Exfoliated and Restacked MoS₂ and WS₂: Ionic or Neutral Species? Encapsulation and Ordering of Hard Electropositive Cations

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Abstract: The relationship between charge and structure in restacked MS₂ (M = Mo, W) has been probed by cation encapsulation and chemical oxidation and characterized by elemental analysis, electron diffraction, X-ray diffraction, and Differential Scanning Calorimetry. Alkali cations have been encapsulated in MoS₂ and WS₂ without the presence of a co-intercalated counterion, suggesting a negative charge in the 0.15–0.25 electrons per M atom range. Electron diffraction studies show ordering of these cations between the layers. Chemical oxidation with I₂ or Br₂ results in a change in the structure of restacked MoS₂, giving rise to a $\sqrt{\sqrt{3}} \times \sqrt{\sqrt{3}}$ superlattice, whereas no change is observed in the structure of restacked WS₂. Differential Scanning Calorimetry studies show that the irreversible exothermic transition to 2H-MS₂ shifts to lower temperature with oxidation. The observed structural distortion and residual negative charge uniquely explain the thermopower measurements, which indicate that restacked MoS₂ and WS₂ are p-type metallic conductors.

Introduction

2H-MoS₂ and 2H-WS₂ are the most stable members of the family of layered dichalcogenides, and find practical application in such processes as hydrodesulfurization (HDS) due to their availability and relatively low cost.¹ Both materials strongly resist attempts to incorporate guest species between their layers.² Li atoms can be inserted into MoS₂ (and WS₂) only upon treatment with very strong reducing agents such as n-butyl-lithium (n-BuLi) or LiBH₄.³,⁴ LiMoS₂ and LiWS₂, however, exhibit a remarkable ability to exfoliate in water by the following redox reaction

$$\text{LiMS}_2 + H_2O \rightarrow (\text{MS}_2)_{\text{single layers}} + \text{LiOH} + H_2(g)$$ (1)

resulting in a collooidally dispersed suspension of single layers.⁴,⁵ The layers can be recovered in a restacked form by filtration, centrifugation, or precipitation. The ability of these materials to exfoliate and to be restacked with relative ease has permitted the encapsulation of a wide variety of guest species which include neutral organic molecules,⁶ polymers,⁷ metal chalcogenide⁸ and metal oxide⁹ clusters, metalloendes,¹⁰ porphyrins,¹¹ and metal cations.¹²,¹³

The authors who first reported the exfoliation of MoS₂ believed that the redox reaction between H₂O and MoS₂ resulted in complete oxidation of the layers, returning the molybdenum to a 4+ oxidation state, because many of the molecules which have been encapsulated are neutral.⁶–⁸,¹⁴ A net drift of the suspended layers toward the anode in an electrophoresis apparatus was observed by these authors, but was attributed to OH⁻ ions associated with the layers which could be displaced by the organic molecules.¹⁵ Subsequent pH studies seemed to support this hypothesis.¹⁶ The increasing number of examples of cationic species which have been encapsulated have suggested to other authors that the layers may retain some negative charge.⁸,¹⁰–¹³,¹⁷ It is rather curious that restacked MoS₂ (and WS₂) can incorporate both cationic and neutral species. The ambiguity of the situation stems from an abundance of both
Li⁺ and OH⁻ generated in the exfoliation process: Li⁺, which could counterbalance a negative charge on the layers when neutral species are intercalated, is a notoriously difficult element to detect; OH⁻, which could co-intercalate with the cationic species, can be confused with residual co-intercalated H₂O.

In addition to the unresolved issues about the oxidation state of the layers, there has also been confusion about the atomic structure of the layers. Reduction of 2H-MoS₂ with n-BuLi or LiBH₄ results in a structural transformation in the layers, causing the geometry around the metal atoms to shift from trigonal prismatic to octahedral.¹⁸ This results in a change in the conductive properties of the material from semiconducting to metallic.¹⁸,¹⁹ This structural change appears to be retained in exfoliated MoS₂, with a structural distortion that results in a $\sqrt{3}a \times a$ orthorhombic superlattice.²⁰²¹ Restacked MoS₂ has also been called 1T-MoS₂ because of the octahedral coordination of the Mo atom. Restacked WS₂ appears to be analogous to restacked MoS₂.²¹ Another material that has been called 1T-MoS₂ is prepared by high-temperature synthesis and subsequent oxidation of K₀.₃₃(H₂O)₀.₃MoS₂.²² Restacked MoS₂ and 1T-MoS₂ were thought to be the same material because both appear to have octahedral metal coordination and both undergo an irreversible exothermic transition to 2H-MoS₂ at around 100 °C.²²,²³ 1T-MoS₂, however, exhibits a $\sqrt{3}a \times \sqrt{3}a$ superlattice.²²,²⁴ The $\sqrt{3}a \times a$ superlattice found in restacked MoS₂ is due to M−M associations resulting in the formation of zigzag chains,²¹ whereas a $\sqrt{3}a \times \sqrt{3}a$ superlattice would involve M−M trimerization.

Are these layers neutral or charged? Why do 1T-MoS₂ and restacked MoS₂ have different superlattices? What is the impact of negative charge on the structure of these materials? If the MoS₂ layers are slightly reduced, how does it affect the electrical conductivity? In this paper we describe our experimental efforts toward answering these questions. The encapsulation of hard, electropositive alkali metal cations was used as a primary tool, and these were chosen due to their relatively poor affinity for OH⁻, which make them perhaps the best species for chemical analyses to determine negative charge. The materials were characterized by X-ray diffraction, electron diffraction, DTA, and elemental analyses. The treatment of LiMS₂ and exfoliated WS₂ with the oxidizing agent Br₂ and concentrated HCl has also been conducted and the products characterized by X-ray diffraction, electron diffraction, and DSC measurements. The structural conclusions presented are supported by thermopower measurements of restacked MoS₂ and WS₂, which address the effects of structure and charge on the nature of their electrical conductivity.

**Experimental Section**

LiMoS₂ and LiWS₂ were synthesized by the LiBH₄ method.¹ MoS₂ was purchased from Cerac. WS₂ was purchased from Alfa Aesar. LiBH₄, acetonitrile, RhCl₃, and CsI were purchased from Aldrich. KCl and BaCl₂·2H₂O were purchased from J. T. Baker. Br₂ and NaCl were purchased from EM Science. Li was purchased from Mallinckrodt. HCl was purchased from Columbus Chemical Industries. All compounds were used as received.

**MoS₂ Aqueous Suspension.** In a glovebox under nitrogen atmosphere, LiMoS₂ (0.1 g, 0.6 mmol) was placed in a 125 mL Erlenmeyer flask equipped with a stir bar and rubber stopper. The flask was removed from the glovebox and 10 mL of deoxygenated deionized H₂O was added. The mixture was allowed to stir for 0.5 h, then the contents of the flask were transferred to a centrifuge tube and centrifuged for 0.5 h. The supernatant was decanted (pH > 12) and to the black gooey solid at the bottom of the tube 10 mL of fresh deoxygenated deionized H₂O was added to rinse away the LiOH. The tube was agitated to resuspend the product, and the mixture again centrifuged for 0.5 h. This rinsing was conducted three times, the supernatant having pH ~12, ~9, and ~7 after each rinse. Then 10 mL more deoxygenated deionized H₂O was added, the tube was agitated to resuspend the product, and the contents of the centrifuge tube were returned to a 125 mL Erlenmeyer flask with a stir bar. The suspension was stirred for at least 0.5 h before further use.

**WS₂ Aqueous Suspension.** In a glovebox under nitrogen atmosphere, LiWS₂ (0.1 g, 0.39 mmol) was placed in a 125 mL Erlenmeyer flask equipped with stir bar and rubber stopper. The flask was removed from the glovebox and 10 mL of deoxygenated deionized H₂O was added. The material was then centrifuged, rinsed, and resuspended in the same manner as MoS₂.

**A₃(H₂O)ₓMoS₂ (Na, K, Rb).** The alkaline chloride salt (1.8 mmol) was dissolved in ~2–4 mL of H₂O. To this solution was added an aqueous suspension of MoS₂ (3:1 excess A⁺). Flocculation occurred immediately. The reaction mixture was stirred for one-half hour and centrifuged and the supernatant decanted. The product was rinsed and centrifuged three times as described in the preparation of aqueous MoS₂, then deposited on a glass slide until dry. Formulas for the products were determined to be Na₃₄(H₂O)₃₂MoS₂, K₃₂(H₂O)₃₀MoS₂, Rb₁₅(H₂O)₉₀MoS₂, and Cs₂₂(H₂O)₃₃MoS₂. In the Cs case CsF was used.

**A₃(H₂O)ₓMoS₂, BaCl₂·2H₂O (0.88 g, 3.6 mmol) was dissolved in ~5 mL of H₂O. To this solution was added an aqueous suspension of MoS₂ (6:1 excess Ba²⁺). Flocculation occurred immediately. The product isolation was analogous to that used for A₃(H₂O)ₓMoS₂.

**A₃(H₂O)ₓWS₂ (Na, K).** The alkaline chloride salt (2.4 mmol) was dissolved in ~3–5 mL of H₂O. To this solution was added an aqueous suspension of WS₂ (6:1 excess Na⁺). Flocculation occurred immediately. The product isolation was analogous to that used above.

**Rb₂₊₃(H₂O)ₓWS₂, RbCl (0.15 g, 1.2 mmol) was dissolved in ~3.5 mL of H₂O. To this solution was added an aqueous suspension of WS₂ (6:1 excess Na⁺). Flocculation occurred immediately. The product isolation was analogous to that above.

**Cs₂₊₃(H₂O)ₓWS₂.** An aqueous suspension of WS₂ was added to 5 mL of a concentrated CsF solution in H₂O (or 5 mL of CsI (2.8 mmol) in water) (7:1 excess Cs⁺). Flocculation occurred immediately. The product isolation was analogous to that given above.

**Li₂₊₃(H₂O)ₓWS₂, BaCl₂·2H₂O (0.29 g, 1.2 mmol) was dissolved in ~5 mL of H₂O. To this solution was added an aqueous suspension of WS₂ (3:1 excess Rb⁺). Flocculation occurred immediately. The product isolation was analogous to that above.

**H₂MoS₂.** In a glovebox under nitrogen atmosphere, LiMoS₂ (0.3 g, 1.8 mmol) was placed in a 125 mL Erlenmeyer flask equipped with a stir bar and rubber stopper. The flask was removed from the glovebox and 30 mL of cold concentrated HCl was added. The reaction mixture was stirred briefly, then centrifuged for a few minutes. The supernatant was decanted, then 30 mL of cold H₂O was added to the solid to rinse,
and the slurry was centrifuged again. This rinsing was repeated two more times, the supernatant after each rinse having pH ~1, ~1, and ~7, respectively. The solid was then slurried in a few milliliters of H₂O and deposited on a glass slide to dry overnight.

**H₂WS₂** In a glovebox under nitrogen atmosphere LiWS₂ (0.3 g, 1.2 mmol) was placed in a 125 mL Erlenmeyer flask equipped with a stir bar and rubber stopper. The flask was removed from the box, and 50 mL of a 0.18 M solution of I₂ in acetonitrile or 50 mL of a 45 mM solution of Br₂ in acetonitrile was added to the solid (5:1 excess I₂/Br₂). The mixture was stirred for different amounts of time ranging from 15 min to 4 days, then was centrifuged and the supernatant decanted. The product was rinsed by resuspending it in 15 mL of acetonitrile and recentrifuging 2 times and then deposited on a glass slide and a Saran wrapped transmission XRD slide to dry.

**Oxidized LiMoS₂.** (a) **Method 1.** In a glovebox under nitrogen atmosphere LiMoS₂ (0.3 g, 1.8 mmol) was placed in a 125 mL Erlenmeyer flask equipped with a stir bar and rubber stopper. The flask was removed from the box, and the solid 50 mL of a 0.12 M MeCN solution of I₂ or the corresponding 75 mL of a 80 mM MeCN solution of Br₂ was added at the solid (5:1 excess I₂/Br₂). The mixture was stirred for varying amounts of time from ~15 min to a week and centrifuged and the supernatant decanted. The product was isolated as described for oxidized LiMoS₂.

(b) **Method 2.** An exfoliated suspension of MoS₂ was prepared as described previously from LiMoS₂ (0.15 g, 0.9 mmol), then centrifuged and rinsed with acetonitrile. The rest of the procedure is the same as in method 1 above.

(c) **Method 3.** LiWS₂ (0.15 g, 0.6 mmol) was used to prepare an exfoliated suspension as described previously. Next 100 mL of a saturated aqueous solution of Br₂ was added. The product was centrifuged immediately for a few minutes, then rinsed with water and centrifuged three times. It was deposited on a glass slide and a Saran wrapped transmission XRD slide to dry.

**Characterization.** Selected area electron diffraction patterns were collected using a JEOL 120 CX transmission electron microscope (TEM). Transmission and reflection powder X-ray diffraction patterns were collected using a Rigaku-Denki/RW4000/2 (Rotaflex) rotating anode X-ray diffractometer using Cu Kα radiation. Differential scanning calorimetry (DSC) measurements were conducted using a Shimadzu DSC-50 instrument under nitrogen flow in sealed aluminum containers at a heating rate of 5 deg C/min. Thermogravimetric analyses (TGA) employed a Shimadzu TGA-50 instrument under nitrogen flow in quartz containers at a heating rate of 2 deg C/min. Energy dispersive spectroscopy (EDS) was used to determine the alkali metal to Mo/W ratio, and a JEOL-JSM-6400V scanning electron microscope was operated at an accelerating voltage of 30 kV using a Tracor Northern 5500 X-ray microanalysis attachment. Thermopower measurements were made with a MMR Technologies Seebeck System.

**Results and Discussion**

**Cation-Encapsulated MS₂.** Addition of exfoliated MoS₂/WS₂ to the alkali halide solution results in immediate flocculation of the suspension. This rapid precipitation, which is not usually observed upon addition of neutral species, strongly suggests that the interaction of the layers with the alkali cations is ionic in nature. Similar behavior is observed upon addition of exfoliated MoS₂/WS₂ to solutions containing Al₁₂O₄(H₂O)₁₂⁻⁺ or tetraphenylphosphonium cations. The samples were characterized by reflectance X-ray diffraction (Figure 1a) and were found to be well ordered, particularly compared to the patterns of samples containing neutral species such as the Co₆S₈L₆ clusters. The predominance of the 00l reflections in the pattern is due to the tendency of lamellar materials to adopt a preferred orientation. All samples exhibited interlamellar d spacings in the range 9.3–9.7 Å (3.1–3.5 Å expansion), indicating co-encapsulation of approximately one monolayer of water.

The flocculated products were found to have the following formulas: Na₀.₁₈(H₂O)₀.₄₅MoS₂, K₀.₂₃(H₂O)₀.₅₅MoS₂, Rb₀.₁₅(H₂O)₀.₇₅MoS₂, Cs₀.₁₂(H₂O)₀.₃₅MoS₂, Na₀.₁₈(H₂O)₀.₃₅WS₂, K₀.₂₁(H₂O)₀.₃₅WS₂, Rb₀.₂₅(H₂O)₀.₄₅WS₂, Cs₀.₁₂(H₂O)₀.₃₅WS₂, and Ba₀.₀₈(H₂O)₀.₂₅WS₂. Thermogravimetric analysis, performed to determine the amount of co-encapsulated water, indicates a range of 0.3–0.45 for x (Figure 1b). Higher x values were found for samples containing Na⁺ and K⁺ and lower values for those containing Cs⁺ and Rb⁺. No halide counterions were detected. Although the presence of OH⁻ ions cannot be completely discounted, the pH of the suspension (~7) and the relatively poor affinity of the alkali cations for OH⁻ ions make their co-encapsulation unlikely.

**Figure 1.** (A) Reflectance X-ray diffraction pattern of Na₀.₁₈(H₂O)₀.₄₅WS₂. The 00l reflections predominate, exhibiting a d spacing of 9.7 Å which corresponds to an expansion of 3.5 Å. (B) TGA of Na₀.₁₈(H₂O)₀.₄₅WS₂ (dotted line), K₀.₂₃(H₂O)₀.₅₅WS₂ (dashed line), and Rb₀.₂₅(H₂O)₀.₃₅WS₂ (solid line). Weight loss corresponds to the loss of co-encapsulated H₂O.

Electron Diffraction Studies of Alkali Cation Encapsulated MoS$_2$. The cation intercalated MoS$_2$ and WS$_2$ samples were also examined by electron diffraction. Both restacked MoS$_2$ and WS$_2$ give rise to electron diffraction patterns which appear to be more simple than they actually are.$^{21}$ Recently, we solved and refined the structure of restacked MoS$_2$ and WS$_2$ from electron diffraction data.$^{21}$ The materials exhibit a superlattice caused by metal–metal associations to form zigzag chains, similar to those observed in WTe$_2$.$^{26}$ This zigzag distortion results in the doubling of one axis of the hexagonal sublattice. As the hexagonal symmetry is destroyed, the new lattice is best described by an $\sqrt{3}$a $\times$ a orthorhombic cell (Figure 2a). Due to their turbostratic nature and the disorder introduced by the exfoliation/floculation process, the diffraction patterns of exfoliated and restacked MoS$_2$ and WS$_2$ are often a “triplet” of these orthorhombic cells, forming an apparent 2a $\times$ 2a superlattice (Figure 2b). Failure to recognize this twinning can lead to incorrect interpretations of the M–M interactions.

The cation intercalated samples are represented by an array of diffraction patterns (Figures 3, 4, and 6) which contain an additional superlattice due to ordering of the electropositive cations in the gallery. The high vacuum found in a TEM ($\sim$10$^{-7}$–10$^{-6}$ Torr) probably results in the removal of most of the co-encapsulated water from the samples. The majority of the patterns appear at first glance to contain a weak 6a $\times$ 6a superlattice relative to the hexagonal sublattice, with distinct variations in the reflections present and the intensity distribution from one pattern to the next. Because of the propensity of these materials for twinning, however, the diffraction patterns are actually quite complicated.

Considering only the orthorhombic lattice caused by the formation of zigzag M–M chains in the host material,$^{21}$ Figures 3a and 3b contain one dominant $\sqrt{3}$a $\times$ a orthorhombic cell with only weak twinning. In the interest of clarity, this $\sqrt{3}$a $\times$ a orthorhombic lattice will henceforth be called the “host-lattice”. A closer examination of Figure 3a reveals that the superlattice caused by the intercalated cations forms strong columns of reflections along the $\sqrt{3}$a* axis of the host-lattice. The superlattice reflections are spaced in thirds between the columns of host–lattice reflections along the $\sqrt{3}$a* axis, indicating a tripling of the a axis. Examination of one of these columns of superlattice reflections reveals a tripling of the $\sqrt{3}$a axis as well, resulting in a $3\sqrt{3}$a $\times$ 3a supercell. Twinning of the host-lattice projects a pseudo 6a $\times$ 6a unit cell.

any superlattice reflections from the cations contained in the columns or rows of host-lattice reflections in Figure 3a. Considering one of the columns of superlattice reflections to find the second cell parameter, the smallest distance between two reflections is 1/3 the length of the (010) reflection of the host-lattice; therefore, the superlattice may be minimally described by the orthorhombic cell $a' \times 3b$ relative to the host-lattice ($a' = \sqrt{3}a$), and $3\sqrt{3}a \times 3a$ (orthorhombic) relative to the hexagonal sublattice of the host material (Figure 3b).

It is logical to conclude that, if the host-lattice is somewhat twinned, the superlattice will be similarly twinned. In this manner the variations in the other diffraction patterns (Figure 4) can be explained by the degree of twinning of the $\sqrt{3}a \times a$ orthorhombic host-lattice and the $3a' \times 3b$ cation superlattice, Figure 4a is very similar to Figures 3a and 3b, but comes from K$_{0.23}$MoS$_2$ rather than Cs$_{0.23}$MoS$_2$ (Figure 3a) or Cs$_{0.13}$WS$_2$ (Figure 3b). The host-lattice is more twinned than the pattern in Figure 3a, but the pattern of cation ordering is essentially the same. Figures 4b and 4c are from crystals of K$_{0.23}$MoS$_2$ and Rb$_{0.14}$MoS$_2$, respectively, that are twinned but are still relatively thin. The distribution of orthorhombic host-lattice cells is uneven, appearing to be stronger in one direction. Consequently, the cation superlattice in these pictures is still stronger in one direction, but does show evidence of twinning. Unlike the previous patterns, the cation superlattice reflections are now found in the columns of reflections along the $\sqrt{3}a'$ axis of the dominant orthorhombic host-lattice (arrows, Figure 4b). This seems to be due to cation superlattices associated with the other (weaker) host-lattice cells. Figure 4d, on the other hand, came from a thicker crystal of K$_{0.23}$MoS$_2$. In this case, the twinning of the host-lattice is so pronounced that the host material exhibits the pseudo $2a \times 2a$ hexagonal lattice which is common in thicker crystals. The crystal is thin enough that the superlattice from the intercalated cations is still visible, but extremely weak. It is twinned in the same manner as the host-lattice, creating a hexagonal “halo” around the pseudo $2a \times 2a$ lattice. The systematic absences of the superlattice (for example, the 200, 130, and the 310) are completely destroyed due to the twinning, generating the pseudo $6a \times 6a$ cation superlattice.

Not all crystals gave rise to well-ordered cation superlattices. Crystals which contain discrete superlattice spots are somewhat unusual; more common are patterns which contain disorder or streaking along the $2a$ axis of the host lattice.

Modeling the Cation Ordering. It is virtually impossible to obtain a diffraction pattern that is completely “single crystal” with respect to the host-lattice and the cation superlattice so that this manner of indexing the patterns might be confirmed; however, it is the best available indexing that can account for the variations in intensities and reflections from one diffraction pattern to the next, all of which can be found within one sample. As such, we have developed a cation ordering model from which an electron diffraction pattern was simulated. It has been designed to resemble the diffraction patterns in Figures 3a, 3b, and 4a, since they are the closest to a “single crystal” pattern (Figure 5). As noted previously, no superlattice reflection is found within a column or row of host-lattice reflections (Figure 3a). The model of cation ordering, depicted in Figure 5a, gives rise to such an electron diffraction pattern (Figure 5b). The cell contains three chains. Alkali cations are placed along the

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure4.png}
\caption{SAED patterns of (A) K$_{0.23}$MoS$_2$, which resembles the patterns in Figure 3, but the degree of twinning is slightly greater; (B) K$_{0.23}$MoS$_2$ and (C) Rb$_{0.14}$MoS$_2$, in which the host-lattice is more twinned but the crystals are still relatively thin; and (D) K$_{0.23}$MoS$_2$, from a thick crystal with a very twinned host-lattice and a “halo” of cation superlattice reflections. As twinning of the host-lattice increases, twinning of the cation superlattice increases, leading to a variety of diffraction patterns.}
\end{figure}
chains in pockets defined by sulfur atoms, where a cation would be expected to reside in the gallery. One-third of the sites are empty in two of the chains; two-thirds of the sites are empty in the third chain. So many alkali cations would not normally be in such close proximity to one another within one layer, however, particularly when one considers the elemental analyses of these samples. More likely this picture represents the superposition of two alternating layers of cations, depicted as white and black. Hence, four of the cations have an occupancy of 0.5 and one cation is fully occupied. This results in a stoichiometry of $A_{0.167}MS_2$, which is consistent with the experimentally determined formula.

It is a necessary condition of the systematic absences that all the alkali cations be in the same kind of site, either “down” or “up” relative to the zigzag chain. The alkali cations occupy only sites which are pointing “up” in the model presented in Figure 5a; however, the sites which are pointing “down” are equally valid sites, so it becomes apparent that this is a possible source of disorder in the samples. The fact that there seems to be no disorder along the $a$ axis indicates that the cations are better ordered along the zigzag chains than between zigzag chains.

A few of the electron diffraction patterns did not have this $3a \times 3b$ superlattice, but had a rather different pattern (Figure 6) corresponding to a $\sqrt{3}a \times \sqrt{3}a$ lattice combined with the pseudo $2a \times 2a$ lattice of the host material, forming a “honeycomb” pattern. The projection of this $\sqrt{3}a \times \sqrt{3}a$ unit cell occupies a smaller area than the previous superlattice (31 Å² vs 161 Å²), which is puzzling when one considers that it is most readily observed for samples in which Ba$^{2+}$ is encapsulated. To reconcile such a lattice with the observed loading of cation one must again employ alternating layers of cations and consider their projection onto the $ab$ plane. For example, in Figure 7a a model has been constructed with four layers of cations, depicted as white, black, gray, and striped circles. The unit cell per MS$_2$ layer is $2\sqrt{3}a \times 2\sqrt{3}a$ (solid line), but the projection is the smaller $\sqrt{3}a \times \sqrt{3}a$ lattice (dashed line). This gives a stoichiometry of $A_{0.09}MS_2$. The simulated diffraction pattern generated from this cation model (Figure 7b) resembles the experimental data.²⁷ It is now possible to understand why cations of different charge can have the same diffraction pattern: they can occupy half as many sites and require twice as many layers to project the appropriate unit cell. This is consistent with the fact that the superlattice is weaker in the samples containing Ba$^{2+}$ than it is in the samples containing Na$^+$ or Rb$^+$.

Oxidation State of M (M = Mo,W) and the Charge of the Layers. The fact that one can see ordering of alkali cations in the MoS$_2$ and WS$_2$ layers without co-intercalation of the halide counterions supports the conclusion that the exfoliated and restacked layers retain residual negative charge. The layers in suspension behave as if they are solvated macroions, precipitating readily in the presence of most cationic species.
and WS₂ to accept co-intercalated OH⁻ ions hinders the quantitation of the negative charge through chemical analyses, as the exfoliation process creates an abundance of OH⁻ ions. These difficulties necessitate the use of "innocent" cations such as alkali metals, as they have poor affinity for OH⁻. This is particularly true for the heavier alkali cations Rb⁺ and Cs⁺ and they are easier to quantify than Li⁺, Na⁺, or K⁺. Although the external OH⁻ ions can largely be removed by rinsing, it is difficult to be certain of their total removal without acidification of the solution. This complicates the situation by increasing the ionic strength of the solution and providing protons, a competing cation that is virtually impossible to unambiguously detect. In addition, if the MoS₂ is in fact slowly oxidized further in solution over time, more OH⁻ ions will be generated. Even restacked MoS₂ or MoS₂ with encapsulated hydrated alkali cations may continue to undergo redox chemistry with intercalated H₂O (see eq 1). Presumably the cations/OH⁻ pairs would remain trapped between the layers, indicating at least the oxidation state at the time of flocculation, but would not reflect the continuum of oxidation states possible for the material over time.

The results of our chemical analyses, which indicate a negative charge in the range 0.10–0.25 per Mo/W atom, are consistent with the results of the analysis of fresh Li⁺ encapsulated samples and are more reliable due to the use of the heavier alkali metal cations. Other studies involving the selective encapsulation of heavy metal ions such as Ag⁺ and Pb²⁺ into MoS₂ and WS₂ have been conducted, and the results indicate a higher negative charge (0.5–0.8 per Mo/W atom). These chalcophilic cations, like the alkali cations, have a poor affinity for OH⁻; however, the samples have been prepared under different experimental conditions, in which the cations were inserted under anaerobic conditions in acidic solutions of moderate ionic strength, inhibiting the formation of colloidal suspension. These results suggest that the continuum of oxidation states possible for MoS₂ and WS₂ is much greater than the range reported in previous studies. The range of negative charge on the Ms₂ layers which we observe is comparable to the range of charge observed in smectite clays, which is not surprising given the similarities in their behavior in aqueous conditions.

Oxidation Reactions of Li₃MS₂. In light of increasing evidence that these materials have a negative charge, Li₃Ms₂ and exfoliated MS₂ were treated with oxidizing agents to see if truly neutral MS₂ could be obtained by oxidizing with I₂ or Br₂ according to

\[ \text{Li}_3\text{MS}_2 + I_2 \rightarrow \text{MS}_2 + x\text{LiI} \]  \[ (2) \]

The oxidized products were characterized by X-ray and electron diffraction studies and by thermal analysis.

Figure 8a contains the selected area electron diffraction pattern of LiMoS₂ oxidized with Br₂ in acetonitrile (MeCN). If LiMoS₂ is first exfoliated in water, then rinsed with acetonitrile, forming Li₁−n(MeCN)ₓLiMoS₂ (n = 0.75–0.85), and subsequently oxidized with Br₂ in acetonitrile, similar patterns can be observed. The pattern resembles the one found for the sample Ba₀₀₂MoO₃ in which a hexagonal array of diffraction spots were inserted under anaerobic conditions in acidic solutions of moderate ionic strength, inhibiting the formation of colloidal suspension. These results suggest that the continuum of oxidation states possible for MoS₂ and WS₂ is much greater than the range reported in previous studies. The range of negative charge on the MS₂ layers which we observe is comparable to the range of charge observed in smectite clays, which is not surprising given the similarities in their behavior in aqueous conditions.

\[ \text{Li}_3\text{Ms}_2 + I_2 \rightarrow \text{Ms}_2 + x\text{LiI} \]  \[ (2) \]
The electron diffraction patterns of WS₂ samples obtained upon oxidation with Br₂ are different from those of MoS₂ samples. Almost all patterns contained only the original $\sqrt{3}a \times a$ lattice, even with repeated sonication and stirring in excess Br₂ for a week. After a week a small amount of 2H-WS₂ could be found, and the amount of diffuse scattering was significantly increased due to decomposition to amorphous product(s). From these results one can conclude that either the product has not been oxidized or restacked WS₂ does not exhibit an alternate superlattice upon oxidation. Although the majority of the product exhibited no change, in almost every sample examined there was a small minority of crystallites which gave rise to a diffraction pattern that could be indexed as a $2\sqrt{3}a \times 2\sqrt{3}a$ lattice. This suggests that even if WS₂ is able to have an alternate superlattice upon oxidation it is not the same as the lattice found in oxidized MoS₂.

**X-ray Diffraction Studies of Oxidized MS₂.** LiMS₂ and Li₁₋ₓ(MeCN)ₓMS₂ were also examined by transmission X-ray diffraction (Figures 9 and 10). Due to the turbostratic nature of these samples induced by the exfoliation/flocculation process, only $hk0$ reflections are visible from the $\sqrt{3}a \times a$ lattice. Interpretation of the X-ray diffraction patterns is more difficult than that of the electron diffraction patterns in part because the peaks are broad. Furthermore, some $h0l$ reflections of the 2H form of the dichalcogenide overlap with the unique $hk0$ reflections from the $\sqrt{3}a \times a$ lattice and the $\sqrt{3}a \times \sqrt{3}a$ lattice. For example, the 200 of the $\sqrt{3}a \times \sqrt{3}a$ lattice overlaps with the 103 of 2H-MS₂. In fact, the presence of the $\sqrt{3}a \times \sqrt{3}a$ lattice cannot be reliably determined by powder X-ray diffraction because the only reflection that is not subject to an overlap problem is the 100, which is extremely weak. The presence of the $\sqrt{3}a \times a$ lattice is more easily monitored because the 210, a moderately strong reflection at $d = 2.10$ Å, does not overlap with peaks from either of the other two phases which may be present in the sample.

The time-dependent behavior of the oxidation of restacked MoS₂ (and LiMoS₂) is illustrated in Figure 9. Initially the $\sqrt{3}a \times a$ lattice dominates (Figure 9a), with the appearance of a shoulder ($d = 1.56$ Å) on the 130 reflection at $2\theta = \sim 59°$ and a new peak at $2\theta = 35°$ ($d = 2.55$ Å), which is not visible in the electron diffraction patterns and is not readily indexed to any of the 3 phases which may be present. At an intermediate stage a new peak appears at $2\theta = 38°$ ($d = 2.35$ Å), which, as mentioned previously, can be indexed as either the 200 of the $\sqrt{3}a \times \sqrt{3}a$ lattice or the 103 of 2H-MoS₂ (Figure 9b). The 110 and the 130 reflections begin to shift to smaller $d$ spacings ($d = 2.78$ to 2.71 Å and 1.61 to 1.59 Å). This is not surprising, because the $\sqrt{3}a \times a$ lattice has the largest $a$ parameter at 3.21 Å; the $\sqrt{3}a \times \sqrt{3}a$ lattice is slightly contracted, as evidenced by the electron diffraction patterns; and in 2H-MoS₂ $a = 3.16$ Å. The 210 peak of the $\sqrt{3}a \times a$ lattice at $2\theta = \sim 38°$ ($d = 2.10$ Å) is still present, and the shoulder at $2\theta = \sim 59°$ has become more pronounced. In the final stage the diffraction pattern no longer contains the peak at $2\theta = 35°$ ($d = 2.55$ Å) or the 210 peak of the $\sqrt{3}a \times a$ lattice at $2\theta = \sim 38°$ ($d = 2.10$ Å), and the 110 and the 130 reflections have shifted to even smaller $d$ spacings ($d = 2.69$ and 1.58 Å). The pattern at this stage contains mostly MoS₂ that has converted to the 2H form.
Figure 9. Transmission X-ray diffraction (XRD) pattern of LiMoS$_2$ oxidized in MeCN with increasing time. (A) Initially the pattern contains the $\sqrt{3}a \times a$ lattice with two new peaks at 2.55 Å (solid black circle) and 1.56 Å (asterisk). (B) A peak at 2.3 Å appears, indexed as either the 200 of the $\sqrt{3}a \times \sqrt{3}a$ lattice or the 103 of 2H-MoS$_2$. (C) The 210 of the $\sqrt{3}a \times a$ lattice has disappeared. The pattern is mostly 2H-MoS$_2$.

Figure 10. (A) Transmission XRD pattern of LiWS$_2$ oxidized with Br$_2$ in MeCN. The black circle marks a peak at 2.55 Å which does not appear to be an hk0 reflection of any of the three expected lattices. The asterisk marks a contribution from the Saran wrap substrate. (B) Transmission XRD pattern of LiWS$_2$ oxidized with Br$_2$ before and after heating. The peak at 2.55 Å (black circle) disappears, leaving 2H-WS$_2$.

The transmission X-ray diffraction patterns of restacked WS$_2$ and LiWS$_2$ upon treatment with Br$_2$ (Figure 10a) resemble those of oxidized restacked MoS$_2$. The peak at $2\theta = 35^\circ$ ($d = 2.55$ Å) appears but, unlike in MoS$_2$, does not disappear with time. Under more rigorous conditions or with time the peak at $2\theta = \sim 38^\circ$ ($d = 2.35$ Å) appears. Given that there is no evidence of a $\sqrt{3}a \times \sqrt{3}a$ lattice by electron diffraction, that peak is probably best indexed as the 103 reflection of 2H-WS$_2$. The disappearance of the 210 peak of the $\sqrt{3}a \times a$ lattice at $2\theta = \sim 38^\circ$ ($d = 2.10$ Å) and the new peak at $2\theta = 35^\circ$ ($d = 2.55$ Å) happens upon heating the material, which converts it to 2H-WS$_2$ (Figure 10b).

The reflection X-ray diffraction patterns contain the basal 001 reflection at 6.05 Å for WS$_2$ and 6.21 Å for MoS$_2$, indicating the deintercalation of most or all of the lithium cations. The basal spacing of WS$_2$ is slightly contracted (0.1 Å) relative to 2H-MS$_2$, but expands upon heating.

Residual negative charge on MoS$_2$ is also substantiated by these diffraction patterns. The structure of restacked MoS$_2$ and WS$_2$, which we recently solved from electron diffraction data and found to be WTe$_2$ type, consists of metal–metal associations to form zigzag chains. As mentioned previously, a material called “1T-MoS$_2$” has been prepared by the oxidation of K$_{0.33}$-(H$_2$O)$_{0.13}$MoS$_2$ and found to have a $\sqrt{3}a \times \sqrt{3}a$ lattice by X-ray diffraction and also by STM studies. The starting material K$_{0.33}$-(H$_2$O)$_{0.13}$MoS$_2$, however, has also been studied by STM and found to have the same structural distortion as restacked MoS$_2$ and WS$_2$. Furthermore, it is evident by the electron diffraction studies presented here that restacked MoS$_2$ can be at least partially converted to “1T-MoS$_2$” upon treatment with Br$_2$ or I$_2$. The exterior of the particle appears to be oxidized, forming the $\sqrt{3}a \times \sqrt{3}a$ lattice, whereas the interior of the particle retains the original $\sqrt{3}a \times a$ structure. Actually in their STM studies of 1T-MoS$_2$ the authors conceded that occasionally they observed the $\sqrt{3}a \times a$ lattice found in their starting material and concluded that it was symptomatic of incomplete oxidation of those samples.

**DSC Studies of Oxidized MS$_2$.** As mentioned earlier, restacked MoS$_2$ and WS$_2$ are metastable, and can be converted to 2H-MS$_2$ by an irreversible exothermic transition upon heating. The 1T- form of MoS$_2$ with the $\sqrt{3}a \times \sqrt{3}a$ lattice has also been reported to be metastable with a comparable conversion. Figure 11a contains a DSC measurement of oxidized MoS$_2$, which has been identified by electron diffraction to contain both the $\sqrt{3}a \times a$ and $\sqrt{3}a \times \sqrt{3}a$ lattices, and a DSC measurement of restacked MoS$_2$ for comparison. Restacked MoS$_2$ undergoes conversion to 2H-MoS$_2$ at 98 °C (at a heating rate of 5 deg C/min). The transition in the MoS$_2$ obtained by oxidizing LiMoS$_2$ with Br$_2$ in acetonitrile occurs at a lower temperature, the broad peak reaching a maximum at 90 °C. Although by TEM it is evident that the material contains more than one kind of lattice, it is not possible to resolve two separate transitions. L$_{1-\gamma}$(MeCN),MoS$_2$ oxidized with Br$_2$ converts rapidly, and a DSC measurement of the material could not be obtained.

The situation is different and somewhat more complicated for the oxidation of WS$_2$ samples (Figure 11b,c). Restacked WS$_2$ undergoes conversion to 2H-WS$_2$ at 195 °C (at a heating rate of 5 deg C/min). WS$_2$ obtained by treating LiWS$_2$ with Br$_2$ in acetonitrile converts at 149 °C, whereas L$_{1-\gamma}$(MeCN),WS$_2$ treated with Br$_2$ in acetonitrile converts at 189 °C. By electron diffraction and transmission X-ray diffraction the materials are structurally identical, containing the $\sqrt{3}a \times a$ lattice. The oxidation was carried out in acetonitrile because aqueous exfoliated WS$_2$ decomposes fairly rapidly upon exposure to Br$_2$, but if the aqueous reaction is isolated within a few minutes it is possible to see a shift in the transition to 183 °C. By

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temperature, from 195 to 149 °C, which is reminiscent of the shift in the transition temperature observed in the MoS₂ system. This shift suggests that oxidation has in fact taken place. Furthermore, reflection X-ray diffraction indicates no residual cations between the layers (i.e., the d spacing is 6.1 Å). The fact that both restacked and oxidized WS₂ have the √3a x a lattice implies that, at least in WS₂, the shift in conversion temperature is not dependent on a structural rearrangement, but rather the degree to which the sample is oxidized. The discrepancy in transition temperature between Br₂ treated LiWS₂ and Br₂ treated Li₁₋₀(MeCN)ₙWS₂ is probably due to limited diffusion in Li₁₋₀(MeCN)ₙWS₂. In LiWS₂ the acetonitrile can solvate the lithium cations, swelling the layers apart and allowing the oxidant to access the layers more intimately, whereas Li₁₋₀(MeCN)ₙWS₂ does not swell in acetonitrile; hence the interior of the particles is inaccessible to the oxidizing agent and the material remains trapped in the incompletely oxidized state that it achieved upon exfoliation in water.

Studies of the structure dependence upon oxidation state in MoS₂ and WS₂ are complicated in part because 2H-MoS₂ undergoes a phase transition upon lithiation in which the coordination environment changes from trigonal prismatic to octahedral. If only a small amount of lithium is introduced the material can remain in the 2H-MoS₂ structure. It has also been observed that the material does not convert to the octahedral structure homogeneously with small amounts of lithium, resulting in a two-phase system. Electrochemical studies which start with 2H-MoS₂ are difficult to interpret due to this problem. The √3a x a octahedral phase (that with the zigzag M–M chains) can be used as a starting point, however. Electrochemical studies of Li₂MoS₂, Kₓ(H₂O)ₓMoS₂, and Kₓ(H₂O)ₓWS₂ which start from the octahedral structure indicate the presence of 4–6 different phases in the range x = 0 to 1. Although some authors have attributed these many phases to cation ordering in the gallery, others have attributed them to charge density waves. The different observed superlattices in MoS₂ suggest that charge density waves are responsible for at least some of these phases. Wypych and co-workers have proposed a scheme containing three different lattices: a 2a x 2a for K₀.₇MoS₂, √3a x a for K₀.₃3(H₂O)ₓMoS₂, and a √3a x √3a for 1T-MoS₂. A comparison of the electrochemical behavior of Kₓ(H₂O)ₓMoS₂ and Kₓ(H₂O)ₓWS₂ reveals that the two materials behave differently at low x values, consistent with the different electron diffraction observed in the oxidation of Li₂MoS₂ and Li₂WS₂ with Br₂.

**Acid Restacked MS₂.** When LiMS₂ is exfoliated in concentrated acid the product should form a proton bronze, HₓMS₂. The transmission X-ray diffraction patterns for the reaction of Li₂MoS₂ and Li₂WS₂ with concentrated HCl (Figure 12a) show that the materials retain the √3a x a lattice and a peak appears at 2.55 Å. The products were examined by electron diffraction and exhibited only the √3a x a lattice with no evidence of an additional reflection at 2.55 Å. In this case, the structure of HₓMoS₂ is the same as that of HₓWS₂, exhibiting no evidence of a √3a x √3a lattice. The reflection X-ray diffraction patterns exhibit basal 00l spacings of 6.05 Å.

If Li₂WS₂ is exfoliated directly in concentrated HCl the DSC

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shows an exothermic transition at 155 °C, whereas if it is first exfoliated in H2O and then concentrated acid is added it exhibits a transition temperature of 191 °C (Figure 12b). Presumably the x values in the products of each reaction, H1W2S2, are different. The discrepancy in the behavior of LiW2S2 and Li1-%(H2O)2WS2 in acidic conditions is similar to the discrepancy upon oxidation with Br2, in which the difference in conversion temperatures could be attributed to a diffusion problem. Exfoliation in concentrated acid provides more oxidizing conditions than exfoliation in H2O before addition of acid. The amount of oxidation during the exfoliation process is important because there is a competition between oxidation and proton encapsulation. Once the material has flocculated its oxidation is limited by diffusion, hence the discrepancy in transition temperatures.

LiMoS2 exfoliated in concentrated acid does not exhibit a shift in its exothermic transition to a lower temperature. The structure of H1MoS2 samples prepared from the reaction of LiMoS2 and Li1-%(H2O)2MoS2 with acid resembles that of their W analogues more than in Br2 solution. There is no evidence of the $\sqrt{3}a \times \sqrt{3}a$ phase in acidic conditions. This suggests that the hypothesis of Golub et al. that MoS2 is fully oxidized upon treatment with acid is not correct, only that protons are now the encapsulated counterion.17

As mentioned previously, the authors who first reported the exfoliation of MoS2 believed that the negative charge of the layers was due to OH− groups associated with the basal planes of the layers. It was believed that exfoliated MoS2 (and WS2) has a point of zero charge (PZC) upon acidification. The authors used the different PZC to create a restacked composite material with alternating MoS2 and WS2 layers, forming a superstructure along the 00l axis.16c Their evidence for a superstructure of alternating MoS2 and WS2 layers was poor. A better interpretation of these results is that the introduction of protons to a homogeneous mixture of exfoliated layers resulted in rapid flocculation, creating a homogeneous mixture of MoS2 and WS2 in the product. They also suggested that PZC occurs at slightly different pH for the edge OH− sites and basal OH− sites, and used this to create a house-of-cards structure for MoS2.16b The evidence for this kind of structure was the low intensity of the 00l reflections in the X-ray diffraction pattern. However, the intensity of the 00l reflections, which is indicative of the degree of order in the flocculated layers, can be influenced by a variety of factors (the ionic strength of the solution, for example), and does not constitute proof of a point of zero charge on the layers.

The peak at 2.55 Å in the transmission X-ray diffraction patterns of H1MS2 and LiMS2 oxidized with Br2 is puzzling, but shifting of the layers relative to one another could allow h0l reflections to appear. A 102 reflection has been observed in some samples of 2H-MoS2 at that d spacing. The peak at 2.3 Å is almost certainly the 103 of 2H-MS2.

An illustration of the different superlattices observed in MoS2 and WS2 due to M−M associations can be found in Figure 13. An ideal 1T-MS2 lattice (not experimentally observed) can distort to form zigzag chains, giving rise to the orthorhombic $\sqrt{3}a \times a$ lattice found in restacked MoS2 and WS2. It can trimerize, giving rise to a $\sqrt{3}a \times \sqrt{3}a$ lattice found in MoS2 upon oxidation with Br2 or I2 (Figure 13c). Finally, when WS2 is treated with Br2, a minority phase with a $2\sqrt{3}a \times 2\sqrt{3}a$ lattice is formed. This distortion could be due to a number of M−M associations, perhaps a trimerization similar to Figure 13c or a tetramerization (Figure 13d).

One question that arises from the behavior of restacked MoS2 upon treatment with Br2 is, why does restacked MoS2, a d2+n system, prefer a $\sqrt{3}a \times a$ distortion, whereas oxidized restacked MoS2 adopts a $\sqrt{3}a \times \sqrt{3}a$ distortion? Also, is oxidized restacked MoS2 a precisely d2 system, or a d2+n system (0 < x < n)? To address these questions, we have investigated the electrical properties of restacked MoS2 and WS2.

**Thermopower Measurements.** As mentioned previously, the reduction of 2H-MoS2 with lithium results in a structural transformation from trigonal prismatic to octahedral metal coordination and a change in properties from semiconducting to metallic. These changes have been explained using a depiction of the band structures for LiMoS2 in both coordination environments, which illustrates a net stabilization in energy upon conversion to octahedral giving a half-filled band with predominantly d orbital character.18 Restacked MoS2 and WS2 retain octahedral coordination about the metal atom,21 and their conductivity has been reported elsewhere4,7b to be metallic. If one simply removes electrons from the half-filled band which was published for LiMoS2, an idealized octahedral d3 system, one should expect an n-type conductor for the d3 system (Figure 14b). Thermopower measurements on restacked MoS2 and WS2, however, indicate that they are p-type (hole) conductors (Figure 14a), with room temperature values of 50 and 20 μV/K, respectively. The structural distortion in restacked MoS2 and WS2 to form zigzag chains obviously should result in a change in the band structure. In fact, distortion of octahedral ML2 d2 systems to form zigzag chains has been predicted by extended Hückel tight binding calculations34 and, for a precisely d2 system, results in a half-filled band (Figure 14a). If, however, the system is actually d2+n, as is the case with restacked MoS2 and WS2, residual negative

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Conclusions

MoS\textsubscript{2} and WS\textsubscript{2} retain some negative charge upon exfoliation and flocculation. Although it is possible to incorporate neutral species, cations can also be encapsulated without a detectable co-encapsulated anion, usually giving rise to very ordered reflectance X-ray diffraction patterns.\textsuperscript{9–13,17} In the studies presented here hard, electropositive alkali cations have been encapsulated in MoS\textsubscript{2} and WS\textsubscript{2} under neutral synthetic conditions. The choice of these cations and these synthetic conditions minimizes the risk of co-encapsulation of OH\textsuperscript{−} ions. The cations order in the gallery, forming additional superlattices. The range of negative charge on the layers appears to be 0.15–0.25 for both MoS\textsubscript{2} and WS\textsubscript{2}, which is consistent with measurements on samples prepared in a similar fashion by other researchers.\textsuperscript{17}

Structural characterization of restacked MoS\textsubscript{2} also supports a negative charge. Restacked MoS\textsubscript{2} and WS\textsubscript{2} have been found by electron diffraction to have the same superlattice as K\textsubscript{0.7}MoS\textsubscript{2}.\textsuperscript{22} Treatment of restacked MoS\textsubscript{2} with Br\textsubscript{2} results in a change from a $\sqrt{3}a \times \sqrt{3}a$ superlattice to a $\sqrt{3}a \times \sqrt{3}a$ superstructure, which is analogous to the superstructure observed in “1T-MoS\textsubscript{2}”, the oxidation product of K\textsubscript{0.7}MoS\textsubscript{2}.\textsuperscript{22} This change in structure upon exposure to an oxidizing agent implies that restacked MoS\textsubscript{2} is incompletely oxidized, and is probably better formulated as Li\textsubscript{i}MoS\textsubscript{2} or Li\textsubscript{i}(H\textsubscript{2}O)\textsubscript{y}MoS\textsubscript{2}.

Restacked WS\textsubscript{2} does not appear to exhibit a structural change upon exposure to Br\textsubscript{2}. However, both restacked MoS\textsubscript{2} and WS\textsubscript{2} exhibit irreversible exothermic transitions which are shifted to lower transition temperatures upon treatment with Br\textsubscript{2}. The shift is quite significant in WS\textsubscript{2}, from 195 to 149 °C in the Br\textsubscript{2}-treated sample, indicating that oxidation has taken place. It is somewhat surprising, however, that oxidation of restacked WS\textsubscript{2} does not result in an alternate superlattice analogous to the $\sqrt{3}a \times \sqrt{3}a$ superstructure observed in oxidized MoS\textsubscript{2}. The products of all thermal conversions are the semiconducting phase 2H-MS\textsubscript{2}, which requires an expulsion of the residual negative charge and explains why the oxidation state affects the transition temperature. The expulsion of the residual negative charge likely results in the reduction of residual H\textsubscript{2}O (or H\textsuperscript{+} in H\textsubscript{2}MS\textsubscript{2}), forming H\textsubscript{2} gas.\textsuperscript{26}

The different phases of MoS\textsubscript{2} produced under various experimental conditions are illustrated in Figure 15a. This scheme is intended to correlate all forms of MoS\textsubscript{2} and the interconversion between forms, and to help clear up any remaining confusion regarding the nature of this system. Exfoliation and flocculation of LiMoS\textsubscript{2} in water results in

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\textsuperscript{(36)} Proton NMR studies of the gaseous species released upon conversion of restacked MoS\textsubscript{2} to 2H-MoS\textsubscript{2} indicated the presence of hydrogen gas. Heising, J.; Kanatzidis, M. G. Unpublished results.
restacked MoS$_2$, which can be more accurately formulated as Li$_{0.2}$MoS$_2$ ($\delta$) based on the chemical analyses of the alkali cation encapsulated products. Oxidation of LiMoS$_2$ in Br$_2$/MeCN results in a mixture of “1T-MoS$_2$” ($\delta$) and Li$_{0.2}$MoS$_2$. LiMoS$_2$ exfoliated in H$_2$O can be converted to the same mixture upon treatment with Br$_2$/MeCN. If LiMoS$_2$ is exfoliated in concentrated HCl it forms H$_x$MoS$_2$, a material with the same superstructure as Li$_{0.2}$MoS$_2$ which does not appear to be oxidized. A similar scheme in Figure 15b illustrates the analogous phases of WS$_2$. A principal difference is that the product of the oxidation of LiWS$_2$ with Br$_2$ in MeCN, called “WS$_2$” ($\delta$), is not structurally different from Li$_{0.2}$WS$_2$. Depending on the preparation, it is possible to isolate products exhibiting a continuum of transition temperatures between 149 $^\circ$C and the transition temperature of Li$_{0.2}$WS$_2$ (195 $^\circ$C). Another difference is that, unlike in MoS$_2$, when LiWS$_2$ reacts with concentrated HCl, the transition temperature of the product (155 $^\circ$C) is closer to that of the oxidized material ($\delta$) rather than Li$_{0.2}$WS$_2$. Given the higher energy of the d orbitals of W, it is not surprising that WS$_2$ is more readily oxidized than MoS$_2$ under comparable experimental conditions.

Clearly the MoS$_2$ and WS$_2$ systems are rather complicated, and the nature of the phase obtained is very sensitive to the experimental conditions used to prepare the product. The term “restacked MoS$_2$” has been used casually in the literature to represent material that has been converted to the 2H form as well as the metastable compound with the $a_\perp$ lattice, and is usually written without a formulation of the negative charge present. In addition, MoS$_2$ and WS$_2$ resemble one another, but there are distinct differences between the two systems. To prevent future confusion researchers should take special care to formulate their products precisely, and also to recognize that restacked MoS$_2$ (and WS$_2$) which has been heated above its conversion temperature is better described by the formula 2H-MoS$_2$ (and 2H-WS$_2$).

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