are larger. For choices besides A, the range of forces is similar. We use E, the furthest starting point in our supercell, as most representative of an AFM experiment for a sample with low doping concentration. The positive and negative $x$ sliding directions are different due to the probe’s asymmetric shape as seen in Fig. 4.

FIG. 7: An example path to create a distribution of the t-intercalated 5L structure, where Re is between the bottom two layers. The energy curve is numerically differentiated to find forces, then those forces are compressed to a distribution. Assuming equal probability for the dopant to be between any of the layers in a real sample, we average the 5L distribution with the 4L, 3L, and 2L, where in each case the Re is between the bottom two layers.
donated from Re to MoS$_2$, which would not vary with number of layers. We tested this with calculations of undoped slabs with extra charge from -0.25e to -1.0e—in all cases, the extra charge is localized on the AFM. This is presumably not a physical effect and relates to the crude model of the AFM tip as well as perhaps difficulties with charge transfer in PBE and LDA,[41] but it makes it not meaningful to calculate AFM forces for such a system. A slab without the AFM tip does not show localization of charge to the surface, but we do find a polarization induced by the presence of Re which would have a long-ranged influence and may account for the differences from pristine. It is not clear whether this is a physical effect however.

We found that when placing the Re atom beyond 2 layers from the AFM, layer-dependence is small. The range of the forces for doped MoS$_2$ is much larger than pristine MoS$_2$. The undoped forces change negligibly between 2 and 3 layers. We also found that adding layers beyond the Re atom did not affect the force distribution, i.e. the 3- and 4-layer systems with Re in the third layer both result in the same force distribution. The weak layer-dependence and reduction in force with number of layers, assuming rigid flat sheets, is incompatible with AFM experiments [15], indicating that an increase in friction is due to changes in puckering.
VI. RAMAN SPECTRA

The standard approach to Raman spectra in DFPT \[22\] calculates atomic Raman tensors via electric-field and atomic displacement perturbations, and then combines these with phonon eigenvectors to obtain the Raman intensities of phonon modes. The formalism is based on the Placzek approximation and a static approximation for the dielectric constant \( \epsilon^\infty \), which is typically valid for sub-gap (non-resonant) incident light.

\[
I_{i,s}^{\nu} \propto |\hat{e}_i \cdot A^{\nu} \cdot \hat{e}_s|^2 \frac{1}{\omega_{\nu}} (n_B (\hbar \omega_{\nu}, T) + 1)
\]  

(2)

where \( I_{i,s} \) is the intensity for incident direction \( i \) and scattered direction \( s \), \( \nu \) is a mode index, \( A^{\nu} \) is the mode Raman tensor, and \( \omega_{\nu} \) is the phonon frequency. The mode Raman tensor is calculated in terms of atomic Raman tensors \( A^{k_{\gamma}}_{lm} \).

\[
A^{\nu}_{lm} = \sum_{k_{\gamma}} A^{k_{\gamma}}_{lm} \frac{w^{\nu}_{k_{\gamma}}}{\sqrt{M_{\gamma}}}
\]

(3)

\[
A^{k_{\gamma}}_{lm} = \frac{\partial^3 U^{el}}{\partial E_l \partial E_m \partial u_{k_{\gamma}}} = \frac{\Omega}{4\pi} \frac{\partial \epsilon_{lm}^{\infty}}{\partial u_{k_{\gamma}}}
\]

(4)

where \( w^{\nu} \) is the displacement pattern of mode \( \nu \); \( k, l, \) and \( m \) are Cartesian directions, \( \gamma \) is an atom index, \( M_{\gamma} \) is the atomic mass, \( \Omega \) is the unit cell volume, \( U^{el} \) is the electronic energy, \( u \) is an atomic displacement, and \( E \) is the electric field. Clearly this approach is only meaningful when a finite \( \epsilon_{\infty} \) can be defined. In this approach, metallic systems, i.e. those without a bandgap, cannot be calculated because of the divergence of the dielectric constant in this case. Practically speaking, any system treated with smearing in ESPRESSO falls in this category.

A true metallic system does not have observable Raman intensity because light will be reflected rather than undergoing Raman scattering, due to a large \( \epsilon_{\infty} \) at the incident frequency. This is typically not the case for a doped system, in particular for low doping concentration. The metallic nature in a small supercell may be due to spurious formation of impurity bands. Moreover, \( n \)-type doping as for Re-doped MoS\(_2\) (see density of states in [35]) in a low-doping limit is expected to leave the bandgap intact and simply move the Fermi level into the conduction bands. In this case, the dielectric constant remains finite at the optical frequencies of incident light for Raman experiments. Indeed this is exactly the situation sought for transparent conductors,\[42\] We also note that many works have reported Raman scattering measurements from Re-doped MoS\(_2\),\[14, 15\] so clearly there must be a way.
to obtain these Raman tensors theoretically. Rather than use prohibitively large supercells and/or perform resonant Raman calculations (e.g. using time-dependent DFT or the Bethe-Salpeter equation), we develop an alternate approach based on the approximation that the atomic Raman tensors are similar to those of pristine MoS$_2$ and/or a similar reference system which has a well-defined gap and can be calculated in the usual way. We use directly calculated phonon displacement patterns and simply substitute those from the reference system in Eq. 3. In practice, this is done by inserting the reference atomic Raman tensors to the files ESPRESSO uses to compute the Raman intensities.

A somewhat related, but more limited approach, has been taken in recent work, in which the Raman intensities from a reference system are used to calculate Raman spectra of a doped system, to avoid the need for explicit calculations on the doped system. The intensities are weighted by the projection of the doped modes onto the pristine modes. The intensity mapping method allows for using classical phonon computations, but we require flexibility in the Raman tensor only and thus can use the more accurate DFPT phonon modes. Moreover, working with only the scalar intensities means losing a significant amount of information about the Raman response; in particular, interference effects are neglected, which can be significant. We will see that this makes small improvements near the pristine Raman-active peaks of Ni-doped MoS$_2$ (around 380 cm$^{-1}$ in Fig. 9). Both methods are less able to predict some modes which are highly local to the Ni (435 cm$^{-1}$ and 470 cm$^{-1}$), but are better at modes which contain both local components and pristine-like vibrations (452 cm$^{-1}$ and 502 cm$^{-1}$).

We tested this method on our previously computed 3 × 3 supercell, t-intercalated, Ni-doped MoS$_2$ which does not require smearing (and thus the Raman tensor is calculable). The relative peak heights are 15% below the full computation as shown in Fig. 9, and the peak height ordering is preserved. We further found that by comparing structures with different Raman tensors against the pristine computation, we can identify which peaks in the spectra are due to geometry changes rather than new Ni-bond related activity. In this case Ni introduces shifts to the active peaks and new peaks related to new modes local to the Ni and activations of existing MoS$_2$ modes that were previously forbidden by symmetry.

In Fig. 10 we test different approximation schemes for the Ni component of the atomic Raman tensor. The intensities in which the Ni and its nearest neighbors’ (NN) contributions were set to zero is the most reductive approximation and is thus furthest from accurate—this
FIG. 9: Raman spectra (in A⁴/amu per MoS₂ unit) of t-intercalated Ni-doped MoS₂ by different methods. The full tensor computation is computed using the Lazzeri method[22]—this is not possible with Re-doped MoS₂. The direct tensor substitution is a slight improvement when compared to intensity mapping[43, 44] method.

is clearest in the muted shoulder of the \(E_{1g}\) peak. It is still useful, however, in interpreting the nature of modes such as the 505 cm⁻¹ peak. The lack of intensity in the NN line means that activity of this peak is highly localized to the Ni atom. The approximation works well near the pristine-active peaks, but fails whenever the activity is semi-local to the Ni atom. Since altering just the Ni’s contribution does not change the pristine-active region much, this method can predict the Re-doped structures’ spectra with little loss in accuracy in this frequency regime.

For the Re-doped case, this approximation is reasonable to consider primarily because the doped bonding network highly resembles the pristine structure. Secondly, we have overwritten the Re contribution to the atomic tensor as Ni in the \(3 \times 3 \times 1\) tetrahedral case. Ni is a transition-metal dopant similar to Re whose contribution we were able to compute directly in the tetrahedral orientation. Given the successful re-creation of the intensities near the pristine-active peaks in Ni-doped MoS₂, we can be confident that the Re-doped peak shifts are similarly accurate.

We find a consistent trend among the Mo-substituted and t-intercalated Re-doped Raman spectra we computed: there is a redshift of both peaks in the t-intercalated case and
FIG. 10: Comparison of the Ni-doped spectra for different approximations of the Ni component of the atomic Raman tensor across three ranges in $A^4$/amu per MoS$_2$ unit (note the different scale for the three plots). The Mo and S atoms use the same elements as the pristine. For the red line, the Ni and its nearest neighbor (NN) S atoms’ contributions to the Raman tensor have been set to 0. For the rest, the Ni atom’s contribution only has been set to 0 (yellow), the same as Mo in pristine (green), and the same as the full computation (blue). The pristine-active modes (b) show the least amount of change, except on the shoulder of the $E_{2g}^1$ peak. At high modes (c) the 435 cm$^{-1}$ and 470 cm$^{-1}$ peaks are highly localized to the Ni and are not computed well. At 505 cm$^{-1}$, the peak is entirely localized near the Ni and its NN, as evidenced by the lack of intensity when those elements are removed from the tensor.

Blue- ($E_{2g}^1$) and red- ($A_{1g}$) shifts in the Mo-substituted case. The t-intercalated behavior is qualitatively consistent with experiments\cite{7, 8, 32, 45}, but inconsistent with others\cite{9, 14}, which is presumably due to different synthesis methods and conditions, and therefore different doping sites (or distributions of sites) in their samples. It is worth noting that Z-contrast imaging\cite{10} is often used to locate the Re dopant, but the basal position of the t-intercalated dopant is the same as the Mo or S site.
FIG. 11: Raman spectra (in A^4/amu per MoS_2 unit) of t-intercalated and Mo-substituted Re-doped MoS_2 as computed by DFPT with substitution of the Raman tensor by those in a pristine computation (Mo and Ni replace the Re atom’s contribution in the Mo-substituted and t-intercalated respectively). The direction of the peak shifts are preserved among the supercell sizes used: redshifts in both peaks when t-intercalated and blue- and redshifts in the \( E_{2g}^1 \) and \( A_{1g} \) peaks respectively while Mo-substituted. Gaussian broadening of 2 cm\(^{-1}\) was used.

The intensity mapping method\[44\] is useful when the phonon modes of doped systems are impossible or impractical to compute directly using expensive methods. Our Raman tensor approximation method is versatile when distinguishing changes in the intensities as being caused by lattice distortions or changes in the charge configurations. The Raman tensor can be replaced with tensors computed at more computationally intensive levels. By replacing specific atomic components (e.g. those of the dopant and its nearest neighbor) we are able to analyze the effect of different atoms in the Raman scattering intensity. For materials with difficult-to-compute phonon modes, such as amorphous materials, the phonon modes may be computed by classical methods while the tensor could use the higher accuracy methods due to lower computational time cost\[22\]. In both methods, the majority of the accuracy rests on using reasonably accurate phonon modes.\[43\]

VII. ELASTICITY

The elastic components were computed using the stress-strain relationship, \( \sigma_i = C_{ij}\epsilon_j \), identically to how we have done previously for Ni-doped MoS_2.\[20\] Strains of -0.002 to 0.002
TABLE II: Relative shifts in the frequency for the computed bulk t-intercalated and Mo-substituted structures with respect to undoped MoS$_2$. T-intercalation results in redshifts of both pristine-active peaks. Mo-substituted results in redshift of the $A_{1g}$ peak, but blueshift in $E_{2g}^1$.

| Dopant Site | Supercell | $A_{1g}$ shift (cm$^{-1}$) | $E_{2g}^1$ (cm$^{-1}$) |
|-------------|-----------|-----------------------------|------------------------|
| t-intercal. | 2 × 2 × 1 | -7.4                        | -2.0                   |
| t-intercal. | 2 × 2 × 2 | -1.3                        | -1.0                   |
| t-intercal. | 3 × 3 × 1 | -5.9                        | -3.2                   |
| Mo-subst.   | 2 × 2 × 1 | -2.8                        | +6.8                   |
| Mo-subst.   | 2 × 2 × 2 | -1.1                        | +0.7, +4.5             |
| Mo-subst.   | 3 × 3 × 1 | -3.1                        | -5.3, -0.34, +9.1      |

in steps of 0.001 were computed in the 3- (z-uniaxial) and 5-directions (xz – shear) using the GD2+PBE computed Mo-substituted, t-intercalated, and undoped structures. These strain directions are important to sliding for two reasons: cell shearing results directly in layer sliding[46] and out-of-plane uniaxial strain is important in deciding the strength of puckering.[15]

The intercalated elastic parameters deviate away from the pristine further than Mo-substitution due to the added bonds in intercalation. A drop in $C_{55}$ for t-intercalation may be related to enhanced sliding since reaching plastic deformation by shearing can be easier. Aside from interlayer sliding, $C_{55}$ also can be related to AFM-type friction.[46] An increase in $C_{33}$ can be related to a weakening of the puckering effect and thus contribute to an altered layer-dependence of friction.[15]
FIG. 12: The $C_{33}$ and $C_{55}$ elastic components are both involved in sliding events through puckering and layer shearing. T-intercalated and Mo-substituted structures for 4×4×1, 3×3×1, 2×2×2, and 2×2×1 supercell sizes are computed.

VIII. CONCLUSION

We have studied the properties of bulk and few-layer Re-doped MoS$_2$ in both t-intercalated and Mo-substituted configurations. We modeled AFM sliding and found a lack of layer dependence beyond two layers, when the sheets are constrained to be flat. Since the relationship does not match the experimentally observed inverse-frictional dependence, the explanation for that phenomenon seems to be related to puckering. Our Raman computations demonstrate an approach to calculate metallic doped systems accurately using atomic Raman tensors from a reference system. We find the t-intercalated Raman spectra shifts in the plots in ways that are consistent with some of the experimental literature (though
they disagree among themselves due to varying sample generation methods). The doped $E_{2g}^1$ peak is less like the pristine peak than the $A_{1g}$ peak in frequency and shape. The direction of the $E_{2g}^1$ peak shift can be used to give evidence to identify the dopant site in experiment—Mo-substitutions show blueshifts while t-intercalated show redshifts.

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