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Nature and origin of unusual properties in chemically exfoliated 2D MoS$_2$

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ABSTRACT
MoS$_2$, in its two-dimensional (2D) form, is known to exhibit many fundamentally interesting and technologically important properties. One of the most popular routes to form an extensive amount of such 2D samples is the chemical exfoliation route. However, the nature and origin of the specific polymorph of MoS$_2$ primarily responsible for such spectacular properties have remained controversial with claims of both T and T’ phases and metallic and semiconducting natures. We show that a comprehensive scrutiny of the available literature data of Raman spectra from such samples allows little scope for such ambiguities, providing overwhelming evidence for the formation of the T’ phase as the dominant metastable state in all such samples. We also explain that this small bandgap T’ phase may attain substantial conductivity due to thermal and chemical doping of charge-carriers, explaining the contradictory claims of the metallic and semiconducting nature of such samples, thereby attaining a consistent view of all reports available so far.

INTRODUCTION
The discovery of an atomically thin layer of graphene from a three-dimensional graphite crystal by Novoselov et al. in 2004 opened up a new avenue of research in two-dimensional (2D) layered materials. Overwhelming attention has been focused on the study of the analogous layered materials since then. Among these, the long known, well-studied, and technologically important is molybdenum disulfide (MoS$_2$), a member of the transition metal dichalcogenide (TMD) family. Although investigations on MoS$_2$ can be traced through decades due to its natural abundance in the earth’s crust, important catalytic properties, and extensive usage as a solid state lubricant, it has seen an exponential increase in the number of publications recently.

Unlike graphene, each layer of MoS$_2$ is three atomic layer thick with a thickness of 6.2 Å in which the planes of Mo atoms are sandwiched between two atomic layers of S with strong in-plane covalent bonding and between Mo and S planes, while such layers of MoS$_2$ with three atomic planes are vertically stacked via weak van der Waals interactions. This allows for easy mechanical exfoliation of single or few layers of MoS$_2$, ideal for investigating 2D form of MoS$_2$. The large van der Waals gap can also allow different ions to readily intercalate between the MoS$_2$ layers.

This route has been often used to chemically exfoliate MoS$_2$ into the 2D form, since such an intercalation typically expands the interlayer separation greatly, reducing the coupling between successive MoS$_2$ layers to an insignificant level.

Bulk MoS$_2$ is semiconducting with an indirect bandgap of 1.2 eV, whereas a monolayer of MoS$_2$ is a direct bandgap (1.8 eV) semiconductor. One of the interesting features of MoS$_2$ is that it can exist in several polymorphic forms, shown in Fig. 1, depending on how the three hexagonal layers of S–Mo–S are stacked above each other. A–B–A type of stacking, with the top and bottom S layers being directly above each other, gives rise to the thermodynamically stable polymorph H [Fig. 1(a)], with six S atoms oriented around the central Mo atom in a trigonal prismatic coordination. In contrast, the unstable T form, shown in Fig. 1(b), has the A–B–C type stacking with an octahedral coordination of S atoms around Mo.

This T polymorph can undergo various Jahn–Teller type distortions, leading to the formation of superlattices with different metal–metal clustering patterns, such as $a_0 \times 2a_0$ with dimerized zigzag Mo chains (T’$^0$) in Fig. 1(c), $2a_0 \times 2a_0$ with tetramer Mo–Mo clusters in a diamond formation (T’$^0$) in Fig. 1(d), and
$\sqrt{3}a_0 \times \sqrt{3}a_0$ with a trimerized clustering ($T'''$) in Fig. 1(e). Such diverse polymorphic forms are of great importance, since their electronic properties vary greatly, with the metastable $T'$, $T''$, and $T'''$ phases being semiconductors with varying bandgaps and the $T$ phase being metallic. Because of this tunability of electronic properties, ranging from wide gap insulator to metal, MoS$_2$ has emerged as a potential candidate for an extraordinarily diverse range of novel applications in different fields, such as transistors, optoelectronics, catalysis, photodetectors, supercapacitors, and even superconductors.

MoS$_2$ can be easily transformed into its various metastable states using different routes. These have been extensively studied and reported in the literature, such as plasma hot electron transfer, mechanical strain, and electron-beam irradiation. However, the chemical routes to achieve such transformation have proven to be the most facile and, therefore, popular ones. Chemical routes, in turn, involve chemical, electrochemical alkali metal intercalation or expansion of the interlayer distance by hydrothermal synthesis. Although, through all the above-mentioned processes, the stable H phase is known to be transformed into one of the metastable states, the structure and electronic properties of the resultant phase have still remained highly contentious with many conflicting claims and ambiguities. Theoretical calculations predict that the Jahn–Teller distorted $T'$ and $T''$ are small bandgap semiconductors and $T'''$ is a ferroelectric insulator. Interestingly, the undistorted $T$ phase is theoretically predicted to be dynamically unstable as phonon dispersion of this phase shows instability at the zone boundary. Despite such distinct properties expected of each variant, most of the experimental papers dealing with such chemically treated samples do not clearly identify the specific phase formed, often using the term $T$ or in few cases $T'$ in a generic manner to denote a metastable phase. There are also several reports where, instead of identifying any crystallographic phase, the additional phases formed due to such chemical treatments are classified by their presumed electronic or transport properties and termed metallic or semiconducting MoS$_2$.

Unfortunately, the generic use of $T$ to denote the metastable form and the frequent claim of a metallic nature have created an impression in the community that the metastable state formed is predominantly the metallic, undistorted $T$ phase and not one of the small bandgap semiconducting, distorted $T'$, $T''$, or $T'''$ phases. We critically scrutinize this dogma by looking at all relevant data already available in the literature to arrive at the contrarian view in this perspective.

**CHEMICAL EXFOLIATION OF MoS$_2$**

Briefly, there are three distinct chemical exfoliation routes employed for MoS$_2$, namely, chemical intercalation, electrochemical intercalation, and hydrothermal or closely related solvothermal synthesis. Schematic representations of these two routes are shown in Fig. 2. Historically, intercalation has been applied to layered

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**FIG. 1.** Top and side views of (a) $H$, (b) $T$, (c) $(1 \times 2)$ supershell, $T'$, (d) $(2 \times 2)$ supershell, $T''$, and (e) $(\sqrt{3} \times \sqrt{3})$ supershell, $T'''$ phases of MoS$_2$. The short Mo–Mo bonds are shown in red for panels (c)–(e). Reproduced with permission from Pal et al., Phys. Rev. B 96, 195426 (2017). Copyright 2017 APS.
materials as a means of exfoliating individual 2D layers from their bulk counterparts in large quantities. Intercalation chemistry plays a key role in a majority of the liquid-based exfoliation methods, which, in contrast to the mechanical exfoliation, presents great advantages for the mass production of 2D materials.\textsuperscript{44,45} The key principle for the intercalation-based exfoliation is to increase the interlayer spacing between individual layers by inserting foreign species. This weakens further the already weak interlayer van der Waals interaction and reduces the energy barrier of exfoliation.\textsuperscript{44}

Although some research on the intercalation of different alkali metals into MoS$_2$ has been reported,\textsuperscript{46–49} most of the attention has been focused on the intercalation of lithium (Li). This is based on the expectation that Li$^+$ ions, with the smallest ionic radius among all alkali metal ions, will easily enter the interlayer space and also because of the potential of such Li-intercalated materials as components of high-power rechargeable batteries. The chemical route of Li-intercalation, developed by Joensen and co-workers, involves treating MoS$_2$ with $n$-butyl lithium ($n$-BuLi) in hexane as the intercalating agent, followed by a water exfoliation step.\textsuperscript{50} The schematic illustration of the procedure is shown in Fig. 3(a). The key step of this procedure is the formation of Li$_x$MoS$_2$ via a slow process, requiring Li-intercalation about 48 h or more. The lithiated solid product is retrieved by filtration and washed with hexane to remove excess Li and organic residues of $n$-BuLi. In the next step of washing with water, the bare alkali ions are immediately solvated by water molecules that form a number of layers in the van der Waals gap, facilitating the exfoliation process and also stabilizing the monolayers in the solvent.

However, for the solvated phase, the Li content is significantly lower than in the intercalated compounds prior to washing with water.\textsuperscript{51} For the solvated phases of these types of compounds, the alkali metals remain almost fully ionized, and the guest (alkali atoms) and host charges (residual negative charges on disulfide layers) remain separated by solvent layers. In the solvated phase, the expansion of interlayer spacing with respect to that of the pristine compound naturally depends on the number of solvent layers formed in the interlayer space, which, in turn, depends on the ionic radius of the intercalated alkali metal. Thus, the distance between the adjacent layers changes in a stepwise manner, depending on whether the solvating molecules form a monolayer or bilayer, as demonstrated in Fig. 3(b).\textsuperscript{51,52}

The hydration energy, characterized by the charge/radius ratio, of Li$^+$ and Na$^+$ is higher due to the smaller radius compared to the other alkali metal ions, leading to the formation of two water layers in the intercalation compound for these two guest ions, whereas all the other cations stabilize with monolayered packing of water in the interlayer space. While we focus our discussion primarily on the Li intercalation route in this article, in view of its pre-eminence in the published literature as the most preferred route, we note in passing many other investigations of chemical intercalation driven exfoliation of MoS$_2$, involving other alkali ions.\textsuperscript{49,53,54}

Electrochemical intercalation allows a considerably higher control on the amount of Li-intercalated while also achieving a faster rate of intercalation for small quantities of the host, compared to the chemical intercalation route. In general, the Li$^+$ electrochemical intercalation [see Fig. 3(c)] is performed in a test cell using a Li foil as the anode, LiPF$_6$ or LiClO$_4$ in propylene carbonate as the electrolyte, and MoS$_2$ as the cathode using galvanostatic discharge at a certain current density.\textsuperscript{55} The advantage of this method is that Li$^+$ insertion can be monitored and precisely controlled so that the galvanostatic
FIG. 3. (a) Schematics of lithium ion intercalation into the MoS$_2$ matrix, (b) representation of the intercalated alkali metal cation with water molecules arranged in monolayer and bilayer, (c) schematics of the electrochemical intercalation method, and (d) voltage–composition curve for the intercalation of lithium into MoS$_2$ to form Li$_x$MoS$_2$. Cutoff voltage is shown with the red dot beyond which Li$_x$MoS$_2$ decomposes forming Li$_2$S. (e) Pure T’ phase of MoS$_2$ prepared through the formation of Li$_x$MoS$_2$ via high temperature solid state synthesis followed by water exfoliation. Panel (d) is reproduced with permission from Benavente et al., Coord. Chem. Rev. 224, 87 (2002). Copyright 2002 Elsevier, and (e) is reproduced with permission from Guo et al., J. Mater. Chem. C 5, 5977 (2017). Copyright 2017 RSC.

VIBRATIONAL STRUCTURE OF DIFFERENT PHASES

Raman spectroscopy has been used routinely in the literature to differentiate different polymorphs of MoS$_2$, as it provides a reliable methodology based on the distinctive vibrational structures expected from each phase. Any spectroscopic, including Raman, transition probability is proportional to the square of the corresponding transition matrix element given by

$$ O_{ji} = \langle \psi_f | \hat{O} | \psi_i \rangle, $$

(1)

where $\psi_i$ and $\psi_f$ are the wavefunctions of the initial and final states of the transition and $\hat{O}$ is the transition operator. For an allowed transition, the integral in Eq. (1) has to be non-zero, which can be simply translated in group theoretical terms by mentioning that for an allowed transition, the direct product of the irreducible
representation of the corresponding terms in Eq. (1) has to contain a function that forms a basis for the totally symmetric irreducible representation. In other words, $\Gamma_r \otimes \Gamma_0 \otimes \Gamma_i$ must contain the totally symmetric irreducible representation for the transition matrix element to be nonzero. The vibrational ground state $\langle \psi_0 |$ of a molecule, relevant for Raman transitions, always transforms as the totally symmetric irreducible representation; therefore, the above general condition, in the context of Raman spectroscopy, requires that the direct product of $\Gamma_r \otimes \Gamma_0 \otimes \Gamma_i$ has to contain a totally symmetric irreducible representation; for Raman spectroscopy, $\tilde{O}$ is the polarizability operator. The irreducible representation $(\Gamma_{\text{ vib}})$, corresponding to the normal modes of vibrations at the zone center $(k = 0)$ of the point group $D_{3h}$ describing the structure of monolayer MoS$_2$ in its $H$ phase, is given by

$$\Gamma_{\text{ vib}}(H) = A_1' + 2E' + 2A_2'' + E'''. \quad (2)$$

Careful inspection of the basis functions of each irreducible representation of the $D_{3h}$ point group reveals that $A_1'$, $E''$, and one of $E'$ are the Raman active modes, which give rise to three peaks in the Raman spectra of this phase.

By carrying out similar analysis on $T$ ($D_{3d}$ point group) and $T'$ ($C_{6h}$ point group) phases, one immediately finds out that the irreducible representations of the normal modes of vibrations are $^{2, 38, 63} \Gamma_{\text{ vib}}(T) = A_{1g} + E_g + 2E_u + 2A_{2u}$,

$$\Gamma_{\text{ vib}}(T') = 6A_g + 3B_g + 3A_u + 6B_u, \quad (4)$$

with the Raman active modes as $A_{1g}$, $E_g$ for the $T$ phase (2 peaks) and $A_g$, $B_g$ ($9$ peaks) for the $T'$ phase. We note that this analysis does not provide any indication of how intense or weak a specific symmetry-allowed Raman signal may be; therefore, it is entirely possible that a symmetry-allowed Raman signal is not observed in an experiment due to its low intensity. In this sense, the above consideration helps to establish a rigorous upper limit on the number of peaks one may observe for a given phase of MoS$_2$ and not the lower limit. Before turning to the available information on the Raman spectra of these samples in the literature, we note the reason to consider the undistorted $T$ phase as a possible candidate despite the undeniable theoretical result that this is an unstable phase that will spontaneously distort itself into one of the lower energy $T'$, $T''$, or $T'''$ phases; in other words, theoretical analysis shows that it is purely unstable and cannot be a metastable state. However, such theoretical analysis bases itself on the long-range periodic structure of the $T$ phase, whereas the observed metastable states of MoS$_2$ coexist as small patches within the domains of the $H$ phase; this leads to several additional effects, such as the finite size effect, strains generated across the two phase boundaries, and possibilities of charge doping, making the real scenario very different from the idealized case considered by theoretical approaches; and many of these additional effects may have the ability to make the finite-sized and embedded and/or charge-doped $T$ phase a metastable phase rather than an unstable phase under the experimental realization.

The above discussion on the maximum number of Raman peaks expected in any given phase of MoS$_2$ is already a powerful tool to probe the possible phases formed. This is further aided by detailed quantum mechanical calculations of the phonon spectrum of each phase, providing quantitative estimates of the various peak positions. For example, in Table I, we have tabulated the theoretically calculated frequencies for the three Raman active modes, namely, $E_{1g}$, $E_{1u}$, and $A_{1g}$ in the $H$ phase of MoS$_2$ from Refs. 12, 38, and 63. We have also shown the experimentally obtained estimates of the Raman peak positions for the $H$ phase. The remarkable agreement between the experiment and calculated values provides us with confidence in determining the specific phases of MoS$_2$ present in any given sample of MoS$_2$ from a scrutiny of its Raman spectrum. With this aim in mind, we have collected every publication on chemically exfoliated MoS$_2$ that also reports the corresponding Raman spectrum. We summarize the comprehensive information available in the literature by tabulating the peak positions of the Raman spectrum in each such publication together with the assignment of the nature of the metastable phase of MoS$_2$, suggested in that publication in Table II. The top three rows of this table provide the summary of all theoretically calculated peak positions, reported for various polymorphs of MoS$_2$ so far in the literature, and we use these values for our own phase identifications of the reported spectra in the last column of this table. When we write $T' + H$ in the last column, we imply that the most intense signal of the Raman spectrum reported in that reference arises from the $T'$ phase, while there are also lower intensity signals present that are due to the presence of the $H$ phase; $H + T'$ implies exactly the opposite scenario. We have arranged the references in the chronological order and grouped them under the year of publication. For a quicker comprehension of all these disparate datasets in Table II, we have represented these results also in the form of a plot in Fig. 4.

Table II and Fig. 4 together make evident a few interesting observations. First, it appears that the claim of the $T$ phase formation was relatively more abundant until about 2017, while the claim of the formation of the $T'$ phase has become relatively more frequent in recent years. We also note that most of the Raman spectra reported in the literature invariably exhibit the signatures of the $H$ phase with peaks appearing at $\sim 382\, \text{cm}^{-1}$ and $\sim 405\, \text{cm}^{-1}$. This suggests that the conversion of bulk MoS$_2$ to its few layered 2D form via chemical exfoliation generally does not lead to a complete

| $H$ | First ($E''/E_{1g}$) | Second ($E'/E_{1g}$) | Third ($A_1'/A_{1g}$) |
|-----|---------------------|----------------------|----------------------|
| Theoretical calculation | 280–286 | 375–385 | 402–408 |
| Experimental value | 286 (very low intensity) | 380–383 | 402–409 |

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1. APL Mater. 8, 040909 (2020); doi: 10.1063/5.0005413

2. 61, 64–67

3. 402–408

4. 61, 64–67
| Reference | Peak positions (cm\(^{-1}\)) | Claim Phase |
|-----------|-----------------------------|-------------|
| 12, 38, 61, 68, and 69 | 280–286 | 375–385 | 402–409 | H |
| 12, 61, and 69 | 258–268 | 356–391 | T |
| 12, 38, 61, and 69-71 | 138–140 146–160 200–209 216–230 286–300 333–336 350 399 412 | T' |
| (2011) | | | |
| 33 | 151 | 229 | 300 | 332 | 382 | 405 | T + H | H + T' |
| (2013) | | | | | | | |
| 42 | 150 | 219 | 327 | 382 | 406 | T + H | H + T' |
| (2014) | | | | | | | |
| 72 | 200 | 225 | 353 | 380 | 405 | T | H + T' |
| (2015) | | | | | | | |
| 73 | 156 | 226 | 299 | 333 | | 405 | T + H | T' + H |
| 60 | 156 | 226 | 284 | 333 | | 377 | 407 | T + H | T' + H |
| 34 | 150 | 200 | | | | 380 | 408 | T + H | T' + H |
| (2016) | | | | | | | | |
| 43 | 146 | 219 | 283 | 326 | | 404 | Metallic | T' + H |
| 67 | 158 | 218 | 334 | 383 | 409 | | | |
| (2017) | | | | | | | | |
| 59 | 150 | | 320 | 380 | 405 | T + H | T' + H |
| 74 | 157 | 229 | 283 | 330 | | 403 | | |
| 37 | 235 | 280 | 336 | | 375 | 404 | | |
| 25 | 156 | 228 | 283 | 330 | | 403 | | |
| 48 | 154 | 219 | 327 | 380 | 404 | T + H | T' + H |
| 32 | 156 | 227 | 330 | 383 | 405.4 | T + H | T' + H |
| 36 | 153.2 | 226.4 | 336.7 | 381.9 | 406.9 | T + H | T' + H |
| Reference | Peak positions (cm$^{-1}$) | Claim | Phase |
|-----------|--------------------------|-------|-------|
| (2018)    |                          |       |       |
| 65        | 156 218 283 333          | 408   | T$^\prime$ + H |
| 62        | 156 228 330              | 383   | 409   |
|           |                          |       | T$^\prime$ + H |
|           |                          |       | T$^\prime$ + H |
| (2019)    |                          |       |       |
| 75        | 187 224 289              | 380   | 405   |
| 76        | 156 ~230 ~290 ~330       |       |       |
| 77        | 153.2 226.5 336.8        | ~380  | ~409  |
|           |                          |       | T$^\prime$ + H |
|           |                          |       | T$^\prime$ + H |
| (2020)    |                          |       |       |
| 78        | 156 220 283 330          | 380   | 404   |
|           |                          |       | T$^\prime$ + H |
|           |                          |       | T$^\prime$ + H |
transformation of the stable H phase to its various metastable T forms. Most importantly, we find that all Raman spectra published so far to provide evidence of metastable states in chemically exfoliated, few layer MoS$_2$ have three or more Raman peaks in addition to those attributable to the presence of H phase in the sample. One notable exception is achieved via a high temperature solid state synthesis of Li$_x$MoS$_2$ and successive exfoliation in aqueous acidic solution, leading to the formation of the homogeneous T$^\prime$ phase instead of the mixtures of H, T, and T$^\prime$ phases. The Raman spectra of this sample are compared with those of a sample synthesized through the traditional intercalation route using n-BuLi in Fig. 3(e). The complete absence of the E$_{2g}^\prime$ mode (383 cm$^{-1}$), characteristic of the H phase, establishes the absence of any H phase in this sample, while the signal due to the E$_{2g}^\prime$ mode is clearly visible in the n-BuLi treated sample mentioned as ref-nanosheets in Fig. 3(e). The clear observation of more than two peaks from the metastable phase in every reported case of Raman spectra, as shown in Table II, establishes the absence of any significant extent of the undistorted, metallic T phase formation in the chemical exfoliation route; this is not entirely surprising in view of the intrinsic instability of the T phase. What is surprising, however, is the often reported metallic nature of the chemically exfoliated MoS$_2$ samples, since the H phase and all metastable distorted phases, such as T$^\prime$, T$^{\prime\prime}$, and T$^{\prime\prime\prime}$, are known to be semiconducting. Since the question of metallic/insulating behavior of any sample is intrinsically connected with its electronic structure, next, we turn to the discussion of electronic structures of such samples.

**ELECTRONIC STRUCTURE CONSIDERATIONS**

Electronic structures of different polymorphs of MoS$_2$ can be rationalized to a large extent in terms of their crystal structures based on the ligand field theory. As shown in Fig. 5(a), the trigonal prismatic coordination of H phase MoS$_2$ splits the five $d$-orbitals of Mo into three groups of energies with the $d_{3z^2}$ orbital as the lowest energy and separated from the remaining four orbitals by a large energy gap. The two $d$-electrons of Mo in MoS$_2$ occupy this lowest energy of the $d_{3z^2}$ orbital making it filled and separated by a large gap from the two sets of empty degenerate levels, namely, $d_{x^2-y^2}$, $d_{xy}$, and $d_{xz}$, $d_{yz}$. In contrast, the octahedral ligand field splitting in the case of the undistorted T phase leads to the splitting of the five $d$-orbitals into lower energy, triply degenerate $t_{2g}$ levels, separated by a large energy gap from the doubly degenerate $e_g$ levels. In this case, the two $d$-electrons of Mo, occupying the triply degenerate $t_{2g}$ levels will give rise to partially occupied states, implying a metallic nature of the system. However, the ground state of the $t_{2g}$ electronic configuration is triply degenerate and is, therefore, unstable toward Jahn–Teller distortions. Such distortions will split the triply degenerate $t_{2g}$ orbitals into a lower lying doubly degenerate orbital group and a higher energy singly degenerate orbital, as shown in the third panel of Fig. 5(a). One may then anticipate the formation of a semiconductor with a small bandgap, controlled by the Jahn–Teller distortions, in such a distorted phase, compared to the bandgap in the H phase determined by the large ligand field splitting.

Depending on the specific distortions of the T phase, lifting the degeneracy of the ground state, one arrives at the various semiconducting T$^\prime$, T$^{\prime\prime}$, and T$^{\prime\prime\prime}$ phases with small bandgaps. While this simplified molecular orbital (MO) diagram provides one with a qualitative expectation of the differing electronic structures for the various crystallographic polymorphs of MoS$_2$, the actual magnitudes of the bandgaps will be determined by the extensive dispersion of the local molecular orbitals in the periodic solid forming bands. This can even induce qualitative changes in the metallic/insulating properties if the dispersive widths of the relevant bands become comparable to or larger than the gaps in the MO energy level diagrams shown schematically in Fig. 5(a). Band structures have been calculated by many groups for various polymorphic forms of MoS$_2$ using a variety of approximations based on different first principles approaches. Such calculations find that the H form of MoS$_2$ is indeed the lowest energy phase and the T form constitutes an unstable phase, undergoing spontaneous distortions to T$^\prime$, T$^{\prime\prime}$, and T$^{\prime\prime\prime}$ structures, in broad agreement with the arguments presented above based on Fig. 5(a). The calculated bandgap of the H phase of MoS$_2$ shows both quantitative and qualitative dependencies on the number of layers of MoS$_2$ involved with the bandgap varying from nearly 1.2 eV for the bulk to about 1.8 eV in the monolayer form; moreover, the nature of the bandgap is a direct one for the single layer, while multilayer H MoS$_2$ presents an indirect bandgap$^{26,28}$ with ample experimental validations$^{29,30}$ of these suggestions. Figure 5(b), showing the band dispersions for a single layer of H–MoS$_2$, exhibits the direct bandgap of 1.67 eV at the k points, consistent with other calculations.$^{31,32}$ The calculated band dispersions for a monolayer of the unstable T-MoS$_2$ show three bands crossing the Fermi level, confirming its metallic nature, as illustrated in Fig. 5(c). The band structures of monolayers of distorted octahedral phases (T$^\prime$, T$^{\prime\prime}$, and T$^{\prime\prime\prime}$) of MoS$_2$ are shown in Figs. 5(d)–5(e).
From these figures, it is evident that both T'' and T''' phases have bandgaps [see Figs. 5(e) and 5(f)] of about 14 meV and 57 meV, significantly smaller than that in the H phase [Fig. 5(b)]. The T' appears to have a Dirac cone formed between B and Γ points, as illustrated in Fig. 5(d). However, it has been shown by some authors that incorporating spin–orbit coupling (SOC) within the Mo 4d in the calculation leads to the splitting of this Dirac cone and opening of a bandgap of ~50 meV [Fig. 5(g)]. There are other reports suggesting the formation of a similarly small bandgap (≤100 meV) for the T' phase by several groups. Since some of these calculations do not involve SOC, the essential role of SOC in forming the bandgap in the T' phase is not fully established. SOC decreases the bandgap of the T'' structure, while the bandgap of the T''' structure is almost unaffected by the SOC, as shown in Figs. 5(h) and 5(i), respectively.

We now focus on experimental investigations leading to claims of formation of specific polymorphs, other than the stable H phase, due to the chemical exfoliations of MoS₂ in the 2D forms. Apart from T and T', mention of other metastable phases, such as T'' and T''', is almost non-existent in the experimental literature. Therefore, the origin and the nature of unusual properties of chemically exfoliated 2D MoS₂ revolve around the primary issues: what is the most abundant additional phase formed, T or T'; and what is the electronic properties of that state? Is it metallic or semiconducting? Theoretical considerations, of course, suggest that the T phase in the extended bulk form is not even a metastable state, but a dynamically unstable state;38,40 in addition, the formation energy of the T phase is quite high compared to that of the T' phase,39 making the formation of the T phase in preference over the T' phase unlikely. As already shown in Table II, several claims of the formation of the T phase were based on additional Raman peaks appearing in the spectra of the exfoliated samples. Many of these publications interpret the T phase formation erroneously citing the original works in Refs. 61 and 70, since these original publications already referred to the formation of the (2 × 1) distorted T phase, which in today's terminology is the T' phase. Since we have discussed the Raman results earlier in this article, we focus our attention to other experimental probes into the nature of the metastable states formed. While the erroneous conclusion of the T phase formation based on Raman studies led.
many groups to conclude, consequently, a metallic nature, there are also reports of some direct investigations of the electronic structure and transport properties that are relevant in the present context. For example, the results of current sensing atomic force microscopy (CSAFM) on MoS$_2$ before and after the chemical exfoliation are shown in Figs. 6(a) and 6(b) in terms of the representative conductivity maps. Curiously, the conductivity map of the pristine H sample in Fig. 6(a) exhibits extreme inhomogeneity, with patches of

FIG. 6. Conductivity maps of (a) pristine MoS$_2$ and (b) chemically exfoliated MoS$_2$. Superimposed on the conductivity map in (b) is the $I$–$V$ plot of the corresponding samples. (c) The absorption spectra of lithium intercalated and exfoliated MoS$_2$ flakes at different annealing temperatures; (d) valence band spectra obtained from mechanically (meMoS$_2$) and chemically exfoliated (ceMoS$_2$) samples along with the calculated valence band of the pure T$'$ phase, inset showing the zoomed-in view of the Fermi energy edge for both the samples; and (e) spectra near the Fermi edges for pristine H and the samples with a different extent of Li$^+$ present in it. Panels (a) and (b) are reproduced with permission from Lukowski et al., J. Am. Chem. Soc. 135, 10274 (2013). Copyright 2013 ACS; (c) reproduced with permission from Eda et al., Nano Lett. 11, 5111 (2011). Copyright 2011 ACS; (d) reproduced with permission from Pal et al., Phys. Rev. B 96, 195426 (2017). Copyright 2017 APS; and (e) Pariari et al., Appl. Mater. Today 19, 100544 (2020). Copyright 2020 Elsevier.
highly insulating regions, marked black on a surprisingly conductive major phase on the surface of a well-known insulating H phase, possibly arising from the limitations of the technique or the sample. On the other hand, more relevant to the present discussion, the map of the chemically exfoliated sample in Fig. 6(b) presents a highly conducting homogeneous surface. The I–V diagram, also shown in Fig. 6(b), was used to assert the metallic nature of the chemically exfoliated sample. In passing, we note that the I–V curve of the exfoliated sample in Fig. 6(b) is unusual with a highly non-ohmic, switching behavior for an extremely small threshold voltage followed by current saturations, not expected of a usual metal. Despite these unusual aspects, these experiments point to a reasonable conductivity of the chemically exfoliated sample. The absorbance data of chemically exfoliated samples have also been used to suggest the existence of the metallic T phase. Reference 33 has also reported the systematic change in the optical absorbance spectra, accompanying the conversion of the metastable phase to the stable one as a function of the annealing temperature. These absorbance spectra are shown in Fig. 6(c). Spectral features, preferentially present in the sample with higher proportion of the large bandgap H phase following the higher temperature annealing, are interpreted as excitonic features. It was argued that the absence of any excitonic peak in the exfoliated sample at room temperature indicated that the as synthesized, exfoliated sample was metallic and, consequently, existed in the T polymorphic form. However, as pointed out in Table 1, the as-synthesized sample in this case exhibited J\textsubscript{1} (151 cm\textsuperscript{-1}), J\textsubscript{2} (229 cm\textsuperscript{-1}), E\textsubscript{1g} (300 cm\textsuperscript{-1}), and J\textsubscript{3} (332 cm\textsuperscript{-1}) peaks in its Raman spectrum, and this is inconsistent with high symmetry of the undistorted T phase. In this context, we note that there is a significant level of absorbance, extending to the longest wavelength displayed in Fig. 6(c), for the chemically exfoliated sample without annealing. This featureless absorbance must be associated with the metastable phase formed, since the absorbance is found to decrease systematically with an increasing conversion of the metastable state to the stable H phase with a large bandgap (~1.8 eV or ~690 nm) with the successively higher annealing temperatures. This allows for the possibility of a small bandgap existing for the metastable phase, since the excitonic peak for that phase will appear in the vicinity of its bandgap. Considering that the various estimates of the bandgap of the T\textsuperscript{′} phase are smaller than 100 meV, the spectral features in Fig. 6(c) do not exclude the possibility of the metastable state being the T\textsuperscript{′} phase with its observable excitonic features lying outside of the wavelengths probed and presented in Fig. 6(c).

It is well-known that the issue of metal/insulator property can be most easily probed by photoelectron spectroscopy as it maps out the electronic structure of the sample. In order to enhance the contribution from the metastable phase to photoelectron spectra, we performed the scanning photoelectron microscopy experiment with a photon beam size down to 120 nm. The photon beam was positioned on the sample to maximize the contribution of the metastable state, and the valence band spectra were obtained from the same spot. A magnified view of the energy region around the Fermi energy is shown in the inset of Fig. 6(d). Clearly, the spectral intensity at the Fermi energy is negligibly small for both the H phases, termed meMoS\textsubscript{2}, and the chemically exfoliated sample (ceMoS\textsubscript{2}), establishing the semiconducting nature of the metastable state, consistent with the interpretation of the formation of the T\textsuperscript{′} phase. The above interpretation, however, does not explain why several past experiments found evidence of substantial conductivity for such metastable states. One possibility, of course, is that the thermally excited charge carriers are substantial for such a small bandgap semiconductor, whereas such charge carriers will be entirely negligible for the large bandgap H phase. In addition, we need to consider the possibility of charge carrier doping of such a small bandgap semiconductor as a plausible origin of the observed conductivity. In order to address this possibility, we prepared samples with a different extent of Li\textsuperscript{+} ions present in it by simply varying the water washing cycle after Li-intercalation. The valence band spectra from the two extremes of washing, namely, no washing at all (termed 0W) and after 12 cycles of washing with water (12W), are shown in Fig. 6(e). These spectra with essentially zero intensity at the Fermi energy establish both samples as small bandgap semiconductors. We also find that the valence band spectrum obtained from the 12W sample is shifted toward the higher binding energy side by almost 0.2 eV, indicating electron doping of Mo\textsubscript{S}\textsubscript{2} by the Li ions. Therefore, it is possible that such charge doping of the chemically exfoliated Mo\textsubscript{S}\textsubscript{2} samples contributes to the conductivity through the polymorphic phase remains T\textsuperscript{′}, as suggested by the Raman frequencies and low photoelectron spectral intensity at the E\textsubscript{2g}.

In summary, we first discussed different routes to chemical exfoliation of bulk Mo\textsubscript{S}\textsubscript{2} that provide the most convenient ways to synthesize copious amounts of 2D Mo\textsubscript{S}\textsubscript{2}. Such chemical exfoliation has been shown to give rise to several polymorphs of Mo\textsubscript{S}\textsubscript{2} in addition to the most stable H phase, and many interesting properties and device applications of such samples have been attributed in the past literature to the presence of these additional phases. Surveying the existing literature, we help to focus on the ambiguities present in identifying the dominant polymorphic phase in such samples and show that the existing literature in terms of Raman spectra provides overwhelming evidence in favor of the T\textsuperscript{′} phase being present, rather than the often stated T phase. Since the T\textsuperscript{′} phase is known to be semiconducting, we then address the puzzling issue of several more direct probes of the electronic structures of these samples, which appears to point to a highly conducting state of such exfoliated samples. We show that the substantial conductivity has to be understood in terms of thermal and dopant induced charge-carrier dopings of the small bandgap T\textsuperscript{′} phase, rather than in terms of the formation of the unstable, metallic T phase.

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