

New crystal structures of the transition metall dichalcogenides

Pavel N. Gavryushkin ^{*1,2}, Nursultan Sagatov¹, and Zakhar I.
Popov³

¹*Sobolev Institute of Geology and Mineralogy, Siberian Branch of
Russian Academy of Sciences, prosp. acad. Koptiyuga 3, 630090
Novosibirsk, Russian Federation*

²*Novosibirsk State University, Pirogova 2, Novosibirsk 630090,
Russian Federation*

³*ИБХФ*

Abstract

1. Проведены предсказания и обнаружены новые (horizontal) структуры, существенно отличающиеся от ранее известных H и T
2. Несмотря на энергетическую метастабильность относительно H и T структур, рассчитанные Фононные спектры подтверждают их динамическую стабильность
3. С помощью автоматизированных топологических алгоритмов проведён поиск топологических аналогов. Все структуры, включая fxt и fes характеризуются уникальными топологами и не имеют структурных аналогов в ICSD. Исключение составляет horH структура, имеющая порядка 50 аналогов среди слоистых структур. Это открывает возможность использования этих структур в качестве подложки при синтезе методом напыления.

Introduction

Transition metall dichalcogenides (TMD) crystallise in four main structural types: CdI₂ (further denoted as C), MoS₂ (further denoted as W), FeS₂ (pyrite-type and less frequently type of marcasite-type). First two structural types are characterised by the layered structures with S-M-S sandwiches bonded by the weak Van-der-Waals bonds. Where instead of S can be also Se and Te. The

*Electronic address: gavryushkin@igm.nsc.ru, p.gavryushkin@ng.nsu.ru; Corresponding author

quasi-2D S-M-S layers attract considerable attention due to their semiconducting, superconducting and magnetic properties. In particular, 2D layers of MoS₂, WS₂, MoSe₂, WSe₂, and MoTe₂ have a direct band gap and can be used as transistors and due to the strong spin-orbit coupling are perspective spintronics.

The top-layer of sulphur in the the sandwich of MoS₂ was successfully changed on the layer of Se with the formation of the so-called Janus SMoSe structure [?]. In the present work based on crystal structure prediction technique and common crystallchemical consideration we reveal new stable Janus and perform their extensive topological analysis. Using topological analysis we analyse uniqueness of the found structures and show its perspective analogues in ICSD database. Preliminary calculations of the electronic structures shows that some of the found structures are direct band gap semiconductors (поправьте меня если я не прав тут). The special paper will be devoted to the results of these calculations.

0.0.1 Crystal structures of MCh₂, M=Mo,W,Vm, Ch=S,Se

At ambient conditions both MoS₂, WS₂, MoSe₂, WSe₂ crystallises in the archetype molibdenite (MoS₂) structure. 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. If the repetition stacking is reproduced through each two layers the structure has hexagonal symmetry and according to Ramsdell notation is denoted as 2H-polytype. As in the present manuscript, we consider only isolated 2D-layers, we will designate them as H-layers.

If the layers of chalcogene atoms are shifted such that the top-layerd is placed in triangular holes formed by the atoms of bottom-layer and such a quasi-2D layers are without a shift one under the other, the 1T-polytype of archetype CdI₂ structure with trigonal symmetry is formed. the archetype CdI₂ (C, 1T polytype) structure is formed. In this case, TM atoms are in octahedral coordination. The separate layers of such a structure will be designate as T-layer.

Considered compounds with Mo, W, and V as TM and S, Se, and Te as chalcogenes are not yet known in the form of bulk crystal with 1T structure. However 1T structure can be stabilised by the impurities of Li atoms or by some deformations (Захар, добавь тут ссылка

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. VS₂ compound is not known. VSe₂ is known in the form 2H structure with additional V adoms in the centers of empty trigonal prisms in between the sandwiches and composition Se₂V_{1.005} V_{1.04}Te₂ 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 characterised by the different coordination polyhedrons, they are similar in the manner of interconnection of these polyhedrons. H structure consists of trigonal prisms MoS_6 (MoS_3Se_3 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 vertex [and each vertical 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 vertex 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^- . The interconnection through the edges but not faces provides the longer distance between high-charged Mo^{4+} 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 enthalpies of fxt and fes structures are higher than that of H structure. However, as well as in H and T structures, each atom of sulphur is 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 well as Mo atoms. Both nets of the Mo atoms and S atoms consists of the geometrically equal triangular loops. Edge-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 \AA^3). In case of fxt structure, the volume of hexagonal cavities (Figure ?? is almost 8 times greater in comparison with H structure (137.8 against 17.7 \AA^3). In contrast to trigonal prisms, the face-sharing of the right octahedra seems to be problematic for quasi 2D structure, as it results in deviation from the flat arrangement (Figure ??b). However, as it will be shown

below, the dynamically stable structures with face sharing deformed octahedra can also be produced.

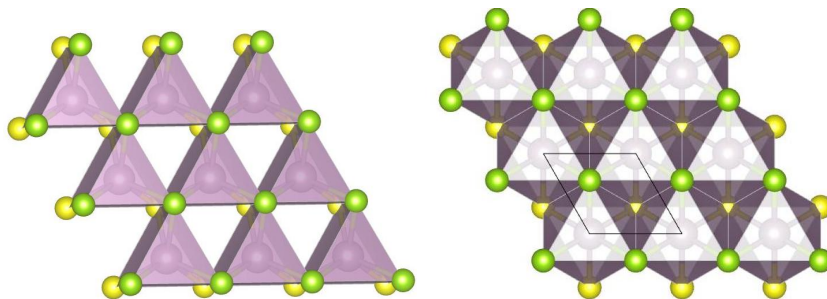


Figure 1: Packing of trigonal prisms and octahedra in H and T structures

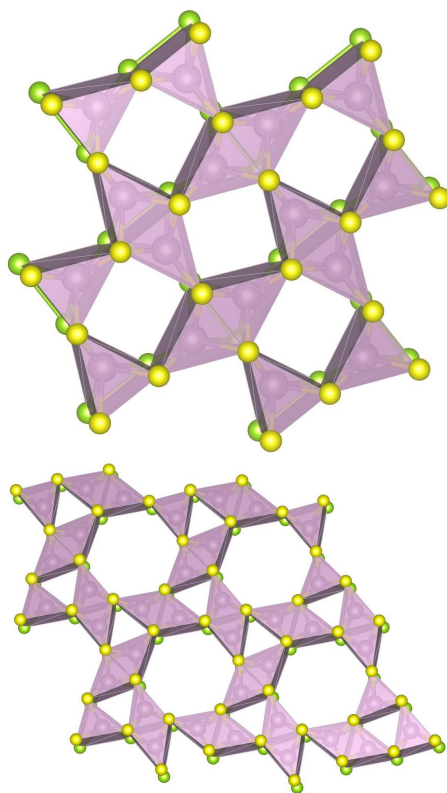


Figure 2: Packing of trigonal prisms in fes and fxt structures.

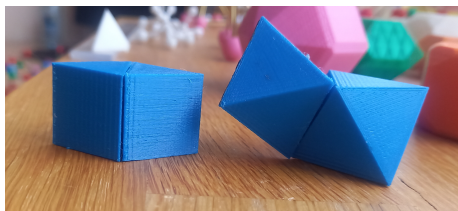


Figure 3: Two face-shared trigonal prisms and octahedra, the deviation from the horizontal plane in the last case is clearly visible

2.2 The new crystal structures

2.2.1 Structures with trigonal prismatic coordination

To compare topologies of H, fes, and fxt structures and produce similar structures with trigonal prismatic coordination, we present the structures as different fillings of the hexagonal net of sulphur atoms (Figure 4). H-structure presents the most symmetric filling similar to chess-board with triangular cells. The fes structure can be also considered as the chess-board, but with doubled triangular cell, having 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, having the form of right hexagons. The second are primitive triangles. The optimisation does not sufficiently change the form of the white loops, only slightly deforming hexagons.

Three new structures were produced by means of the filling of triangles in the hexagonal net of the sulphur atoms, named test1, test2, and test3. We failed to produce new structures obeying the local charge balance, i.e. the structures in which each vertex of the trigonal prism is common for two other prisms. In the structure test1, each sulphur atom is common for two or four filled prisms, in test2 and test 3 – for 2, 3, and 4 (Figure 4). Test 3 structure is different from other structures in that it is characterised by the presence of trigonal prisms with two common faces, while in all other structures prisms have no more than one common face. This results in the shortening of the Mo–Mo–Mo distance, for Mo atoms placed in the neighbouring trigonal prisms. Optimisation of test 3 structure sufficiently affects the arrangement of sulphur atoms coordinating these closely spaced Mo atoms, as well as atoms themselves. In the final structure the net of sulphur atoms is not the hexagonal one and coordinations of some of Mo atoms, change from trigonal prismatic to subsquare quadratic.

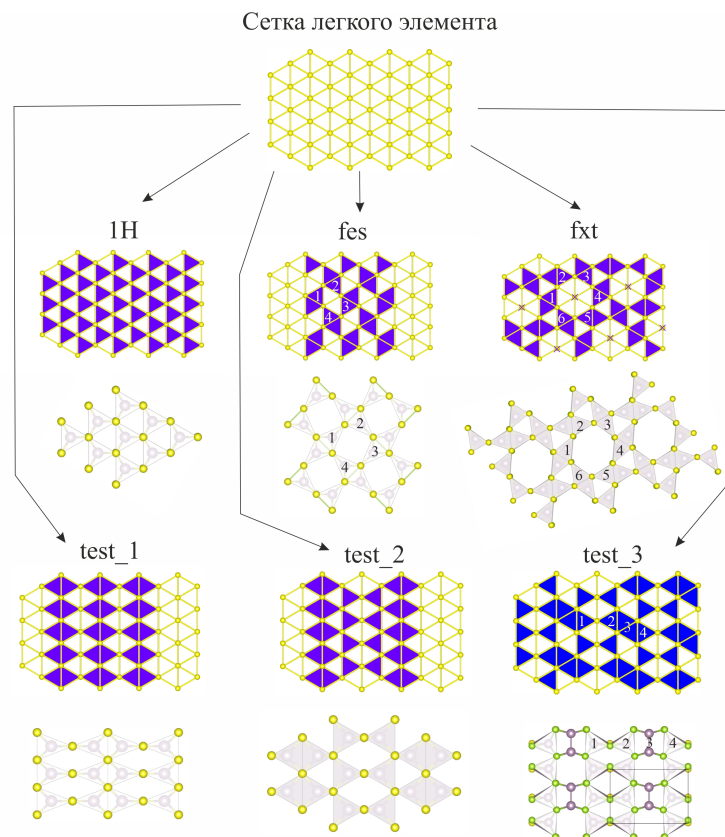


Figure 4: The initial and optimised structures of MoSSe. Тут нужно убрать связь Mo-Mo для test3 и возможно показать Mo3 в профиль

Another structure characterising by trigonal prismatic coordination was found by means of USPEX code. It is sufficiently different from all the considered above structures in that three-fold axes of trigonal prisms are parallel to the plane of sulphur atoms. As the result the loops of the net sulphur atoms is not more hexagonal, but square. This structure was called Hhor (from H-horizontall)

2.2.2 Structures with octahedral coordination

As it was mentioned above T structure, composed of closely packed octahedra does not give such a flexibility as H-structure, as contact of octahedra through the face results in the coorigation of the plane of sulphur atoms. One such a structure with face-shared octahedra have been found with AIRSS code. In this structure each octahedra have four common edges and one common face. The presence of the common face results in the sufficient corrugation of the layers of sulphur, in contrast to earlier considered structures, which a relatively flat

ones. This structure was called T-hor.

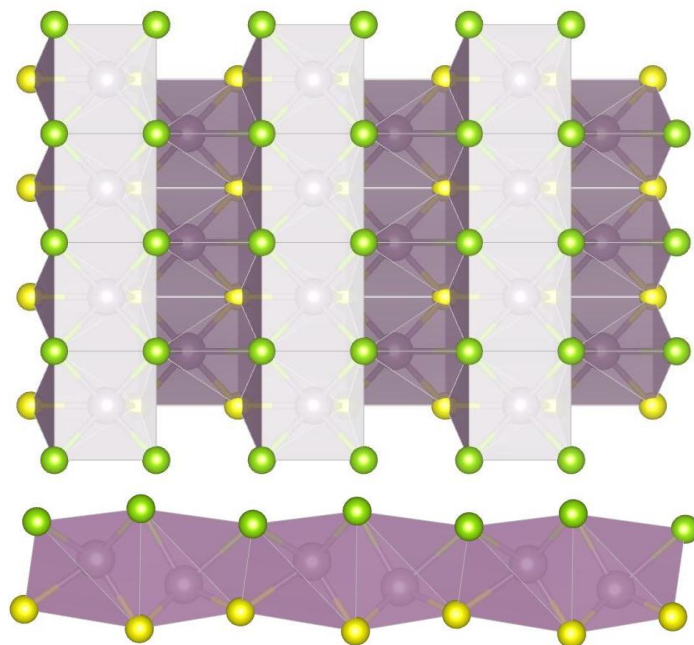


Figure 5: H-hor crystal structure perpendicular and along the layer.

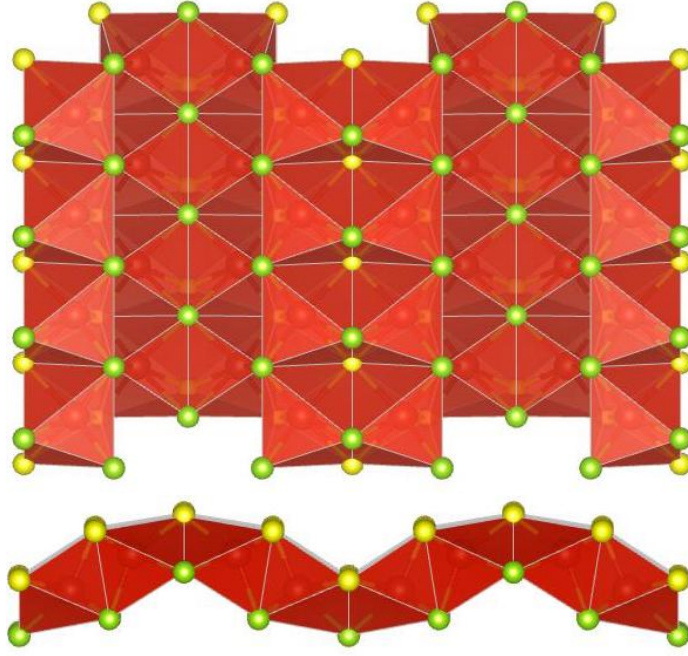


Figure 6: T-hor crystal structure perpendicular (left) and along(right) the layer.

2.3 Stability of the predicted structures