

**substance: (transition metal)(V)<sub>2</sub> compounds**

**property: crystal structure, chemical bond of transition element dipnictides**

In nonmetallic transition-element pnictides not more than 4 cation valence electrons are engaged in the cation-anion bonds, therefore the semiconducting compounds  $TV_n$  ( $n \geq 2$ ) as well as the chalcopnictides T–V–VI all contain polyanions. The most stable configuration of the cation d electrons is nonmagnetic  $d^6$  and thus octahedral (although distorted) coordination ( $\approx t_{2g}^6$ ) is predominant. Structures that match this requirement for  $TX_2$  compositions are the pyrite and the marcasite structure as well as the pararammelsbergite structure. The pyrite structure is a rocksalt structure where the single anions are substituted by polyanions  $[X_2]$ , oriented along the body diagonals. Each anion X thus acquires 1 X + 3 T neighbors which together form a distorted tetrahedron. The marcasite structure is closely related to the rutile  $TiO_2$  structure and can be derived from a cation-deficient NiAs structure, i.e. from a distorted hexagonal anion close packing. Whereas in pyrite the  $[TX_6]$  octahedra are connected via corners they share two opposite edges in marcasite. In the marcasite structure the deformation of the  $[TX_6]$  octahedron is more pronounced than in the pyrite structure. Frequently the marcasite type is met in the low-temperature modification while the pyrite type occurs in the high-temperature or high-pressure modification. The pararammelsbergite structure, which is isopuntal with brookite  $TiO_2$ , represents a combination of pyrite and marcasite.

In the compounds with low-spin  $d^6$  cations no distortion of the  $[TX_6]$  octahedron is required in order to warrant nonmetallic properties. The distortions found may be due to geometrical constraints only. With a cation in octahedral coordination carrying less than six excess valence electrons, however, the  $t_{2g}$  band would be incompletely filled. Metallic behavior can be avoided only by splitting this d-band by means of additional distortions or cation-cation bonds. The loellingite branch of the marcasite family indeed reveals such strong structural distortions which at the same time lead to distinctly shortened metal-metal distances within the metal chains along the  $c$  axis ( $T - T = c$ ). Loellingites form with  $d^4$  and  $d^2$  cations. The case of the antiferromagnetic semiconductor  $CrSb_2$  raises doubts that metal-metal bonding is the driving force for the loellingite-type contractions of the marcasite structure [68H, 72G, 74K2, 79K].

Some kind of metal-metal bonding appears to occur in the low-spin  $d^5$  compounds  $TX_2$  and  $TX_2Y$  which crystallize in the arsenopyrite structure. The metal atoms, which are equidistant in the chains of the loellingites, are shifted out of the centers of the  $[TX_6]$  octahedra such as to form T – T pairs separated from the neighboring pairs. The bonding within these T – T pairs is gradually weakened at higher temperatures and in  $CoAs_2$ ,  $CoSb_2$  and  $RhSb_2$  a second-order transition to the loellingite structure is observed [77K].

Various models for the chemical bonding in pyrites, marcasites and arsenopyrites have been proposed [65H, 65P, 70B, 71K, 72G, 72H, 74K1, 74K2, 75J]. Molecular-orbital calculations [81T] support Goodenough's model [72G] which ignores T – T interactions. Attention is focused upon the T – X – T angles which differ substantially among the three structure types. Direct T – T d orbital interaction, on the other hand, is argued to be small.

The  $PdP_2$  structure owes its existence to the particular stability of the diamagnetic  $d^8$  configuration of  $Ni^{2+}$  and  $Pd^{2+}$ . In this structure type anion chains spiralling along the  $a$  axis are connected by cations in such a way that the latter acquire a square-planar coordination while the anions see four neighbors ( $2P + 2T$ ) at the apices of a strongly deformed tetrahedron.

## References:

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