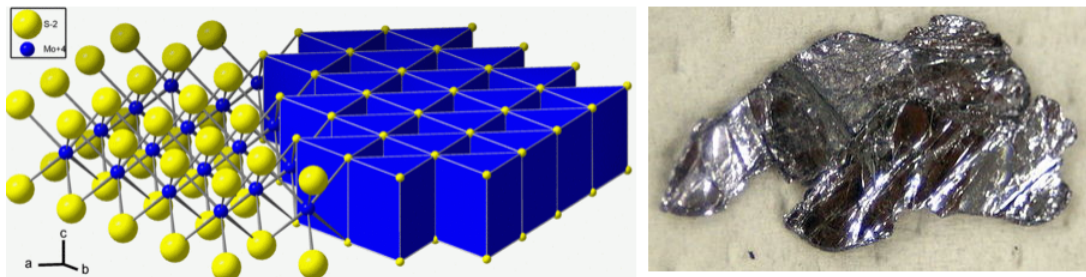


8.6: Bonding in TiS_2 , MoS_2 , and Pyrite Structures

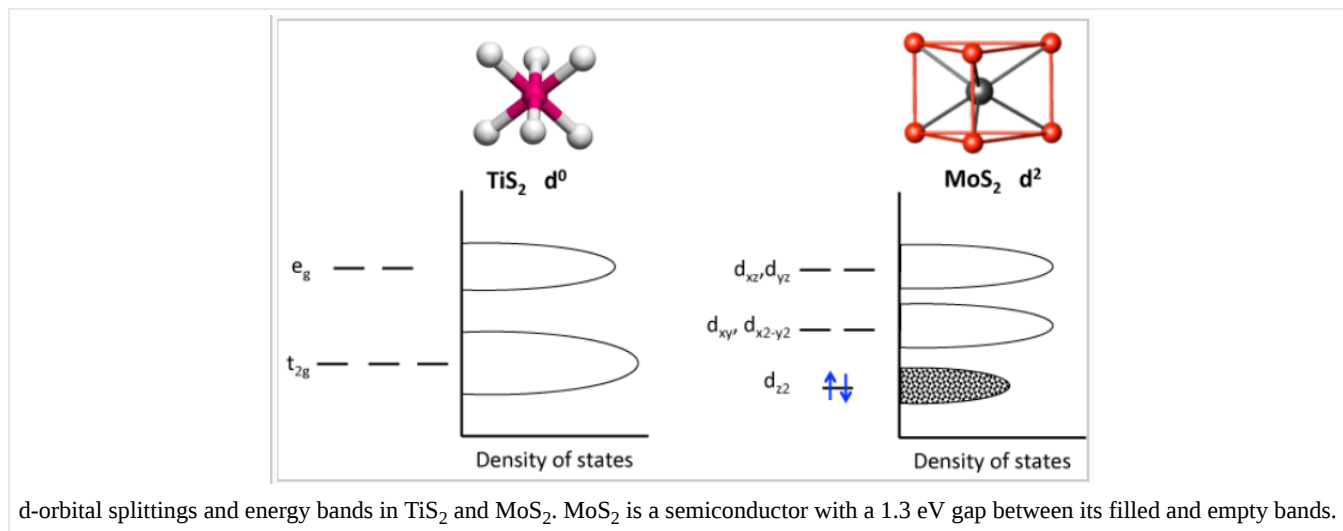
Many layered dichalcogenides, such as TiS_2 and ZrS_2 , have the CdI_2 structure. In these compounds, as we have noted above, the metal ions are octahedrally coordinated by S. Interestingly, the structures of MoS_2 and WS_2 , while they are also layered, are different. In these cases, the metal is surrounded by a **trigonal prism** of sulfur atoms. NbS_2 , TaS_2 , MoSe_2 , MoTe_2 , and WSe_2 also have the trigonal prismatic molybdenite structure, which is shown below alongside a platy crystal of MoS_2 .



The coordination of the metal ions by a trigonal prism of chalcogenide ions is **sterically unfavorable** relative to octahedral coordination. There are close contacts between the chalcogenide ions, which are eclipsed in the stacking sequence **AbA/BaB/AbA/BaB...** (where "/" indicates the van der Waals gap between layers). What stabilizes this structure?

The molybdenite structure occurs most commonly in MX_2 compounds with a **d^1 or d^2 electron count**. The figure below compares the splitting of d-orbital energies in the octahedral and trigonal prismatic coordination environments:

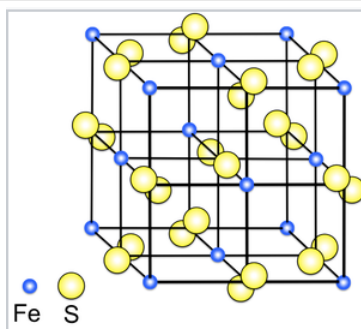
The trigonal prismatic structure is stabilized in MoS_2 by filling the lowest energy band, the d_{z^2} . The d_{z^2} orbital which points vertically through the triangular top and bottom faces of the trigonal prism, has the least interaction with the sulfide ligands and therefore the lowest energy. The d_{xz} and d_{yz} orbitals, which point at the ligands, have the highest energy. The d_{z^2} orbital is lower in energy in this structure than the t_{2g} orbitals are in the octahedral structure of TiS_2 .



Because it has an unfilled t_{2g} band, TiS_2 is relatively easy to reduce by intercalation with Li. For this reason, LiTiS_2 was one of the first intercalation compounds studied by Stanley Whittingham, who developed the concept of the non-aqueous lithium ion battery in the early 1970's.^[3] Because it has a filled d_{z^2} band, MoS_2 is harder to reduce, but it can be intercalated by reaction with the powerful reducing agent n-butyllithium to make Li_xMoS_2 ($x < 1$). Atoms in the van der Waals planes of these compounds are relatively unreactive, which gives MoS_2 its good oxidative stability and enables its application as a high temperature lubricant. Atoms at the edges of the crystals are however more reactive and in fact are catalytic. High surface area MoS_2 , which has a high density of exposed edge planes, is used as a hydrodesulfurization catalyst and is also of increasing interest as an electrocatalyst for the reduction of water to hydrogen.

Layered metal dichalcogenides, including MoS_2 , WS_2 , and SnS_2 , can form closed nanostructures that take the shape of multiwalled onions and multiwalled tubes. These materials were discovered by the group of Reshef Tenne in 1992, shortly after the discovery of

carbon nanotubes. Since then nanotubes have been synthesized from many other materials, including vanadium and manganese oxides.



The pyrite (FeS_2) crystal structure. The structure is related to NaCl, with Fe^{2+} and S_2^{2-} ions occupying the cation and anion sites.

Although early (TiS_2) and late (PtS_2) transition metal disulfides have layered structures, a number of MS_2 compounds in the middle of the transition series, such as MnS_2 , FeS_2 and RuS_2 , have three-dimensionally bonded structures. For example, FeS_2 has the **pyrite structure**, which is related to the NaCl structure. The reason is that FeS_2 is not $\text{Fe}^{4+}(\text{S}^{2-})_2$, but is actually $\text{Fe}^{2+}(\text{S}_2^{2-})$, where S_2^{2-} is the disulfide anion (which contains a single bond like the peroxide anion O_2^{2-}). S^{2-} is too strong a reducing agent to exist in the same compound with Fe^{4+} , which is a strong oxidizing agent. Because FeS_2 is actually $\text{Fe}^{2+}(\text{S}_2^{2-})$, it is a 1:1 compound and adopts a 1:1 structure.

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