

Metavalent bonding under pressure: the case of orpiment

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Metavalent or resonant bonding is a recently proposed new class of bonding that is intermediate between p-type covalent bonding and metallic bonding. It characterizes a new family of materials known as “incipient metals” [1]. Metavalent bonding occurs in materials where there is a deficiency of valence electrons in the unit cell to form a large number of bonds, such as in octahedrally-coordinated rocksalt-related structures occurring in GeTe, SnTe, PbSe, PbTe, Sb₂Te₃, Bi₂Te₃, Bi₂Se₃, Sb, Bi and AgSb₂Te₄.

The main characteristics of metavalent bonding are: i) a much higher cation coordination than that assumed with the 8-N rule; ii) very high Born effective charge and optical dielectric constant as compared to typical covalent materials; iii) high mode Grüneisen parameters of phonons and low wavenumbers of optical phonons as compared to typical covalent materials; and iv) a moderately high electrical conductivity caused by the small bandgap which stems from the partial delocalization of electrons between several bonds.

Arsenic sulfide (As₂S₃), and in particular the monoclinic polymorph (α -As₂S₃), aka mineral orpiment, is one of the ores of As together with realgar (α -As₄S₄) and arsenopyrite (FeAsS) minerals [2]. In particular, orpiment and realgar are known since ancient times, where realgar was used as a red pigment and orpiment as a gold-like pigment (*Aurum pigmentum* in latin), hence his mineral name orpiment [3].

Despite existing several high-pressure studies on orpiment [4], many of its properties are not well known even at ambient pressure. In particular, the behavior of its structural, vibrational and electronic properties both at room and high pressure are far from being understood. Here, we present a joint experimental and theoretical study of the structural, vibrational and electronic properties of orpiment under compression, which unveils the internal mechanisms that emerge in orpiment during compression. We discuss the equation of state and the internal polyhedral compressibility, the symmetry and behavior of the Raman-active modes and the of the electronic band structure of orpiment under compression and compare them to its parent binary compounds.

Our X-ray diffraction and Raman measurements together with theoretical calculations evidence the presence of an isostructural phase transition around 25

GPa leading from a three-fold coordination of As atoms at room pressure to an As coordination larger than five above 25 GPa (see Figure 1).

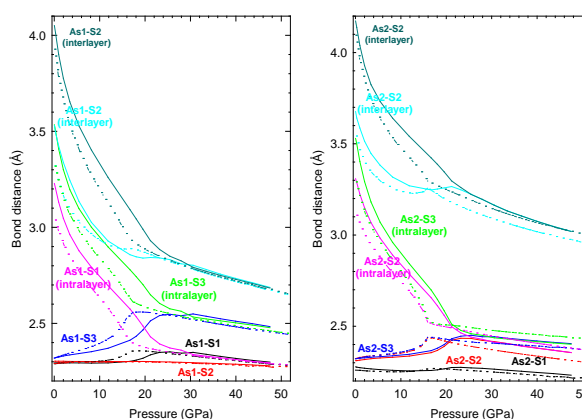


Figure 1. Theoretical pressure dependence of the interatomic distances in orpiment with (solid) and without (dashed) van der Waals interactions.

The behavior of the structural parameters, Raman and infrared vibrational frequencies and optical bandgap of orpiment under compression can be understood on the light of the metavalent bonding concept; i.e. above 25 GPa, orpiment undergoes a transition from a solid featuring intra-layer p-type covalent bonds and inter-layer van der Waals bonds to a solid with intra-layer and partially inter-layer resonant bonds. This behavior is similar to that recently found for GeSe, where a pressure-induced intra-layer metavalent bonding is observed above 40 GPa after a first-order phase transition [5]. On further compression, full metallization of orpiment is predicted, which is observed above 40 GPa.

In summary, pressure transforms orpiment, a layered semiconductor with p-type covalent bonds and van der Waals interactions at room pressure, into an incipient metal, with metavalent bonds, above 25 GPa, and finally into a metal, with metallic bonds, above 40 GPa. We propose that this path from covalent bonding to metal bonding going through metavalent bonding is also followed by many other compounds with IV-VI and V₂-VI₃ stoichiometry as well as by their related ternary and multinary compounds.

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