Atomic structure and Edge Magnetism in MoS_{2+x} Parallelogram Shaped Platelets†

J. Karthikeyan,[a] Vijay Kumar,[b,c‡] and P. Murugan*[a]

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[a] *CSIR Central Electrochemical Research Institute, Karaikudi - 630 006, Tamil Nadu, India*
[b] *Dr. Vijay Kumar Foundation, 1969 Sector 4, Gurgaon 122 001, Haryana, India*
[c] *Center for Informatics, School of Natural Sciences, Shiv Nadar University, Chithera, Gautam Budh Nagar 203 207, Uttar Pradesh, India*

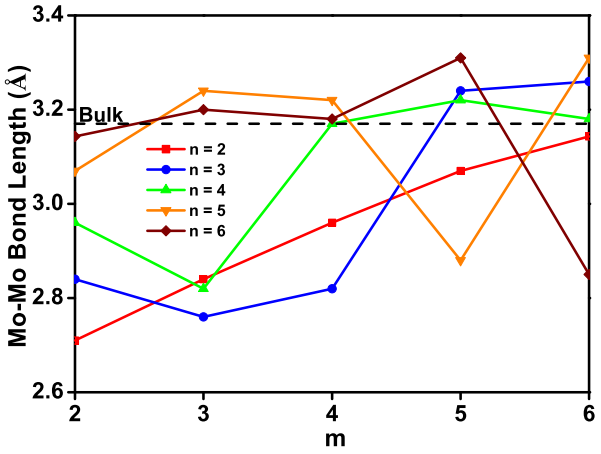

Fig. S 1 The mean Mo-Mo bond distance in triangular metallic corner which was observed in 100% S covered side of (*n*,*m*) parallelogram platelets. Horizontal dotted line shows the bulk Mo-Mo bond distance. For $m = n$, the bond distances are short except for (4,4) platelets.

From our calculations, we observed that at the corner of 100% S covered side of the platelets with $m = n$, three Mo atoms are strongly bonded with each other and form a triangular metallic corner which is shown in Fig. S1. These Mo atoms are surrounded by polysulfide S_2^{2-} ions. Note that the Mo-Mo bond distance at this corner is always the lowest for all the platelets with $m = n$, except for the (4,4) platelet.

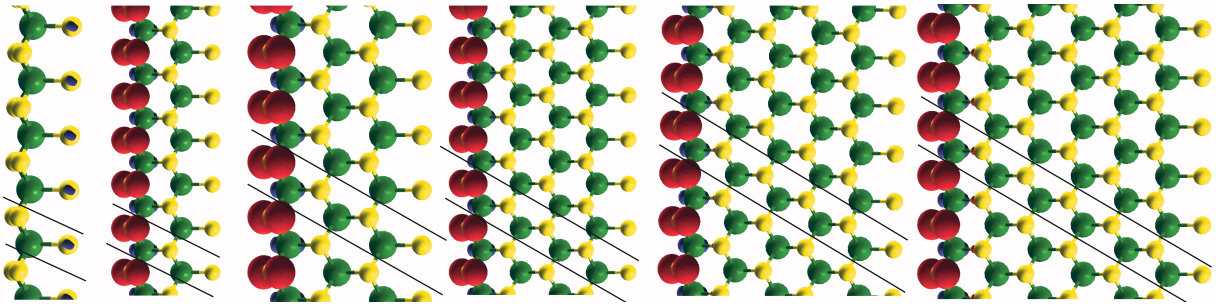

Fig. S 2 Spin density distribution of optimized (m,∞) nanoribbons with m = 1 - 6 and the isosurface value of 89×10^{-3} e^{-}/ Å^3. The green and yellow balls correspond to Mo and S atoms, respectively and the lines represent the periodicity of the unit cell

Figure S2 shows that the magnetism in nanoribbons arises only from S(2c) atoms at 50% S covered side which is true for platelets also. It also infers that p_z orbital contributes to the moment in S(2c) atoms. The observed total magnetic moment for all nanoribbons except (1,∞) is close to 0.65 μ_B which is due to the same number of edge S(2c) atoms in the unit cell of all the nanoribbons. The non magnetic nature of (1,∞) can be well explained by the results obtained from platelet case; it is because of the attachment of S(2c) atoms and the dimer with the Mo atom.

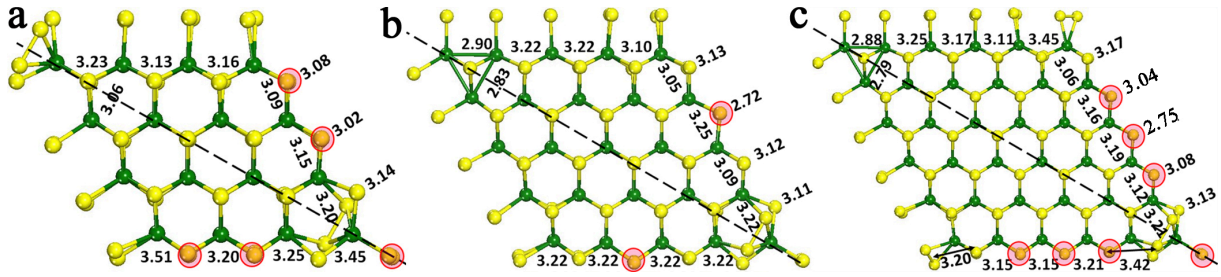

Fig. S 3 Ball and stick model of the optimized structure of a) (4, 4), b) (5, 5), and c) (6, 6) platelets. Green and yellow balls correspond to Mo and S atoms, respectively. The bond distances of the edge Mo-Mo atoms and S(2*c*)-S(2*c*) atoms (along the edges) are shown in between those atoms. Further, S(2*c*)-S(2*c*) bond distances (perpendicular to the plane of the platelet) are written along the direction perpendicular to the edge. S atoms carrying magnetic moments are marked by pink colored circles. Dotted line depicts the mirror symmetry.

As the bond distance is the governing parameter of magnetism in these platelets, we measured various Mo-Mo, Mo-S, and S-S bond distances in (4,4), (5,5), and (6,6) platelets and these are shown in Fig. S3. Platelets having equal *m* and *n* values possess mirror symmetry. Apart from the separation between S(2*c*)-S(2*c*) bond distances, edge Mo-Mo interaction also plays a crucial role in magnetism of some S(2*c*) atoms. We observed that the moment on S(2*c*) atoms occurs when Mo-Mo atoms are separated by a distance above 3.1 Å. Below this distance, Mo-Mo atoms interact strongly, and it leads to quenching of the moment on S(2*c*) atoms. In addition to S(2*c*) atoms, sulfur dimer also carries magnetic moments at the corner of 50% S covered side, which is due to the fractional charge transfer from Mo atoms.