Critical electronic structures controlling phase transitions induced by lithium ion intercalation in molybdenum disulphide

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We report on first-principles studies of lithium-intercalation-induced structural phase transitions in molybdenum disulphide (MoS_2), a promising material for energy storage in lithium ion batteries. It is demonstrated that the inversion-symmetry-related Mo-S p - d covalence interaction and the anisotropy of d -band hybridization are the critical factors influencing the structural phase transitions upon Li ion intercalation. Li ion intercalation in 2H- MoS_2 leads to two competing effects, i.e. the 2H-to-1T transition due to the weakening of Mo-S p - d interaction and the D_{6h} crystal field, and the charge-density-wave transition due to the Peierls instability in Li-intercalated 2H phase. The stabilization of charge density wave in Li-intercalated MoS_2 originates from the enhanced electron correlation due to nearest-neighbor Mo-Mo d - d covalence interaction, conforming to the extended Hubbard model. The magnitude of charge density wave is affected by Mo-S p - d covalence interaction and the anisotropy of d -band hybridization. In 1T phase of Li-intercalated MoS_2 , the strong anisotropy of d -band hybridization contributes to the strong Fermi surface nesting while the d -band nonbonding with S- p facilitates effective electron injection.

MoS_2 , phase transition, charge density wave, p - d interaction, first-principles

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Molybdenum disulphide (MoS_2) is increasingly important for a variety of applications in electronics [1–3], optics [4–6], hydrogen storage [7], catalysts [8,9], lubricants [10,11], and double-layer capacitors [12]. The quasi-two-dimensional structural characteristic facilitates lithium ion intercalation and extraction, analogous to that in graphite [13,14]. The much higher capacity of MoS_2 (600–1200 mA h/g) than that of graphite/graphene (372–900 mA h/g) makes MoS_2 an excellent candidate for fabricating high-capacity and rechargeable lithium ion batteries (LIBs) [15–26]. Clearly, the electrochemical performance of MoS_2 is closely related to the structural phase transitions induced by Li ion intercalation [14,27]. This leads to the imperative need for understanding the mechanism of intercalation-induced phase transitions in order to realize its full electrochemical potential for energy storage.

It is commonly believed that upon Li ion intercalation

MoS_2 may undergo a 2H-to-1T phase transition, in which the local MoS_6 unit transforms from the original trigonal prism into an octahedron [28–31]. This belief is challenged by a recent *in situ* XRD result which indicates amorphization of MoS_2 host, rather than the formation of 1T phase [32]. On the other hand, the first-principles calculations predict a Fermi-surface-driven charge density wave (CDW) in Li-intercalated 1T- MoS_2 [33], which is featured by a Mo plane distortion with diamond pattern [33–36]. Another type of Mo plane distortion with zigzag-chain pattern is reported for single-layer and restacked MoS_2 [37,38]. We have demonstrated in a recent calculation that the CDW formation in Li-intercalated 1T- MoS_2 coincides with the maximization of chemical hardness of Li-intercalated MoS_2 host [27]. However, ambiguity exists in understanding of the mechanisms of both 2H-to-1T transition and CDW stabilization. Especially the issue concerning whether Li-intercalated 2H- MoS_2 can undergo a CDW transition similar to that in the 1T counterpart have not been addressed.

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All these hamper the understanding of experimentally observed inconsistency and thus further improvements in performance. Additionally, although the electronic structures of 2H- and 1T-MoS₂ and Li-intercalated compounds (e.g. 2H- and 1T-LiMoS₂, and the CDW phase of 1T-LiMoS₂) have been studied intensively [39–44], the critical electronic properties governing relative phase stability (with and without Li ion intercalation) and electron injection have not been revealed, imposing difficulties in uncovering the mechanisms of structural phase transitions.

The target of this theoretical work is twofold, first, to identify the critical electronic states near Fermi surface associated with phase stability and outer electron injection due to Li ion intercalation, and second, to analyze the mechanisms of intercalation-induced phase transitions of MoS₂. It is demonstrated that the inversion-symmetry-related Mo-S *p-d* interaction and the anisotropy of *d*-band hybridization are the critical factors influencing the structural phase transitions. When Li ions are intercalated, 2H-MoS₂ may transit to 1T phase due to the weakening of Mo-S *p-d* interaction and the *D*_{6h} crystal field. It is found that CDW exists not only in Li-intercalated 1T-MoS₂ but also in the corresponding 2H counterpart, with a relatively weak magnitude in the latter due to the inversion-symmetry-related Mo-S *p-d* interaction. The CDW transition in Li-intercalated 2H-MoS₂ may compete with the 2H-to-1T transition, perhaps leading to a structural disorder corresponding to the observed amorphization of MoS₂ host. The stabilization of CDW in Li-intercalated MoS₂ can be ascribed to the enhancement of electron correlation due to nearest-neighbor Mo-Mo *d-d* interaction.

1 Structures and computational details

MoS₂ crystal consists of S-Mo-S tri-layer slabs held together by weak vdW force. Changes in the ion arrangement within an S-Mo-S slab may lead to two typical building blocks, i.e. trigonal prism and octahedron. Three polytypes, i.e. trigonal 1T, hexagonal 2H, or rhombohedral 3R, have been experimentally obtained. The structural models are representatively shown for 1T and 2H phase in Figure 1. In this work, initial unit-cells for these polytypes are constructed from experimental lattice parameters and internal coordinates [45–47].

Structural differences of these three polytypes are summarized in Table 1. Point groups of 1T, 2H, and 3R phases are *D*_{3d}, *D*_{6h}, and *C*_{3v} respectively. Both *D*_{3d} and *D*_{6h} have inversion symmetry, while *C*_{3v} does not. For the *D*_{3d} point group of 1T phase, inversion centers are at Mo sites. For the *D*_{6h} point group of 2H phase, they are at interstitial octahedral sites within vdW gaps, even though the trigonal prismatic MoS₆ unit has no inversion center.

Octahedral and tetrahedral interstitial sites for 1T and 2H phase are shown in Figure 1. These are potential sites for Li

Figure 1 Perspective views of structural models and building blocks for 1T- and 2H-MoS₂. The corresponding unit cells are indicated by the black-line boundaries containing atoms labeled with red symbols. Octahedral and tetrahedral interstitial sites in the vdW gap are represented by red and blue crosses, respectively.

ion intercalation. The number of tetrahedral sites is twice that of octahedral sites. Within a vdW gap, interstitial sites can be separated into three layers, with one octahedral interstitial layer sandwiched by two other tetrahedral interstitial layers. The three interstitial layers displace each other by one third of the diagonal line length in the (001) face.

Total energy calculations are performed within the framework of density functional theory (DFT), as implemented in the Vienna Ab-initio Simulation Package (VASP) [48]. Interactions of electrons with ion cores are represented by the projector augmented wave (PAW) potential [49]. A cutoff energy of 400 eV is used for the plane-wave expansion of wave functions. Integrations over Brillouin zone use Monkhorst-Pack special *k* point mesh of 18×18×4 for the 2H and 3R unit-cells, and 18×18×8 for the 1T unit-cell, and 8×8×8 for the unit cell of the CDW phase of 1T-LiMoS₂ (denoted thereafter as C1T-LiMoS₂) [33] respectively. Structural relaxations are performed with all the forces acting on ions smaller than 0.005 eV/Å. Energy uncertainties due to the selection of cutoff energy and *k* point sampling are smaller than 0.002 eV/ion. For pure MoS₂, the vdW correction in Grimme's DFT-D2 scheme [50] is used for structural determination. This gives overall deviations smaller than 1.1% for *a*, *c*, and thickness *T*, and a deviation smaller than 2% for θ of S-Mo-S from the experimental values, as shown in Table 1. For Li-intercalated systems, we use only PBE for calculations because vdW interactions are expected to be suppressed by Li-host electrostatic interactions. As a comparison, optimized structural parameters for C1T-LiMoS₂ are listed with other available theoretical and experimental values in Table 2. In general, our calculations agree well with the experiment of Mulhern [30]. We also test the effect of vdW correction and find that the prediction of *c* is worsened remarkably relative to the result of pure

Table 1 Structural and energy properties of 2H-, 3R- and 1T-MoS₂ calculated at the GGA-PBE level corrected with van der Waals interactions^{a)}

	2H	3R	1T
Stacking	cBcbCb	cAcBcBaBa	cAb
Point group	D_{6h}	C_{3v}	D_{3d}
c/a	3.887	5.799	1.872
$d_{\text{Mo-S}}$ (Å)	2.416	2.416	2.430
$d_{\text{Mo-Mo}}$ (Å)	3.196	3.198	3.225
$d_{\text{S-S}}$ (Å)	3.119	3.116	3.637
Inter-slab distance (Å)	6.212	6.182	6.036
Volume (Å ³ /f.u.)	54.940	54.755	54.351
E_{tot} (eV/f.u.)	-22.457	-22.457	-21.665
E_1 (eV/f.u.)	-170.733	-169.807	-166.532
E_2 (eV/f.u.)	149.056	148.134	145.685
E_{vdW} (eV/f.u.)	-0.780	-0.784	-0.818

a) $d_{\text{Mo-S}}$ and $d_{\text{Mo-Mo}}$ denote bond lengths of Mo-S and Mo-Mo respectively. $d_{\text{S-S}}$ denotes the inter-ionic distance of two nearest neighboring S ions bonding on different sides of Mo planes. The inter-slab distance indicates the separation between two neighboring Mo planes. In the line of 'stacking', capital letters means the positions of Mo and the lowercase the positions of S.

Table 2 Optimized cell parameters at the PBE level compared to the FLAPW results and the experimental one for C1T-LiMoS₂

	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)
Exp. [28]	6.720	6.720	6.294	90	90	120
Exp. [30]	6.75–6.80	6.75–6.80	6.26	90.0	90.0	121.2
FLAPW [33]	6.70	6.70	6.39	90	90	120
This work	6.85	6.80	6.28	90.13	90.10	121.43

GGA. It is noted that the FPLAPW calculations [33] agree with the experiment of Py et al. [28] only in the prediction of a and b , but not c . Therefore, it is not necessary to include vdW correction for LiMoS₂. In our PBE optimization, the original hexagonal lattice distorts slightly into a triclinic one, resulting in a total energy reduction of ~50 meV/f.u.

2 Results and discussion

2.1 Electronic properties: p - d interaction and d -band hybridization

Band structures of relaxed 2H, 3R, and 1T phases are compared in Figure 2(a). 2H phase has an indirect band gap of 0.93 eV, smaller than the experimental one of 1.29 eV [51], in agreement with previous DFT calculations [46,52]. The valence band maximum (VBM) is at Γ and the conduction band minimum (CBM) lies midway between Γ and K. Similar to 2H phase, 3R has an indirect fundamental band gap of 0.86 eV. However, the VBM is shifted from Γ to A and the CBM is shifted from the midway of Γ -K to H due to the band folding effect induced by the increase of stacking periodicity of S-Mo-S slabs along the c axis. In contrast to 2H and 3R phases, 1T bands present the feature of metal, which

is ascribed to the D_{3d} symmetry of MoS₆ building blocks.

Mo-4d and S-3p constitute the major valence band of MoS₂. Under D_{6h} point group, the five degenerate Mo-4d orbitals split into two doubly-degenerate states e (d_{xz} , d_{yz}) and e' (d_{xy} , $d_{x^2-y^2}$), and one singly degenerate state a (d_z^2), as shown in Figure 3. The latter two hybridize with each other due to the mirror reflection with respect to the x - y plane crossing Mo ions, resulting in the fundamental band gap in the d -band manifold and the energy reduction of the a -subband. The hybridized a -subband (mixing with d_{xy} , $d_{x^2-y^2}$, and d_z^2) can bond covalently with S- p to form a bonding p - d state and an antibonding (p - d)* one, reducing the energy of occupied states. It is different for D_{3d} symmetry in that Mo-4d orbitals split into an e_g state (d_{xz} , d_{yz}) and a t_{2g} state (d_{xy} , $d_{x^2-y^2}$, d_z^2). The bonding of t_{2g} to S- p is forbidden because of the inversion symmetry centered at Mo sites.

The evolution of Mo-S p - d mixing in MoS₂ lattice is presented in Figure 4. The squares of coefficients of each angular momentum wave functions for the highest occupied valence band of 2H- and 1T-MoS₂ are extracted from the first-principles calculations respectively. They are summed up along the K- Γ -M route for S- p and Mo- d , as shown in Figure 4(a) and (c). For 2H phase p and d can mix independent on k . For 1T phase, on the contrary, the mixing is forbidden at Γ but weakly permitted for k points away from Γ . It is obvious that the majorities of p and d are distributed in different parts, i.e. p state is centralized around Γ , but d state away from Γ . This inversion-symmetry-related p - d interaction indicates that covalent bonding is stronger in 2H phase than in 1T phase. In the following, it will be seen that Mo-S p - d interaction imposes significant effect on electron injection due to Li ion intercalation and the magnitude of CDW in Li-intercalated MoS₂.

Figure 4(b) and (d) indicates the effect of k dispersion on the d -state hybridization for the highest occupied valence band of 2H- and 1T-MoS₂, respectively. In 2H phase, the d -state hybridization is formed by d_{xy} , $d_{x^2-y^2}$, and d_z^2 , which are distributed nearly symmetrically at the two sides of Γ except for the boundaries, indicating it is generally isotropic. In 1T phase, in contrast, k dispersion leads to anisotropic hybridization, i.e. the hybridization is changed from the original (d_{xy} , $d_{x^2-y^2}$, d_z^2) to orientation-dependent new combinations. This hybridization anisotropy also exists in lower valence bands, such as band B and C shown in Figure 2(a). It will be shown in the following that the anisotropy of d -state hybridization of edge bands determines the Fermi surface shape, which affects the CDW transition of Li-intercalated MoS₂.

The partial density of states (DOS) in Figure 2(b) show that the formation of band gap in 2H phase correlates indeed first to the strong hybridization between d_z^2 and (d_{xy} , $d_{x^2-y^2}$), and then to the strong Mo-S p - d covalence interaction that lowers the a -subband further. The energy reduction induced by both d -subband hybridization and p - d covalence

Figure 2 (a) Band structures of relaxed 2H-, 3R- and 1T-MoS₂ along the high-symmetry points (connected by red lines) shown in the irreducible Brillouin zone of a hexagonal unit-cell. The Fermi energy is set to be energy zero point, denoted by dotted line. (110)-plane projected partial charge density for the valence band maximum and conduction band minimum of 2H phase are presented together. Charge density value decreases according to the color change from red to green and then to blue. (b) and (c) are the partial density of states of 2H- and 1T-MoS₂, respectively.

Figure 3 Energy-level diagram of molecular orbital model for *p-d* interaction under *D*_{6h} group.

interaction stabilizes the 2H phase at ground state. Since the $4d^2$ electronic configuration of Mo⁴⁺ leads to a full occupation of the lowest *a*-subband, 2H phase is a semiconductor. In the partial charge profiles in Figure 2(a), one can easily identify the *p-d* bonding characteristic of the VBM and the antibonding characteristic of the CBM. The antibonding part is overlapped in energy with the hybridized *e'*-subband.

1T phase is metallic because the t_{2g} -band remains weak bonding with S-*p* and partially filled under the $4d^2$ electronic configuration of Mo⁴⁺. Figure 2(c) shows that the t_{2g} -band is constituted mainly by d_{xy} , $d_{x^2-y^2}$ and d_z^2 , rather than d_{xy} , d_{yz} , and d_{xz} assumed previously [40]. The e_g -band is composed of d_{xz} and d_{yz} . We find that in the t_{2g} -band only d_{xy} has substantial overlap with S-*p* due to *k* dispersion, in contrast to the case of 2H phase where d_{xy} , $d_{x^2-y^2}$ and d_z^2 all have strong covalence with the latter. This accounts for the weak Mo-S *p-d* covalence in 1T phase, leaving the electronic bands crossing the Fermi level determined primarily by the crystal-field. The Fermi surface is formed by three bands denoted by A, B, and C in Figure 2(a). The rising of A-band in the midway of both Γ -M and Γ -K is due to the fact that Mo-4*d* is higher in energy than S-3*p*.

2.2 Phase stability of MoS₂ polytypes

Since different polytypes of MoS₂ have the same element

Figure 4 Coefficient squares of p and d orbitals along the path K- Γ -M for the top valence band (shown by red lines in Figure 4) of MoS₂. (a) and (b) are for 2H-MoS₂, and (c) and (d) for 1T-MoS₂.

constitution and differ only in the symmetry, direct comparison of stability in terms of relative energy is possible because their cohesive energies can be referred to the same reference energy, i.e. the formula-unit (f.u.) total energy when all the atoms are separated infinitely. This is the standard total energy approach in the first-principles structure determination.

In normal state, 2H and 3R are more stable than 1T, as could be seen from the f.u. total energies E_{tot} in Table 1. This is natural because both d -subband hybridization and Mo-S p - d covalence in 2H and 3R can lower the total energies by lowering the occupation state energy, as indicated above. Under current computational accuracy, the energy stability is identical for 2H and 3R. This indicates that stacking order is less important than slab symmetry in structural stabilization. To quantify the origin of stability, one can compare the different contribution to the Kohn-Sham total energy [53] from

$$E_1 = \sum_i \varepsilon_i + \int n(\vec{r}) \left\{ \varepsilon_{xc} [n(\vec{r})] - \mu_{xc} [n(\vec{r})] \right\} d^3r \quad (1)$$

and

$$E_2 = -\frac{1}{2} \iint \frac{n(\vec{r}_i)n(\vec{r}_j)}{|\vec{r}_i - \vec{r}_j|} d^3r_i d^3r_j - \frac{1}{2} \iint \frac{Z_i Z_j e^2}{|\vec{R}_i - \vec{R}_j|} d^3R_i d^3R_j. \quad (2)$$

E_1 is a sum of the total KS band energy and XC energy, an indication of the occupation state energy. E_2 presents the classic Coulomb repulsion energy, containing the electron-

electron Hartree energy and the ion-ion Ewald energy only. Note that E_1 and E_2 are all finite number and their sums are the normal total energy by the first-principles methods. Therefore, one can use them for relative energy comparison between the polytypes. The vdW energy is defined as [50]

$$E_{\text{vdW}} = -\frac{s_6}{2} \sum_{i=1}^{N_{\text{at}}-1} \sum_{j=i+1}^{N_{\text{at}}} \frac{C_{ij}^{ij}}{R_{ij}^6} f(R_{ij}), \quad (3)$$

where parameters in eq. (3) are assigned according to [44]. As shown in Table 1, E_1 is higher by ~ 0.93 eV/f.u. for 3R than for 2H. However, the difference of $E_2 + E_{\text{vdW}}$ between 2H and 3R cancels that of E_1 exactly, resulting in an identical energy stability of them. For 1T phase, on the contrary, the relative rising magnitude of E_1 (4.201 eV/f.u.) with respect to that of 2H is much larger than the relative decrease magnitude of coulomb energies (3.371 eV/f.u.) between them, leading to the lower stability of 1T than 2H and 3R. The large increase of E_1 is a result of the change of crystal-field splitting and the absence of Mo-S p - d interaction due to the occurrence of inversion symmetry centered at Mo sites. It is clear that crystal-field stabilization is the major reason for the stability of 2H phase, which is reinforced by Mo-S p - d interaction.

2.3 Phase stability upon Li intercalation: 2H-to-1T transition

It is commonly believed that the 2H-to-1T phase transition occurs at the 1.1 V voltage plateau of discharging curve

[23,24,28]. During the transition, the ion ratio between Li and Mo changes continuously in the range of (0, 1). To model Li ion intercalation in this range, we construct a $3 \times 3 \times 1$ super-cell for 2H-MoS₂ and a $3 \times 3 \times 2$ super-cell for 1T-MoS₂ from their primary unit-cells, respectively. The two super-cells have equivalent Mo and S ions. By studying the change of relative energy of the two polytypes and the evolution of electronic structures around Fermi levels during Li ion intercalation, one can figure out the driving force for the 2H-to-1T phase transition. Since Li ions can fill every vdW gap with a continuously variable Li content [54], we assume two principles for Li ion introductions, (1) each vdW gap may be intercalated with equal amount of Li ions, and (2) within each vdW gap, Li ion distribution should be as uniform as possible to maximize the Li-Li interionic separation. Following these principles, the intercalated structure is expected to have the smallest Coulomb repulsion.

As indicated in Figure 1, there are two kinds of interstitial sites available for Li occupation. One is at octahedral sites and the other is at tetrahedral sites. Unlike the Li ion occupation at octahedral sites, the occupation of one Li ion at a tetrahedral site increases the lattice stress along the diagonal line direction of (110) face. As a result, the lattice can distort into a monoclinic shape and the Li ion is expelled out from the tetrahedral site. Therefore, to keep the configuration stable, two neighboring tetrahedral sites belonging to different interstitial layers within a vdW gap should be occupied simultaneously (i.e. forming a Li-ion pair). In this way, the stresses induced by the two Li ions cancel each other and the intercalated structure becomes stable.

To quantify the stability of Li intercalation at these possible sites, we define the formation energy of intercalated Li as $E_f = E_{\text{tot}} - E_{\text{MoS}_2} - nE_{\text{Li}}$. Here E_{tot} is the total energy of lithiated MoS₂, E_{MoS_2} is the total energy of pure MoS₂ host, E_{Li} is the total energy of body-centered cubic Li metal, and n is the number of intercalated Li ions. If one Li ion is introduced at an octahedral site, the intercalated structure Li-MoS₂ forms. The calculated E_f is -1.593 and -1.895 eV/f.u. for 2H and 1T phase respectively. If a Li-ion pair is introduced at two tetrahedral sites in the manner discussed above, Li₂MoS₂ may form. The calculated E_f of half the Li-ion pair (i.e. one tetrahedral interstitial Li ion) becomes -0.693 and -0.636 eV/f.u. for 2H and 1T phase respectively. These calculations indicate that (1) octahedral sites are more favorable for Li ion intercalation than tetrahedral sites, regardless of whether the host phase is 2H or 1T; and (2) Li ion intercalation can be more easily realized in 1T phase than in 2H phase. Therefore, the following studies will focus on Li ion occupation on octahedral sites.

By tracking different Li contents (0, 0.11, 0.33, 0.44, 0.56, 0.67, 0.78 and 1), one gets the evolution of relative stability between 2H and 1T in terms of the relative energy $E_{1T} - E_{2H}$ (Figure 5). The total energy E_{1T} of 1T-Li_xMoS₂ decreases with increasing Li content, indicating 1T phase

Figure 5 Li-content-dependent relative total energy of 1T phase with respect to 2H phase. The total energy of 2H phase is set to be zero point. For Li content beyond $\sim 56\%$, the total energy of 1T phase is lower than that of 2H phase.

becomes energy favorable for Li intercalation. When Li percentage per MoS₂ is beyond $\sim 56\%$, 1T-Li_xMoS₂ turns out to be more stable than 2H-Li_xMoS₂, consistent with the experimental indication by Py et al. [28] and pointing to the falling of the first voltage plateau at 1.1 V, which accounts for $\sim 60\%$ capacity of fully lithiated LiMoS₂. Details will be addressed in our future publication combined with our own experimental characterization.

Although possible structural disorder due to random Li occupation may slightly change electronic state at the bands near Fermi levels, a general trend with continuing electron injection into antibonding states is to weaken Mo-S *p-d* covalence interaction. This may bring two effects. First, the average Mo-S bond length is lengthened from 2.416 Å in 2H-MoS₂ to 2.450 Å in 2H-Li_xMoS₂ ($x = 0.56$). As a result, the crystal-field splitting is diminished and the crystal is destabilized. Second, since *p-d* interaction is incompatible with center-inversion symmetry, the weakening of this interaction breaks the restriction of symmetry and enables the transition to the D_{3d} configuration. Another result of electron injection is that Mo 4*d* electronic configuration changes from d^2 to d^3 . The latter term has been found energetically favorable under D_{3d} group to stabilize crystal-field [55].

2.4 Formation and stabilization of CDW after Li intercalation

Li-intercalated normal 1T phase is subject to the Peierls instability originating from Fermi surface nesting [33]. This is generally associated with two mechanisms: first, electrons are injected into previously unoccupied *d*-states, increasing the electron density on Mo and nesting the Fermi surface simultaneously, and second, the electron density is spatially modulated accompanied by a periodic lattice distortion (PLD) with complicated ionic patterns featured by reduced symmetry. Different from the electron self-modulation in such CDW materials as NbSe₂, TiSe₂ and TaSe₂ [56–58], the modulation of electron density in Li-intercalated MoS₂ requires outer electron injection and depends on the symmetry of host matrix (1T or 2H). It is shown here that the

Peierls instability exists also in the Li-intercalated 2H-MoS₂, which results in the formation of a CDW weaker than that in the 1T counterpart.

Under the D_{6h} symmetry of 2H lattice, only the lowest conduction band α form nested Fermi surface, as seen from Figure 6(a) for 2H-LiMoS₂. Electrons brought in with Li ion are added on the antibonding channel constituted by $(p-d)^*$ state and e' -band. The filling of e' -band increases the electron density on Mo, while the filling of $(p-d)^*$ state leads to repelling between Mo and S which impedes Mo ion clustering. Since the hybridization of antibonding α -band (by d_{xy} , $d_{x^2-y^2}$, and d_z^2) keeps approximately isotropic in the K- Γ -M plane, similar to the isotropic hybridization of the highest valence band in 2H-MoS₂ (Section 2.1), the Fermi surface nesting is moderate (Figure 6(c)). Therefore, a relatively small distortion is expected in 2H-LiMoS₂, resulting in the

CDW phase of LiMoS₂ (denoted thereafter to be C2H-LiMoS₂).

To verify this conjecture, we examine a $(4\times 4\times 1)$ 2H-LiMoS₂ supercell in which Mo planes are initially distorted according to the diamond pattern in C1T-LiMoS₂ [33]. This construction is reasonable because the nesting directions of 2H phase are the same as those of 1T phase, as seen by comparison of Figure 6(c) and (d) (indicated by green arrows). In this way a strong initial Mo plane distortion is assumed that all the three nesting directions leads to Mo-Mo bonding. After careful structural relaxation, the original Mo clusters degenerate into zigzag chains with an average Mo-Mo bond length 2.92 Å, indicating that the initial distortion remains only in two directions. The derived C2H-LiMoS₂ has an orthorhombic lattice with a space group Pmma and point group D_{2h} , as shown in Figure 6(e). The

Figure 6 (a) and (b) are the band structures of 2H- and 1T-LiMoS₂, respectively. The energy bands crossing the Fermi level are highlighted by colored lines. (c) and (d) show the Fermi surface profiles (from top view) of the bands with the corresponding colors in (a) and (b), respectively. For displaying the green regions which are covered by the blue region, the latter is drawn transparently in (d). Green arrows indicate three directions of nesting. (e) and (f) are top-view models of single-slab C2H- and C1T-LiMoS₂, respectively. Mo ions are denoted by large green spheres. S ions are denoted by moderate yellow spheres and Li ions are denoted by small pink spheres.

partial DOS of C2H-LiMoS₂ in Figure 7(a) shows that *d*-state dominates around the Fermi level reflecting the effect of Mo clustering. However, this new phase is a metal with no gap opening but only a valley in the half-filled *e'*-subband manifold because the CDW distortion is not strong enough to induce a strong electron localization. Note that a similar metal-to-metal CDW transition occurs in 1T-TiSe₂ [59]. Additionally, Mo plane distortion with zigzag chains appears also in single-layer and restacked MoS₂ [37,38] and CDW has been experimentally reported for 2H-structured Na_xTaS₂ [60]. We have verified that the zigzag shape of Mo arrangement is maintained for smaller Li content down to 56%.

The 2H-to-C2H transition results in an energy reduction of ~0.15 eV/f.u. for LiMoS₂. Although smaller than that of ~0.30 eV/f.u. induced by the transition to 1T phase, the difference of energy reduction between the two transitions shrinks for smaller Li content. When Li content is 56%, the energy reduction due to the 2H-to-C2H transition is ~23 meV/f.u., slightly larger than that induced by the 2H-to-1T transition (~16 meV), indicating a possible competition between Mo plane distortion and S triangle rotation during Li ion intercalation. As a result, local disorder of arrangement and rotation may occur, perhaps corresponding to the observed amorphization after discharging at the 1.1 V voltage plateau [32].

Only when the transition to 1T phase finishes, the further

transition to C1T-LiMoS₂ is possible. Under the *D*_{3d} symmetry of 1T lattice, there is no bonding between S-*p* and Mo-*d*. The former is centralized around Γ while the latter away from Γ (Figure 3). Injected electrons will fill initially the S-*p* state and then the Mo-*d* state, leading to an increase of electron density on Mo sites finally. This is natural because injected electrons are more likely captured by electronegative atoms first. The absence of antibonding (*p-d*)* state in this case ensures a substantial increase of electron density on Mo.

Figure 6(b) and (d) shows that the Fermi surface nesting of 1T-LiMoS₂ is mainly formed by the β band (blue line). The hybridization of β band is anisotropic in the K- Γ -M plane, similar to the anisotropic hybridization of the highest valence band in 1T-MoS₂ (Section 2.1). In the direction Γ -K, band β is featured mainly by *d*_{xy}, mixed with moderate *d*_{yz} (not shown). While for Γ -M, all five *d* states are involved. As a result, $\beta_{\Gamma-K}$ (i.e. band β along Γ -K) has relatively stronger electron localization than that of $\beta_{\Gamma-M}$, reflected by the more flat dispersion of the former. Therefore, for a given Fermi energy much more *k* points are involved in the direction Γ -K than in Γ -M, accounting for the strong nesting of Fermi surface (Figure 6(d)).

The real-space modulation of electron density is constrained within Mo planes because, first, all the nesting directions are parallel to Mo planes, and second, the major composition of $\beta_{\Gamma-K}$ (*d*_{xy}) is within Mo planes. As a result,

Figure 7 (a) and (b) are the partial density of states of C2H- and C1T-LiMoS₂, respectively. For C1T-LiMoS₂, only Mo-*d* and S-*p* are shown. (c) Band structures of relaxed C1T-LiMoS₂ along the *k* point path shown in Figure 4. Partial charge density distribution corresponding to the valence band maximum and conduction band minimum are plotted and projected onto Mo planes. Top view of the primitive-cell model of C1T-LiMoS₂ is presented together. Mo ions are denoted by large green spheres. S ions are denoted by moderate yellow spheres and Li ions are denoted by small pink spheres.

Mo ions cluster together to form diamond pattern, with an average bond length 2.93 Å (Figure 6(f)). Since mainly d -band is filled in this stage, Mo-Mo bonding is enabled by increased d -electron interactions. We plot the energy bands of C1T-LiMoS₂ along the same k point path as that of 1T phase, although the C1T phase distorts slightly into a triclinic lattice. As shown in Figure 7(c), the C1T phase is an insulator having a large band gap of ~ 1 eV. Both its edge bands present very flat dispersion, an indication of electron correlation enhancement, similar to that in TiSe₂ [58]. The partial DOS in Figure 7(b) proves that those edge bands are dominated by Mo- d , indicating that the enhancement of electron correlation mainly comes from the d -band localization due to enhanced nearest-neighbor Mo-Mo d - d interaction. This is supported by the charge profiles representing Mo-Mo d - d interaction shown in Figure 7(c). It is seen that d - d interaction leads to a bonding characteristic at VBM and an antibonding characteristic at CBM, similar to the case of p - d interaction in 2H-MoS₂.

The stabilization of CDW in Li-intercalated MoS₂ (in both 2H and 1T lattice) can be ascribed to the same nature of the Mott-Hubbard type transition [61,62]. However, the former is featured by two distinct characteristics. First, the enhancement of electron correlation is not on-site but comes from Mo-Mo d - d interaction, which results in electron localization within the domains formed by clustered Mo ions and prevents electron itinerating among the domains. This conforms to the extended Hubbard model which stresses the contribution of nearest-neighbor interaction [63]. Second, the magnitude of CDW in Li-intercalated MoS₂ is affected by Mo-S p - d covalence interaction and Fermi surface nesting, which are governed by initial symmetry (trigonal prism or octahedron) and outer electron injection (Li ion intercalation). For example, the strong Mo-S p - d covalence interaction due to the absence of inversion centers in 2H-LiMoS₂ weakens Mo-Mo d - d interaction and prevents electron localization, resulting in a moderate distortion and a zero or small band gap after the CDW transition, as is the case of the 2H-to-C2H transition. The opposite applies when the undistorted phase has a vanished Mo-S p - d covalence interaction, which results in strong Mo clustering and a large band gap in the CDW phase, like the 1T-to-C1T transition. This argument also explains the similar phenomenon in group V dichalcogenides such as NbSe₂ and TaSe₂, i.e. the CDW in 1T phase is stronger than that in 2H phase [13].

3 Conclusion

In summary, we use first-principles methods to study the mechanism of intercalation-induced phase transitions of MoS₂. The inversion-symmetry-related Mo-S p - d interaction and the anisotropy of d -band hybridization are the critical factor influencing the structural phase transitions. We suggest that doping (e.g. iodine) and/or decreasing material

size to nanometer scale may change electronic interaction and hybridization, and controls the structural phase transitions during charging and discharging. Li ion intercalation in 2H-MoS₂ leads to two competing effects, i.e. the transition to 1T phase and the Mo plane distortion in 2H lattice. The Peierls instability exists in both 2H and 1T hosts of Li-intercalated MoS₂ while results in a stronger PLD in the latter. The stabilization of CDW in Li-intercalated MoS₂ is related to the enhanced electron correlation due to Mo-Mo d - d covalence interaction, which can be weakened by Mo-S p - d covalence interaction however. In 1T phase of Li-intercalated MoS₂, the d -band nonbonding with S- p ensures effective electron injection, and the hybridization anisotropy of d -band leads to strong Fermi surface nesting. Since the technological importance of MoS₂ originates from its quasi-two-dimensional electronic structures, the insights gained in our work are helpful to the development of high-energy-density LIB with the band engineering as an important means to tailor the electrochemical performance.

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