

# New crystal structures of the transition metall dichalcogenides

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## Abstract

## Introduction

Transition metall dichalcogenides (TMD) crystallise in four main structural types: type of CdI<sub>2</sub> (further denoted as C), type of MoS<sub>2</sub> (further denoted as W), type of pyrite and less frequent type of marcasite. First two structural types are characterised by the layered structures with S-M-S sandwiches bonded by the weak Van-der-Waals bonds. The 2D layers attracts considerable attention due to their semiconducting, superconducting and magnetic properties. In particular, 2D layers of MoS<sub>2</sub>, WS<sub>2</sub>, MoSe<sub>2</sub>, WSe<sub>2</sub>, and MoTe<sub>2</sub> have a direct band gap and can be used as transistors and due to strong spin-orbit coupling are perspective spintronics.

The top-layer of sulphur in the the sandwich of MoS<sub>2</sub> was successfully changed on the layer of Se with formation of the so-called Janus SMoSe structure [?]. In the present work based on crystal structure prediction technique and common crystalchemical consideration we reveal new stable Janus structures of Mo, W and V and perform their extensive topological analysis. The special paper will be devoted to the electronic properties of the found structures.

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### 0.0.1 Crystal structures of MCh<sub>2</sub>, M=Mo,W,Vm, Ch=S,Se

At ambient conditions both MoS<sub>2</sub>, WS<sub>2</sub>, MoSe<sub>2</sub>, WSe<sub>2</sub> crystallises in the archetype molibdenite (MoS<sub>2</sub>) structure (W, 2H polytype). In these structure atoms of chalcogenides form close-packed layers placed exactly one under another along c-axis. TM atoms occupy center of trigonal prismatic cavities between the layers. Different stacking of such a 2D layers produce different polytypes, but they are out of scope of the present work, where we consider only isolated 2D-layers.

If the layers of chalcogene atoms are shifted such that the top-layerd is placed in triangular holes fromed by the atoms of bottom-layer, the archetype CdI<sub>2</sub> (C, 1T polytype) structure is formed. In this case, TM atoms are in octahedral coordination.

Considered compounds are not yet known in the form of bulk crystal with 1T structure

V is different from W and Mo in that it does not produce dichalcogenides at ambient conditions or this compounds needs some additional factors for stabilisation. VS<sub>2</sub> compound is not known. VSe<sub>2</sub> is known in the form 2H structure with additional V adoms in the centers of empty trigonal prisms in between the sandwiches and composition Se<sub>2</sub>V<sub>1.005</sub> V<sub>1.04</sub>Te<sub>2</sub> has not-layered structure with isolated clusters.

## 1 Methods

## 2 Results

### 2.1 Similarity and differences of H, T, fxt and fes structures

H and T structures Although H and T structures are charactersied by the different coordination polyhedrons, they are similar in the manner of interconnection of these polyhedrons. H structure consists of trigonal prisms MoS<sub>6</sub> (MoS<sub>3</sub>Se<sub>3</sub> for Janus structures), and T structure – of the octahedra of the same composition (Figure??H1T). Each trigonal prism share all three vertical edges with the neighboring prisms and does not share any faces. As the result each vertice [and each verical edge] of the trigonal prism is common for three prisms (Figure??H1T). Similarly in T structure, each octahedron share all edges inclined to the plane of sulphur atoms with neighbouring octahedra, and each vertice is common for three octahedra (Figure??H1T). Bond valence of Mo–S bond is nearly equal to +4/6 and there are necessary three such a bonds on the sulphur atom to compensate its negative charge of 2<sup>-</sup>. The interconnection through the edges but not faces provides the longer distance between high-charged Mo<sup>4+</sup> ions, reducing the energy of Coulomb interaction. Thus in full accordance with Pauling rules, the arrangement of trigonal prisms and octahedra corresponding to H and T structures is most energetically favourable (Table ??), in full accordance with the well known Pauling rules [?].

fxt and fes structures The topology of recently found fes and fxt structures principally is different from that of H structure in the manner trigonal prisms are connected not only through edges but also through the faces. The whole structure can be constructed from the two edge-connected trigonal prisms (Figure ??b). As the result, the enthalpis of fxt and fes structures are higher than that of H structure. However, as well as in H and T structures, each at sulphur are connected to three Mo atoms in fxt and fes structure, providing the mentioned local charge balance. As we will show below the local charge balance is not the obligatory requirement for the dynamical stability of the structure.

H and T structures provide the most homogenic distribution of sulphur as we as Mo atoms. Both nets of the Mo atoms and and S atoms consists of the geometrically equal triangular loops. Eadge-sharing interconnection of trigonal prisms realised in fxt and fes structure inevitably leads to the appearance of the cavities bigger than that in H and T structures. In fes structure the cavities are in the form of the slightly compressed cube (Figure ??). The volume of these cavities is almost two times large than the volume of the cavities in H structure ( $38.8$  against  $17.7 \text{ \AA}^3$ ). In casse of fxt structure, the volume of hexagonal cavities (Figure ?? is almost 8 times greater in comparison with H structure ( $137.8$  against  $17.7 \text{ \AA}^3$ ). In contrast to trigonal prisms, the face-sharing of the rights octahedra seems to be problematic for quasi 2D structure, as it is results in deviation from the flat arrangement (Figure??b). However, as it will be shown belown, the dynamically stable structures with face sharing deformed octahedra can also produced.

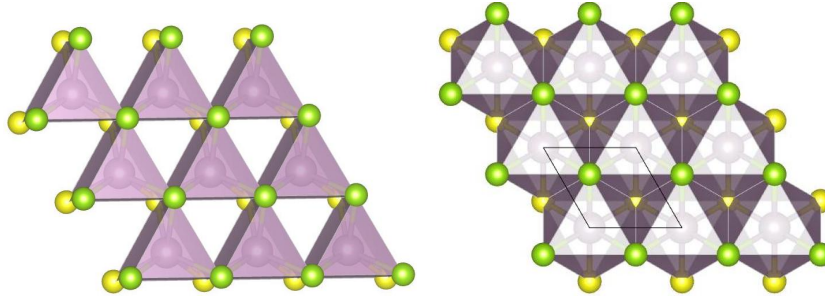


Figure 1: Packing of trigonal prisms and octahedra in H and T structures

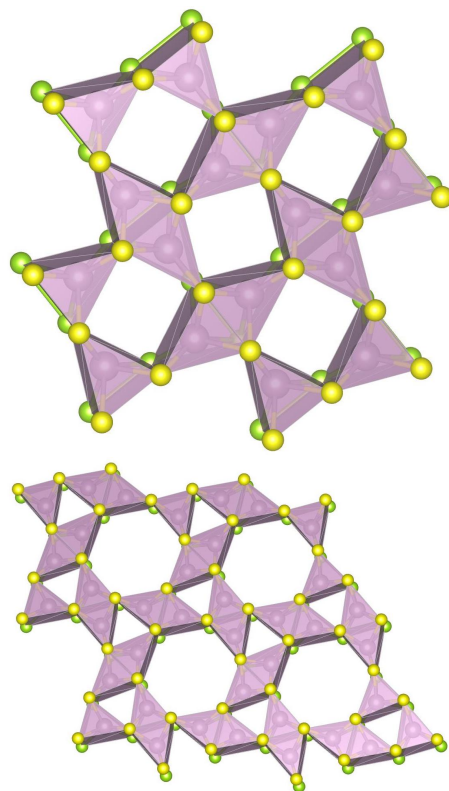


Figure 2: Packing of trigonal prisms in fes and fxt structures.

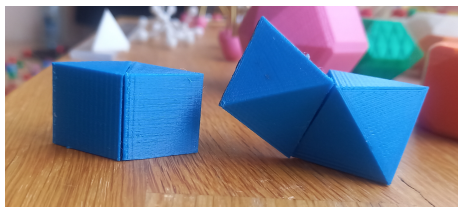


Figure 3: Two face-shared trigonal prisms and octahedra, the deviation from the horizontal plane in the last case is clearly visible

## 2.2 Construction of the structures with trigonal prismatic coordination

To compare topologies of H, fes, and fxt structures and produce similar structures with trigonal prismatic coordination, we present them as different fillings of the same hexagonal net of sulphur atoms (Figure 4). H-structure presents

the most symmetric chess-board filling. Fes structure can be also considered as the chess-board, but with doubled triangular cell. In the initial fes structure constructed in such a manner, white cells have the form of rhombuses. After optimisation these rhombuses transform in the described above right squares. In fxt structure the white loops are of two types. The first are three doubled triangular (rhombuses) connected through the faces. They have the form of right hexagons. The second are primitive triangular. The optimisation does not sufficiently change the form of these white loops, only lightly deforming hexagons.

Four new structures were produced by means of the filling of triangles in the hexagonal net of the sulphur atom, named as test1, test2, test3, and test4. We failed to produce new structures obeying the local charge balance, i.e. the structures in which each sulphur vertex is common for three trigonal prisms, and only global charge balance in test1, test2, test3, test4 structure is obeyed. In test1 structure, S-vertices are common for two or four filled prisms, in test2 and test 3 – for 2, 3, and 4 (Figure 4). The net of the light element of test3 structure, produced based on the net of H structure by the deletion and shift of some atoms (Figure 4).

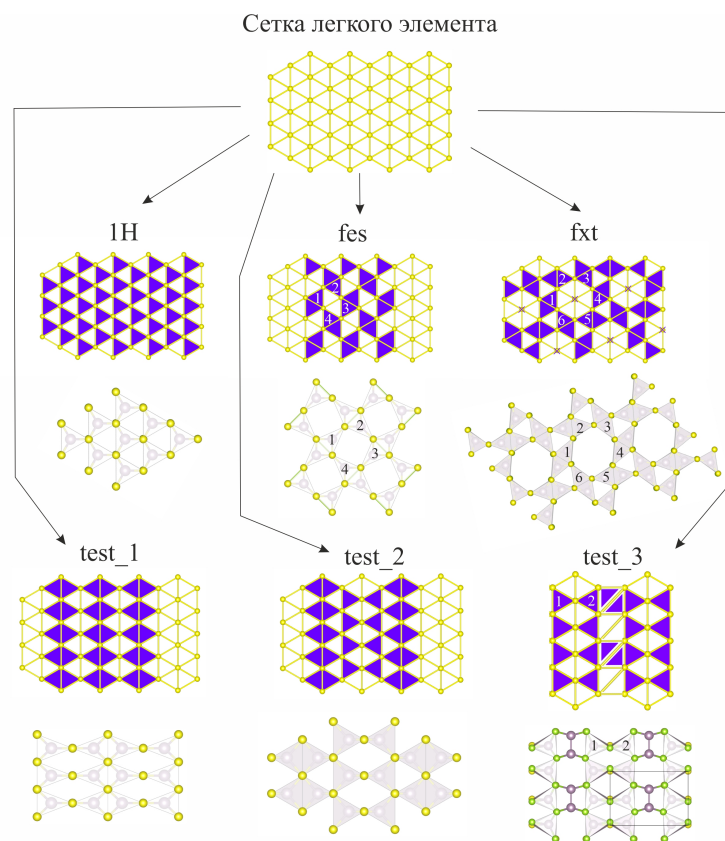


Figure 4: The construction of the new structures based on H structure of MoSSe