Fluorite-related framework in the Pd$_{11}$As$_2$L$_2$ family of crystal structures

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Recently, the crystal structures of palladium minerals with common formula Pd$_x$As$_y$L$_z$ (L=Sb, Te, Bi) were studied [1]. Isomertieite, Pd$_{11}$As$_2$Sb$_2$ (I), and törnroosite, Pd$_{11}$As$_2$(Te,Bi)$_2$ (II), are cubic, sp.gr. Fd-3m, Z=8, unit-cell parameters for (I): a=12.297(5) Å, V =1859.3(2) Å$^3$; for (II): a=12.350(2) Å, V=1883.6(4). Minerals are structurally isotype.

Isomertieite and törnroosite are intermetallic compounds, but their crystal structures can be described in terms Pauling polyhedrons. Palladium atom is considered as a center of a polyhedron, and As, Sb (or Te) atoms are considered as ligands. There are three types of Pd polyhedrons in the structure: PdAs$_3$ tetrahedra, PdSb$_3$As or PdTe$_3$As tetrahedra, and PdSb$_3$As or PdTe$_3$As$_2$ octahedra. Pd polyhedrons share common edges forming three-dimentional framework.

Fluorite-related framework can be seen in the isomertieite crystal structure type. The framework of F-centered tetrahedra (FCA)$_3$ is one of classic description of fluorite crystal structure. Kang and Eyring [2] used anion-centered tetrahedra for description of the rare earths oxides. Fluorite-related frameworks are made by four types “fluorite module” in the Kang-Eyring systematic. Krivovichev [3] extended Kang-Eyring system for to the wide range of fluorite-related structures with vacancies in both anion and cation sites.

**Fluorite modules of D**$_1$ and U$^3$ types can be described in the structure of isomertieite and törnroosite. They are built up from seven tetrahedrons: six PdL$_x$As tetrahedra and one PdAs$_3$ tetrahedra. The *supemodule* in the Pd$_{11}$As$_2$L$_2$ structure is made by 8 fluorite modules. The *supemodule* has p x q x r dimensions equal 2x2x2 (according to Krivovichev system). Alternation of modules D$_1$ and U$^3$ types in the unit-cell is: layer 1 D$_1$ U$^3$ U$^3$ D$_1$ / layer 2 U$^3$ D$_1$ D$_1$ U$^3$. Four Pd-octahedra are joined together via common edges in a clusters. Pd-octahedra clusters located in a cavities of the tetrahedral framework.

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References


**Figure 1.** Fluorite modules (a) and their alternation (b, c); and tetrahedral framework (d) in the isomertieite structure type.

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