

**substance: (transition metal)-V-VI compounds**  
**property: crystal structure, chemical bond**

Most of the semiconducting TXY pnigochalcogenides are ternary analogs of the corresponding binary phases with the same cation d electron configuration. Therefore, these phases may exist in a disordered high-temperature modification as well as in an ordered low-temperature modification. In the ternary pyrites, marcasites, pararammelsbergites and in the arsenopyrites the cations are in distorted octahedral coordination while the anions possess  $3T + 1(X,Y)$  neighbors at the apices of a distorted tetrahedron. In the ternary pyrites anion ordering is possible in at least four variants [73E], but only two of them were detected until now. One of these is the cubic ullmannite type, space group  $T^4 - P2_13$ , met in the high-pressure modification of CoSbS. The other ordered variant is the cobaltite type of pseudocubic CoAsS and of orthorhombic PtGeSe, space group  $C_{2v}^5 - Pca2_1$ . In the known ordered variant of marcasite, which is similar to arsenopyrite, one of the glide planes is absent, and this reduction of the symmetry transforms the space group from  $D_{2h}^{12} - Pnnm$  to  $C_{2v}^7 - Pn2_1m$ .

In pararammelsbergite  $\alpha$ -NiAs<sub>2</sub> the anions occupy two sets of the general positions 8(c) of space group  $D_{2h}^{15} - Pbca$ . Thus, ordering is possible within the same space group. In this structure type layering of the cation coordination octahedra perpendicular to the *c*-axis is based on pyrite-type {100} planes alternating with marcasite-type {101} planes. In the pararammelsbergite-type modification of CoSbS (paracostibite) these alternating layers have every second "arsenopyrite" layer in reverse orientation. The pyrite-type layers contain the Sb atoms while the S atoms are located within the marcasite-type layers [75R].

In the ternary marcasites (as well as in the ternary pyrites and pararammelsbergites) with  $d^6$  cations short cation-cation contacts are avoided. No ternary  $d^4$  loellingite (like e.g. "MnAsSe", in analogy to FeAs<sub>2</sub>) has been synthesized until now. In  $d^5$  arsenopyrites nonmetallic properties require a splitting of the half-filled d-subband, and this is attained by displacing the cations within the chains along  $[101]$ , which corresponds to the original marcasite *c*-axis. In these strings the  $[TX_3Y_3]$  octahedra share  $X...X$  edges alternating with  $Y...Y$  edges. The distortion of the structure on forming cation pairs leads to monoclinic symmetry and space group  $C_{2h}^5 - P2_1c$ . All atoms occupy general positions 4(e), and ordering is again possible within the same space group.

A unique structure with no binary analog is exhibited by PdPS and isostructural PdPSe. In these compounds the metal atoms adopt a diamagnetic  $d^8$  configuration with square-planar coordination as in PdS<sub>2</sub> and PdP<sub>2</sub>. In the layer structure of PdPS structural elements of both binaries can be detected (PdS<sub>2</sub> crystallizes in a strongly elongated, layered pyrite structure). Instead of the infinite P chains of PdP<sub>2</sub>, however, polyanions  $[S - P - P - S]^{4-}$  are present in PdPS. Phosphorus is tetrahedrally coordinated by  $1S + 1P + 2Pd$ . Sulfur has one P and two Pd neighbors. The lone electron pair which complements the tetrahedral coordination of S points towards the adjacent sandwich and is responsible for the Van der Waals bonding.

**References:**

- 73E Entner, P., Parthé, F.: Acta Crystallogr. B29 (1973) 1557.  
75R Rowland, J. F., Gabe, E. J., Hall, S. R.: Can. Mineralogist 13 (1975) 188.