

substance: TP₄ compounds

property: crystal structure, chemical bond of transition metal tetraphosphides

Since the same cation d electron configurations as met in the transition-element tetraphosphides occur also in the TX₂ phases the corresponding structures bear similar features. In all these structures the metal atom is octahedrally coordinated by 6 P atoms. The phosphorus atoms form ten-membered rings which are condensed to two-dimensional nets. Thus, half the P atoms are connected to 3 P + 1 T, while the remaining P atoms have 2 P + 2 T neighbors, all being in roughly tetrahedral coordination. In order to fill the anion valence band two cation valence electrons are thus required for the cation-anion bonds. The various TP₄ structure types differ in the way of connecting the [TP₆] octahedra, which is dictated by the cation d electron configuration. Thus, in the orthorhombic modification of FeP₄, in CdP₄-type RuP₄(r) and OsP₄(r), the [TP₆] octahedra are linked via corners as they are in the low-spin d⁶ pyrites, e.g. in PtP₂. Monoclinic FeP₄ and triclinic RuP₄ are reminiscent of the normal d⁶ marcasites. In marcasites, however, the strings of edge-sharing octahedra have infinite length, while in FeP₄ and RuP₄ there are units of three and two octahedra, respectively. Based on the low-spin d⁵ configuration of the cation the orthorhombic structure of ReP₄ is the analog to the arsenopyrite structure of CoP₂: Anion double octahedra containing the Re pairs are connected via corners. The same cation d electron configuration is met also in MnP₄, which occurs in three polymorphs. The structure of each of these MnP₄ modifications as well as that of CrP₄ and of orthorhombic FeP₄ can be generated by an appropriate stacking of identical puckered T_nP_{4n} nets. The differences in the structures arise through different linking of the [TP₆] octahedra. In the monoclinic 8-layer modification of MnP₄ four octahedra share edges to form a linear array of two Mn pairs. These units are connected with each other via corners only. In the triclinic 6-layer modification such units are linked via edges. In the 2-layer modification the T_nP_{4n} nets are stacked on top of each other. Distortions arise through the pairwise bonding of Mn atoms of adjacent nets. The near-neighbor environments in the three MnP₄ modifications are very similar. Half the phosphorus atoms are surrounded by 2 Mn + 2 P. The remaining P atoms have 1 Mn + 3 P neighbors. Thus the distorted tetrahedral coordination of the P "anions" is due to bonds to the cations based on electron back donating.

The cations in CrP₄ and in isotypical MoP₄ have a d⁴ configuration as it is the case for the cations in the loellingites. Again the cations form infinite chains which, however, go zigzag instead of straight, and this may account for the (probably) metallic character of CrP₄ and MoP₄ [72J].

References:

72J Jeitschko, W., Donohue, P. C.: Acta Crystallogr. B28 (1972) 1893.