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Nature of low dimensional structural modulations and relative phase stability in $\text{Re}_x\text{Mo(W)}_{1-x}\text{S}_2$ transition metal dichalcogenide alloys

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We report on the various types of Peierls like two dimensional structural modulations and relative phase stability of 2H and 1T poly-types in the $\text{Re}_x\text{Mo}_{1-x}\text{S}_2$ and $\text{Re}_x\text{W}_{1-x}\text{S}_2$ alloy system. Theoretical calculation predicts a polytype phase transition cross over at ~ 50 at. % of Mo and W in ReS_2 in both monolayer and bulk form, respectively. Experimentally, two different types of structural modulations at 50% and a modulation corresponding to trimerization at 75% alloy composition are observed for $\text{Re}_x\text{Mo}_{1-x}\text{S}_2$ and only one type of modulation is observed at the 50% $\text{Re}_x\text{W}_{1-x}\text{S}_2$ alloy system. The 50% alloy system is found to be a suitable monolithic candidate for metal semiconductor transition with minute external perturbation. ReS_2 is known to be in the 2D Peierls distorted $1T_d$ structure and forms a chain like superstructure. Incorporation of Mo and W atoms into the ReS_2 lattice modifies the metal-metal hybridization between the cations and influences the structural modulation and electronic properties of the system. The results offer yet another effective way to tune the electronic structure and poly-type phases of this class of materials other than intercalation, strain, and vertical stacking arrangement. *Published by AIP Publishing.*

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INTRODUCTION

Atomically thin transition metal dichalcogenides (TMDs) are considered to be the next generation platform for future electronics and offer numerous novel device applications based on their unique excitons, spin, and valley properties.^{1–11} The most explored members in the family i.e., MoS_2 and WS_2 possess a direct band gap in the monolayer form but undergo transition to an undesirable indirect band gap material for a number of layers two and more.^{5,12,13} The stable crystal structure of MoS_2 and WS_2 is 2H (space group 194; $P6_3/mmc$) with a direct band gap of 1.88 and 1.9 eV, respectively, for the monolayer. On the other hand for ReS_2 , the band gap remains direct even in the bulk form due to weak interlayer van der Waals and electronic coupling.¹⁴ The stable crystal structure of ReS_2 is 2D-Peierls distorted $1T_d$ (space group 2: $P\bar{1}$) where chains made of Re_4 clusters form the quasi two dimensional superstructure with a band gap of 1.55 eV for the monolayer. The metastable unmodulated 1T phase of MoS_2 is demanding due to its metallicity that is indispensable for carrier transport, injection and in the modulated $1T_d$ form shows excellent hydrogen evolution activity (HER).¹⁵ The most stable configuration in the modulated 1T form of MoS_2 and WS_2 is a $2a \times a$ superstructure as in the case of ReS_2 .^{15–17} These superstructures are reported to have a band gap of 0.1–0.2 eV and 0.14 eV, for MoS_2 and WS_2 , respectively.^{15,17} Throughout the text “ $1T_d$ ” is used to represent the chain like superstructure in all cases.

As already mentioned above, the 1T and modulated $1T_d$ poly-types of both MoS_2 and WS_2 are metastable. However, due to their useful properties, various attempts have been made to stabilize these poly-type structural forms.^{18–21} Most of the reports are based on intercalation method using alkali metals, e.g., Li, and K where structural transitions between various poly-types take place during loading of alkali metals at the interlayer spacing with the end application as rechargeable batteries. Among various reports, Li and alkali metal intercalation was reported to stabilize the $1T_d$ form of both MoS_2 and WS_2 through hybridization between metals forming a quasi 2D chain. Li intercalation of MoS_2 powders in water formed a $2a \times 2a$ superstructure as confirmed by X-ray diffraction.²² On the other hand, K intercalation stabilizes two different forms of the modulated structure of MoS_2 depending on the K concentration, i.e., trimerization of Mo with superstructure ($a\sqrt{3} \times a\sqrt{3}$) ($x \approx 0.3$) and tetramerization of Mo with superstructure $2a \times 2a$ ($x \leq 0.3$).²³ The presence of two different superstructures in this case was confirmed by a scanning tunneling microscopy (STM) technique.

Relative stability of various types of superstructure modulations in Li intercalated MoS_2 , i.e., LiMoS_2 was previously investigated by first principles calculations.¹⁹ It was found that the $(2a \times 2a)$ superstructure formed by tetramerization of cations was more stable (by 0.5 eV) compared to trimerized ($a\sqrt{3} \times a\sqrt{3}$) structural modulation. This opened a band gap of about 1 eV. However, later studies based on both experimentation and theory revealed that it is $2a \times a$ type periodicity forming chain like structure the most stable modulated form of MoS_2 .¹⁶ It was also pointed out that a

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charge density wave (CDW) phenomenon was at the origin of such structural modulation that was associated with a partially nested Fermi surface and the stabilization is localized around the Fermi level. The destabilization due to strain occurs mainly in the $3p$ of the Sulphur part which is compensated by electronic stabilization in the $3d$ of the Molybdenum part. Although energetically least stable, the trimerized modulated structure was predicted to be the thinnest ferroelectric material.²⁴

There is a lot of interest in the community to understand and control various structural poly-types of monolayer TMDs by different means for their efficient utilization in energy, optoelectronics, and novel devices apart from immense interest in fundamental science.^{3–8,25–28} Among recent reports, intermediate steps of structural transition from trigonal prismatic 2H to octahedral 1T phases have been studied by electron microscopy.²⁰ Three different types of distortions or sub-superstructures are observed by HRTEM as transient states involving a shear mechanism. These are (2×1) , (2×2) and $(\sqrt{3} \times 1)$ and the combinations between them. The d electron system for various superstructures changes as follows, d^2 for 2×1 (zigzag clustering), $d^{3/4}$ for $(\sqrt{3} \times 1)$ (ribbon chain clustering), and d^3 for 2×2 (diamond chain clustering). In another report, Li intercalated MoS₂ shows the presence of a bi-phase structure, i.e., both 2H and combination of 1T and 1T_d (2×1).¹ Different structural phases form coherent interface at the boundary. The structure changes from 1T_d to 1T by e^- beam exposure. The transition from 1T_d to 2H is a multi-step process and goes via different metastable structures. In the case of WS₂, 1T is found to be more stable than MoS₂. After annealing at different temperatures, the structure does not transform to the 2H phase completely and defects are believed to stabilize the residues of the 1T phase.

Formation of a metastable tetramer diamond unit along with zigzag chains with a new orientation formed by e^- beam irradiation of the zigzag 1T phase of Li intercalated WS₂ has been reported.¹⁷ In the 1T zigzag starting phase, both tetramer and triangular clusters were present. The presence of triangular clusters in K intercalated 2H-MoS₂ has already been predicted theoretically¹⁸ and experimentally confirmed.²⁹ Theoretically, the energy difference between the two meta-stable structures is found to be 0.1 eV per formula unit. The stabilization of the local tetramer in the present case is due to the electronic charging effect. It was argued that the observed distortion is not a charge density wave (CDW) phenomenon but rather Jahn Teller (JT) type introduced by a weakening of the W-S bonds leading to electronic instability. However, ReS₂ is not a Jahn Teller type as argued before because the gap opens in the d bands at the Fermi level as confirmed by modern first principles calculations.^{10,13,29}

Thus, in the present report, stabilization of 1T_d structural form of Re_xMo_{1-x}S₂ and Re_xW_{1-x}S₂ alloys has been explored by both theory and experiment. Theoretically, a structural cross over is observed at approximately 50% alloy composition in both monolayer and bulk form. In this context, the stability of the metallic 1T phase of MoS₂ upon 25% Sn substitution was predicted theoretically.³⁰ There are some

reports where Re incorporation into MoS₂ forms nanotubes, fullerene, and nanoparticles reported to show beneficial effects on HER activity.^{31–36} Taking theory as a guide experimentally, only 50% alloy composition is synthesized in both the cases. However, for the Re_xMo_{1-x}S₂ alloy, two different compositions, i.e., 50% and 75% and for the Re_xW_(1-x)S₂ case mostly homogeneous 50% alloy composition was obtained after the synthesis procedure. In the case of the Re_xMo_{1-x}S₂ alloy, two different types of modulations, i.e., tetramer (type I) and trapezoid like modulations (type II) or two different modulations between two different cations for 50% and a trimer modulation, are observed for 75% alloy composition. The observation of stable trimerized structural modulation is important as this could be useful as a thinnest platform for ferroelectric devices.²⁴ On the other hand in Re_xW_{1-x}S₂, the alloy formation is homogeneous and only one type, i.e., tetramer modulation (type I) is observed along with some areas with different modulation vectors probably due to slightly varying composition in these areas. The energy difference between the metallic and semiconducting ground states with slightly differing structural parameters is found to be very small; 90 and 40 meV for the 50% Re_xMo_{1-x}S₂ and Re_xW_{1-x}S₂ alloys, respectively. This could be an excellent monolithic candidate for the metal-semiconductor transition with minute external perturbation suitable for application as a nanoscale switching device. Overall, the results show that the alloy can be formed between these important material systems with a differing stable structural form of the terminal compounds, i.e., 2H and 1T_d and the various structural modulations observed offer yet another way to controlling the electronic structure of this system other than intercalation, strain, and vertical stacking arrangement. While high resolution electron microscopy revealed the details of such modulated structures, the density functional theory (DFT) based calculations throw light on the implications on the electronic properties of such an alloy system.

MATERIALS AND METHODS

Re_{0.5}X_{0.5}S₂ (X = Mo and W) alloys were synthesized following a similar synthetic procedure reported earlier for ReS₂.¹³ In short, rhenium (wire, 1.0 mm diameter, 99.97%, Alfa Aesar), molybdenum/tungsten (powder, 99.9%, Sigma Aldrich/powder, 99.8%, Sigma Aldrich) and sulfur (powder, –325 mesh, 99.5%, Alfa Aesar) were taken in the stoichiometric ratio (1:1:4) and sealed in an evacuated (10^{-5} mbar pressure) quartz tube. The tube was then heated to 200 °C at the rate of 10 °C/h followed by annealing at that temperature for 2 h in order to avoid any possible explosion due to the high vapor pressure of sulfur. Next, the temperature was increased to 900 °C at a rate of 20 °C/h and annealed for 120 h after which the furnace was shut down and the sample was allowed to cool to room temperature naturally. The final product was fine black powder.

All the high resolution phase contrast transmission electron microscopy (HRTEM, in ICMS, India) and Z-contrast high angle annular dark field imaging (HAADF, in KAUST, Saudi Arabia) were performed in a FEI TITAN aberration

corrected 80–300 keV TEM. Powder alloy samples were sonicated for 40 min to exfoliate monolayer materials for TEM imaging and energy dispersive spectroscopy (EDS) analysis.

Computational method

The electronic structure calculations were performed using density functional theory (DFT) as implemented in Wien2k code.³⁷ Wien2k uses linearized augmented plane waves as the basis and considers all electrons into the calculation. We have used the following structures for the present calculation: monolayer and bulk form of 2H and 1T MoS₂, WS₂, ReS₂, and various alloys between them and also considering structural modulations for ReS₂ and some of the intermediate alloy composition. (The schematic of calculated structures is shown in various figures while describing the results and also some in the [supplementary material](#)). For the construction of bulk (1T/2H) and monolayer (1T/2H) Re_xMo(W)_{1-x}S₂ alloy structure, various sizes of supercells depending on Re concentrations were constructed, e.g., (i) $4 \times 4 \times 1$ supercell for 6.25% Re, (ii) $4 \times 2 \times 1$ for 12.5% Re, (iii) $2 \times 2 \times 1$ for 25% and 75% Re, and (iv) $2 \times 1 \times 1$ for 50% Re. A Γ centered $30 \times 30 \times 1$ and $30 \times 30 \times 18$ k point mesh was used for a single formula unit cell of monolayer and two formula unit cell of bulk. The number of the k-mesh points was reduced proportionally for the larger supercell.

For bulk MoS₂ and WS₂ calculation, a unit cell consisting two formula units was considered with Bernal stacking along the *c*-direction. DFTD3 was introduced for dispersion correction which considers van der Waals interaction between the layers.³⁸ In the case of monolayer calculation, 16 Å vacuum was added between the layers in order to prevent interlayer coupling. The optimization of lattice parameters and atomic position for the MoS₂, WS₂ and distorted

ReS₂ model was performed using the generalized gradient approximation (GGA) exchange-correlation functional of Perdew, Burke, and Enzerhof (PBE).³⁹ The criteria of convergence for force, energy and electronic charge were set below 1 mRy/a.u., 0.0001 Ry and 0.001 e, respectively. The relaxed lattice parameters of MoS₂, WS₂, modulated ReS₂, and all other alloy structures considered for the present calculations are shown in Table 2 ([supplementary material](#)). The muffin tin radii and RMT were chosen in such a way that they do not overlap. The $K_{\max}$ was set at 7.00/RMT.

RESULTS AND DISCUSSION

We begin with the experimental structural description and associated superstructures observed by high resolution transmission electron microscopy in both Re_xMo_{1-x}S₂ and Re_xW_{1-x}S₂ alloy systems. As mentioned earlier, the most stable structure of ReS₂ is 1T_d (space group 2: $P\bar{1}$) and for MoS₂ and WS₂ it is 2H (space group 194: $P6_3/mmc$). ReS₂ is known to be in a 2D Peierls distorted 1T_d structure where four Re atoms hybridize to form Re₄ clusters. Incorporation of Mo and W atoms into the ReS₂ lattice modifies the metal-metal hybridization between the cations and influences the structural modulation and electronic properties of the system. Figure 1(a) is the typical 1T_d ReS₂ structure where four Re atoms together hybridize to form a tetramer Re₄ cluster forming a quasi two dimensional chain like superstructure. The calculated superlattice spots corresponding to 1T (one of the S hexagons is rotated by 30° with respect to other Re and S hexagons) and periodic modulations/superstructure ($2a \times a$) are indicated with two different color circles. The lattice parameter of monolayer ReS₂ is $a = 6.4308$ Å, $b = 6.4912$ Å, and $\gamma = 119.03^\circ$. The typical stable 2H and distorted 1T structure of MoS₂ and WS₂ is shown in Figures 1(b) and 1(c). Kindly note that the length of the edges and

FIG. 1. Schematic structural models of (a) 1T_d ReS₂ (b) 2H MoS₂/WS₂, (c) 1T MoS₂/WS₂, and polytypes. The side view of each of polytype is also shown. (d) Schematic supercell unit for the superstructure phases of 1T_d structure with various structural parameters defined by a_1 , a_2 , a_1' , a_2' , a , b , and γ . These structural parameters are used throughout the text to define various superstructures observed. Also, various colors indicate different types of metal-metal hybridization bonds possible in the systems.

the angle between them of the modulated structural units can be different along different directions for the same superstructure periodicity depending on the alloy composition. Therefore, in order to distinguish such modulations between different alloy systems, we take help from the geometry by drawing a rhombus with four cations at the corners as shown in Figure 1(d). Two different directions are defined as a_1 and a_2 , with an obtuse angle between them as γ . Another two parameters are defined as a_1' and a_2' along the original a_1 and a_2 directions, which will define the distance between the hybridized units along the two different directions. The supercell lattice parameters of the system are also defined in terms of repeat vectors a and b (Fig. 1(d)). This is helpful to describe in detail the nature of modulation vectors and their strength along distinct directions, which in the literature either various nomenclature or dimensionality of modulations (1D or 2D) was used to define such structures. However, distortions can be quasi 2D with different lattice vectors and strength along different directions and therefore, we have used this definition to distinguish the various structural distortions observed in both the alloy systems. Additionally, the bonding lines between cation-cation represent hybridization and various types of hybridization possibilities are also indicated in the same figure. For both the alloys, all the structures are found to be the $1T_d$ poly-type form with different types of superstructures depending on the alloy composition. All the structural parameters obtained from theoretical and experimental observations are given in the [supplementary material](#).

Alloy of $\text{Re}_x\text{Mo}_{1-x}\text{S}_2$

Three different types of structural modulations or superstructures are observed in this alloy system depending on the

composition. Out of three, two different modulations are observed for the same 50% and the third one with a trimerize type modulation for 75% $\text{Re}_x\text{Mo}_{1-x}\text{S}_2$ alloy case. Percentage numbers in the alloys indicate the composition in terms of either Mo or W in the host ReS_2 lattice. There are areas where pathways of poly-type structural transition are observed due to gradual changes in Re concentrations and are also described. The EDS analysis for 50% alloy is shown in the [supplementary material](#) (Fig. S7).

Type I modulation of 50% $\text{Re}_x\text{Mo}_{1-x}\text{S}_2$

Figure 2(a) shows the modulation for the monolayer alloy. Alternate rows are filled by either Re and Mo atoms. This gives rise to the different modulations of lattice parameters along different directions. This is schematically shown in the inset. The Mo-Mo, Re-Re, and Re-Mo distances are 2.88, 2.80, and 2.68 Å, respectively. The acute angle γ of the rhombus is 74° . a_1' and a_2' are 2.9, and 2.7 Å. The FFT (fast Fourier transformation) equivalent to the periodic diffraction pattern of the image is shown in Figure 2(d). FFT also shows the signature of the $1T_d$ phase. The superlattice spots corresponding to the $1T_d$ phase are strong along one of the directions that correspond to the parallel planes containing only Re and Mo atoms. The observed modulation in this case is similar to the ReS_2 but with different lattice vectors. The Z-contrast line scan profile identifying Re and Mo in a column is shown in Figure S2 ([supplementary material](#)).

Type II modulation of 50% $\text{Re}_x\text{Mo}_{1-x}\text{S}_2$

For the same 50% alloy composition, a unique structural modulation is observed in some areas particularly near the surface regions and to the best of our knowledge this type of structural modulation is not known in the literature

FIG. 2. Various types of superstructures observed in the case of $\text{Re}_x\text{Mo}_{1-x}\text{S}_2$ alloy. Two different types of structural modulations are observed in $1T_d$ phase with $X_{\text{Re}} = 50\%$, (a) type I, where alternate rows are filled either by Re or Mo atoms giving rise to a superstructure which can be defined by $2a \times 2a$ supercell and (b) type II where the superstructure can be defined by two different $4a \times 2a$ supercells. The corresponding FFTs are shown in (d) and (e) where characteristic spots confirming the $1T$ phase and structural modulation are marked with white and yellow circles, respectively. The major difference between superstructure (a) and (b) is a two different metal-metal hybridization length (see text for details). (c) A trimer structure modulation is also observed with $X_{\text{Re}} = 25\%$ areas, where Mo atoms form corner sharing triangular arrangement. The corresponding FFT is shown in (f). The structural parameters derived from experimental images are given in the [supplementary material](#) and indicate that they are closer to the ideal hexagonal system in the case of (c) and triclinic type in case of (a) and (b). The orange circle corresponds to the upper lattice spot. The scale bar is 0.5 nm.

(Fig. 2(b)). Two consecutive parallel lines are marked along which modulation of cations is different, i.e., one short and another large distance periodic structural modulation. This can also be thought of in terms of two independent 1D Peierls distorted atomic chains or 2D type with doubling the edge of one side of the supercell unit. Considering all four atoms from the consecutive rows, a trapezoid like geometry can be identified or in other words the structural parameters can be described using two numbers of rhombuses and doubling the side along one direction (inset of Figure 2(b)). The lattice parameters are shown in the same figure. FFT also reflects the corresponding symmetry (Fig. 2(e)). The distances between the atoms, which are short and long, are 2.42 Å and 2.69 Å, respectively. This trapezoid structure can be stabilized in both tetramer type of modulation like Re_4 in ReS_2 (2D chain) and NN configurations (1D chain) depending on Re concentration as shown in Figure S3.I (supplementary material).

Trimerized modulation of 75% $\text{Re}_x\text{Mo}_{1-x}\text{S}_2$

In this case, a trimerized modulation is observed as shown in Figure 2(c). The triangles are indicated in the figure along with the schematic (inset in Fig. 2(c)) and the length of the edges is equal to each other and is 3.2 Å. At the center of the large hexagon, the Re atom is occupying the site as marked with the blue circles. The structure can also be described by two parallel lines with one of them completely occupied by Mo atoms and another one is alternately filled by Mo and Re atoms. The distance between the Mo-Re atoms is 2.8 Å. The γ is 109° in this case. The FFT shows the signature of the 1T_d phase along with structural modulation (Fig. 2(f)). The observation of stable trimer modulation is significant in the sense that such a structure was predicted to be the thinnest ferroelectric in the case of MoS_2 .²³ The present alloy offers a stable trimer system without an intercalation route and might be amenable for a possible thinnest ferroelectric device fabrication. The Mo-Mo distance in the trimmer is ~ 3.2 Å. The Re-Mo or Re-Re bond distance in the trimmer is ~ 2.8 – 2.9 Å as shown in the HRTEM images in Figure S4 (supplementary material).

In some areas, pathways of phase transition between 2H to 1T_d structure are observed due to gradual changes in Re concentrations as shown by both HRTEM and HAADF images (Figs. 3 and 4). This is an accidental finding and involves different intermediate phases depending on local Re distributions. Four distinct intermediate transition phases have been identified as shown in Figure 3. The transition from 2H to 1T_d takes place via simultaneous rotation and gliding of one of the two S planes of the 2H crystal structure. As mentioned before, the Re-Re, Re-S bond length is shorter compared to Mo-Mo, Mo-S counterpart because of the smaller ionic radius of Re. The gradual decrease in the Metal-S bond length due to introduction of Re atoms at Mo sites can be observed for the intermediate phases in going from 2H to 1T_d and these are indicated and tabulated in the same figure. The intermediate phase IV is similar to the intermediate stripe phase reported earlier for the hydrogenated 2H MoS_2 surface.⁴⁰ As already mentioned, the

presence of four different phases is due to different distribution of Re in the MoS_2 lattice which can clearly be observed in the Z contrast image and the route from 2H to 1T_d transition is indicated by arrows in Figure 3. This image shows clearly the movement of the S plane due to Re incorporation into the lattice and extent to which the plane will move depends on the local population of Re. Figures 4(b)–4(e) are showing the atomically resolved images from areas with single Re substitution, two Re atoms forming a dimmer, three Re atoms forming a trimmer, and four Re atoms forming a tetramer, respectively. The various metal-metal and metal-S bond lengths are also mentioned. It is found that the smallest Re-S bond length in mono atomic doping is 1.39 Å ($\text{Re}_1\text{-S}_1$) and for dimmer is 1.42 Å ($\text{Re}_2\text{-S}_3$) and 1.65 Å ($\text{Re}_1\text{-S}_3$). The area where four Re atom forming tetramer the metal-metal distance is 2.7 Å and 2.9 Å which is similar to the Re-Re distance in ReS_2 . Example line profiles identifying two different metals for various clustering are shown in the inset. A gradual S plane rotation (along with gliding of the plane) is observed from 2H to 1T_d phase and associated modulation of the structure due to hybridization between cations. A detailed schematic representation showing the correlation between the movements of the S plane with Re content for various intermediate phases observed experimentally is given in Figure 3 and this contain very rich structural variation in this 2D alloy system. The continuation of Figure 3 is clearly visible in the HAADF STEM image in Figure S5 (supplementary material). It is worth investigating the electronic properties of such intermediate phases, which is part of further work. The simulated diffraction pattern of distorted 1T phases from the theoretical crystal structure is well compared with selected area diffraction (SAD) in Figure S9 (supplementary material).

Alloy of $\text{Re}_x\text{W}_{1-x}\text{S}_2$

In this case, the alloy composition (i.e., 50%) is homogeneous in most of the regions probed and no variation in structural modulation is observed unlike the $\text{Re}_x\text{Mo}_{1-x}\text{S}_2$ alloy system except few areas where the deviation in modulation is observed probably due to slight variation in composition. This is due to good mixing between W and Re atoms as they are next to each other in the Periodic Table and have an almost equal atomic size. This slight variation in the composition cannot easily be determined between W vs. Re atoms, unlike Mo vs. Re atoms where the atomic number difference is high. We describe the detailed observation below;

Type I modulation of 50% $\text{Re}_x\text{W}_{1-x}\text{S}_2$

This is exactly similar to the 50% $\text{Re}_x\text{Mo}_{1-x}\text{S}_2$ alloy system described earlier with alternating layers of W and Re atoms as indicated in Figure 5(a). This gives strong superlattice spots in the FFT image which corresponds to the parallel planes containing mono-type atoms (Fig. 5(b)). This is a quasi 2D system and the geometrical parameters are given in Table 3 in the supplementary material which are slightly different compared to the MoS_2 counterpart. The angle γ is 80° between the a_1 and a_2 directions. The W-W, Re-Re, and Re-W distances are 2.78, 2.68 Å, and 2.43 Å, respectively. We

FIG. 3. (a) Is the HRTEM image showing the pathway of phase transition from 2H to 1T_d through the intermediate metastable state. The phase transition occurs via rotation and gliding of the upper S plane and is also indicated. SI and SII lines are the position of the upper S plane before and after the S plane movement while the bottom S plane is static. Re doping modulates cation (metal) as shown in yellow color. (b) Display the magnified view of gliding and rotation of upper S plane associated with intermediated phases. (c) Shows Mo-S bond length in distorted and undistorted MoS₂. (d) Is the schematic to represent evolution of the 1T_d phase from 2H through different intermediate phases. The experimentally derived metal-S bond lengths in different states are listed in the table. The scale bar is 1 nm.

do not observe type II modulation in this case like in the Re_{0.5}Mo_{0.5}S₂ alloy system.

Variation in type I modulation in Re_xW_{1-x}S₂

In some areas, variation in the lattice parameters of superstructure modulation is observed (Fig. 5(c)). This may be because of slight variation in W composition in the alloy in these areas. The two different areas are marked corresponding to regions with more 1D and 2D like modulation (Fig. 5(c)). The modulation vectors and lattice parameter for the supercell are indicated. The mechanism for 1D to 2D transition is shown in Figure S3 (supplementary material).

Density functional theory based calculation was carried out as a function of Mo and W concentration for Re_xMo_{1-x}S₂ and Re_xW_{1-x}S₂ alloy systems in both monolayer and bulk form (Fig. 6). The data of cohesive energy against alloy composition for monolayer for two different alloys are given in Figures 7(a) and 7(b) (see supplementary material for the

bulk). The cohesive energy corresponding to 2H and unmodulated 1T polytypes is indicated by different colors points. All the 1T forms of unmodulated alloys are metallic and expected to have imaginary phonon mode similar to 1T MoS₂ or ReS₂ and render them unstable and undergo 2D Peierls structural modulation.²⁴ Therefore, for some alloy composition, e.g., 25, 50, and 75 at. %, modulated 1T_d structural calculation was carried out to investigate the relative stability with respect to its un-modulated and 2H counterparts. One can observe that at ~50 at. % alloy composition a structural cross over between 2H and 1T_d takes place and the modulated structure is the most stable beyond that composition (see the data for 75%). Therefore, it can be expected that for this composition range the alloy would be stable in the modulated 1T_d form. Experimental results suggest that for the Re_xMo_{1-x}S₂ alloy system, the 1T_d modulated structure is stable even at 75 at. % in addition to 50 at. %, however, with a trimer type modulation. The initial calculations do not suggest the formation of such structural modulations

FIG. 4. (a) The STEM HAADF images show the phase transition from 2H to 1T_d through intermediate metastable phases. This is equivalent to Figure 3 but with the direct detection of Re atoms in the lattice. (b) Is the 1T_d phase and the (g) corresponding line scan showing two S peaks in between two metal atoms. (c)–(f) Show monoatomic, two, three, and four (tetramer geometry, Re₄) atom clusters in Re doped MoS₂. The figure (g), (h), and (i) are the line scan showing Re dopant corresponding to figure (b), (c), and (d), respectively. The scale bars are 0.5 nm for (a), and 0.2 nm for (b)–(f).

FIG. 5. (a) HRTEM image and (b) corresponding FFT showing the 1T_d phase with structural modulation for $X_{\text{Re}} = 50\%$ $\text{Re}_x\text{W}_{1-x}\text{S}_2$ alloy. This is similar to Type I modulation observed in the case of $\text{Re}_{0.5}\text{Mo}_{0.5}\text{S}_2$. (c) Some areas show strength of structural modulation along different directions, i.e., 2D vs. 1D, probably due to slight variation of W/Re concentration and the corresponding FFTs are shown in (d) and (e). The scale bar is 1 nm.

and defects might be playing a role stabilizing such structure through the electronic charging effect.⁴¹ It will be worth investigating both theoretically and experimentally the electronic properties of such an alloy superstructure for the stable in-plane dipole domain structure for thinnest ferroelectric devices and beyond the scope of the present discussion.²⁴ Similarly, it will also be worth investigating any novel properties arising from the type II or trapezoid type modulation for the 50% $\text{Re}_x\text{Mo}_{1-x}\text{S}_2$ alloy system as part of the future exploration. The relative energy difference between the 2H and 1T_d form of structural poly-types at 50% alloy composition is 90, 40 meV for monolayer $\text{Re}_x\text{Mo}_{1-x}\text{S}_2$ and $\text{Re}_x\text{W}_{1-x}\text{S}_2$ alloys, respectively. The relative energy difference between the 2H semiconductor and 1T metallic phase of MoS₂ and WS₂ is ~ 0.25 eV and 0.35 eV, respectively, which are one order of magnitude higher than the 50% alloy case. The relative stability of the 1T phase in the SnS₂-MoS₂ alloy system investigated earlier reported a cross over at ~ 60 at. % of Sn in the MoS₂ lattice and all the alloys are found to be metallic in nature.³⁰ The modulated 1T_d structure corresponding to 50% alloy composition for both the cases ($\text{Re}_{0.5}\text{Mo}_{0.5}\text{S}_2$ and $\text{Re}_{0.5}\text{W}_{0.5}\text{S}_2$) is shown in Figure 7. The lattice parameters are indicated with the help of rhombus geometry defined earlier. The structure is semiconducting with a band gap of

FIG. 6. Relative stability of 2H vs. 1T polytype of monolayer (a) $\text{MoS}_2\text{-ReS}_2$ and (b) $\text{WS}_2\text{-ReS}_2$ alloys as a function of Re concentration. Compositions and the corresponding energy values are marked with different colors. Approximately, at $X_{\text{Re}} = 50\%$, a structural cross over is observed between 2H and 1T and 2H and 1T_d polytypes. Also, (a) shows the energy values of different structural ground states for 50% $\text{Re}_x\text{Mo}_{1-x}\text{S}_2$ alloys. The inset is the zoomed energy values for 50% alloy composition for various structural configurations.

0.317 eV and 0.115 eV for $\text{Re}_{0.5}\text{Mo}_{0.5}\text{S}_2$ and $\text{Re}_{0.5}\text{W}_{0.5}\text{S}_2$ alloys, respectively (Figs. 7(b) and 7(c)).

However, with slightly different atomic configurations for the same composition, both metallic and semiconducting states are also found to be stable with a smaller energy difference (supplementary material). The difference between these later structural states and the most stable structural configuration is the atomic distances between two different cations. The most stable configuration is obtained if the Mo-Mo (or W-W) and Re-Re distances are different than the single

value and this is because of the different sizes of the atoms which are also reflected in different lattice parameters of the individual crystals. The energy difference between semiconducting and the metallic ground states is also small, 90 and 40 meV for $\text{Re}_{0.5}\text{Mo}_{0.5}\text{S}_2$ and $\text{Re}_{0.5}\text{W}_{0.5}\text{S}_2$ alloys, respectively. This is extremely important in the sense that by small external stimuli, e.g., strain, charge or photon energy can tune the conductivity of such a system with the slight modification of atomic arrangement within the same host lattice. This can be useful as a switch, sensors, and many novel

FIG. 7. The most stable 1T_d structure of $X_{\text{Re}} = 50\%$ (a) $\text{Re}_x\text{Mo}_{1-x}\text{S}_2$, (d) $\text{Re}_x\text{W}_{1-x}\text{S}_2$ alloy. Both the structures are semiconducting and the corresponding band structure and density of state are given (b) and (c), (e) and (f) for $\text{Re}_{0.5}\text{Mo}_{0.5}\text{S}_2$ and $\text{Re}_{0.5}\text{W}_{0.5}\text{S}_2$ alloys, respectively.

nanoscale electronic devices through metal-semiconductor transition.^{42,43} Although similar possibility exists between structural polytypes, i.e., between 2H and 1T/1T_d in the family, the energy difference is significantly higher, i.e., ~0.25–0.35 eV and only an alkali metal intercalation route has been shown to be able to control such structural transitions in a reversible way. This is in contrast to irreversible transitions in the SnS₂-MoS₂ based alloy reported earlier where the similar transition is composition dependent.³⁰ The reversible metal-semiconducting transitions between H and T' phases of W_{0.67}Mo_{0.33}Te₂ by charge mediation were also predicted theoretically with the small energy difference between the two structural polytypes.⁴²

The nature of valence and conduction bands for 50% Re_xMo_{1-x}S₂, Re_xW_{1-x}S₂ alloy cases is briefly described below. The conduction band maximum (CBM) and the valence band maximum (VBM) of MoS₂ are made of Mo d_{z^2} orbital. In the case of ReS₂, both the VBM and CBM have significant contributions from $d_{x^2-y^2}$ and d_{xy} orbitals. In the case of MoS₂, the direct transition occurs from K (VBM) to K (CBM) and for ReS₂, it is from Γ (VBM) to Γ (CBM). For the two alloy cases, we have found a stable semiconductor state for both Re_{0.5}Mo_{0.5}S₂ and Re_{0.5}W_{0.5}S₂ with the triclinic state having *P*1 crystallographic symmetry. The Brillouin zone and the symmetry points used for plotting band structure are shown in the [supplementary material](#) (Fig. S10). The VBM energy value at M point is comparable with R point but the CBM energy at M point is lowest for Re_{0.5}Mo_{0.5}S₂. The Re_{0.5}Mo_{0.5}S₂ structure shows a fundamental and direct band gap of 0.317 eV with fundamental transition between M and M (Fig. 7(b)). An indirect transition from M to X having band gap of 0.115 eV is found for Re_{0.5}W_{0.5}S₂ (Fig. 7(e)). Figures 7(c) and 7(f) show that for Re_{0.5}Mo_{0.5}S₂, the fundamental direct band transition has significant contribution from Mo d_{z^2} , and $d_{x^2-y^2}$ orbitals at VBM and d_{xy} orbital at CBM and similarly the fundamental indirect band transition for Re_{0.5}W_{0.5}S₂, is primarily due to the Re $d_{x^2-y^2}$ orbital at the VBM and W d_{xy} orbital at the CBM. The band structure and DOS for other stable configurations are shown in Figure S8 and the related lattice parameters are listed in Table 2 ([supplementary material](#)).

CONCLUSIONS

In summary, alloy formation, 2H vs. 1T_d structural stability, and electronic structure between MoS₂/WS₂ and ReS₂ have been explored both by theory and experiment. Theory indicates a structural cross over between 2H and 1T_d at approximately 50% alloy composition for both the system. Experimentally, two different structural modulations for 50% and a trimerized modulation are observed in Re_{0.25}Mo_{0.75}S₂ and only tetramerized modulation is observed for WS₂-ReS₂ alloy systems. The trimer modulation could offer the stable thinnest platform to explore the ferroelectric device. The 50% alloy system is found to be a suitable monolithic candidate for metal semiconductor transition with minute external perturbation. The results show yet another way to tune the various structural types and the

corresponding electronic structure in this important class of material systems.

SUPPLEMENTARY MATERIAL

See [supplementary material](#) for HRTEM, Z-contrast STEM HAADF image, schematic model, EDS, Band structure and DOS, table contains lattice parameter of the Re_{0.5}Mo_{0.5}S₂ and Re_{0.5}W_{0.5}S₂ alloy system.

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