

08.2-39 PREPARATION AND CRYSTAL STRUCTURE OF $\text{Ce}_2\text{Cu}_2\text{P}_5$. By M. H. Möller and W. Jeitschko, Lehrstuhl für Anorganische Chemie III, Universität Dortmund, D-4600 Dortmund 50, West-Germany.

The title compound was prepared by reaction of the prereacted elemental components in an alumina container under vacuum. Single crystals were isolated from the solidified melt. They crystallize with a pseudotetragonal subcell of symmetry $I4/mmm$ and lattice constants $a = 3.91$ and $c = 19.645 \text{ \AA}$. The true symmetry is orthorhombic with lattice constants $a = 5.522(2)$, $b = 5.550(2)$, $c = 19.645(8) \text{ \AA}$; $Z = 4$. The structure was solved by Patterson and difference Fourier syntheses. The present conventional R-value is 0.035 for 37 variable parameters and 963 independent structure factors. For the 340 superstructure reflections the R-value is 0.114. The structure (Fig. 1) is closely related to those of the $\text{PbFCl-ThCr}_2\text{Si}_2$ family. The slabs centered at $z = 1/4$ and $3/4$ with the stackings of the Ce, P, Cu, P, Ce atoms are virtually identical to those found in the ThCr_2Si_2 structure. The differences arise through the clustering of the P atom layers around $z = 0$ and $1/2$ (P atoms 5 to 8). These atoms give also rise to the superstructure: they are considerably displaced from their positions in the tetragonal subcell. Furthermore these positions are only partially occupied. This is especially so for the positions P(7) and P(8), where the occupancy parameters are equal or less than one half, which corresponds to a composition of $\text{Ce}_2\text{Cu}_2\text{P}_{5-x}$. Several isotypic compounds in the systems lanthanoid - Cu, Ag - pnictogen have been prepared.

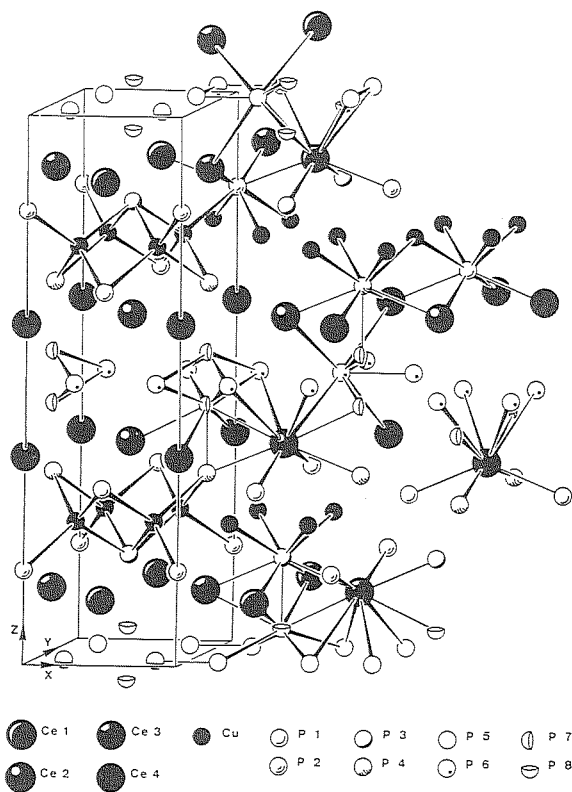


Fig. 1. Crystal structure of $\text{Ce}_2\text{Cu}_2\text{P}_{5-x}$

08.2-40 PREPARATION AND CRYSTAL STRUCTURE OF Re_2P_5 , A DIAMAGNETIC POLYPHOSPHIDE WITH PLANAR Re_4 -CLUSTERS. By R. Rühl and W. Jeitschko, Lehrstuhl für Anorganische Chemie III, Universität Dortmund, D-4600 Dortmund 50, West Germany.

Single crystals of the new compound Re_2P_5 were obtained by reaction of the elemental components in a tin flux. They are triclinic, space group $P\bar{1}$, $a = 8.229(4)$, $b = 8.336(10)$, $c = 7.329(4) \text{ \AA}$, $\alpha = 112.28(4)$, $\beta = 87.11(4)$, $\gamma = 110.18(4)^\circ$; $Z = 4$. The structure was determined and refined from single-crystal counter data to a conventional R-value of 0.038 for 4675 independent reflections and 129 variable parameters. All Re atoms are approximately octahedrally coordinated by P atoms. The ReP_6 octahedra are condensed by edge-sharing in two chemically very similar, but crystallographically different planar groups of four, one of which is shown in Fig. 1. All P atoms are tetrahedrally coordinated by Re and P atoms. In stressing ionicity, the P atoms may be considered as forming homonuclear polyanions with groups of two and four P atoms. One kind of P atoms has only Re neighbors, while others form an infinite branched chain. This great variety in the coordination of the P atoms suggests similar strengths of the P-P and P-Re bonds. Chemical bonding in Re_2P_5 may be rationalized with a simple covalent model where two electrons are counted for all short near-neighbor interactions. In this way the Re atoms obtain oxidation numbers +3 and +4 (d^4 and d^3 systems respectively). The compound is diamagnetic and thus all spins are compensated by Re-Re bonds via edges of the condensed ReP_6 octahedra within the clusters. The structure is closely related to that of paramagnetic Re_6P_{13} . Differences in bond lengths can be correlated with possible band structures of the two compounds.

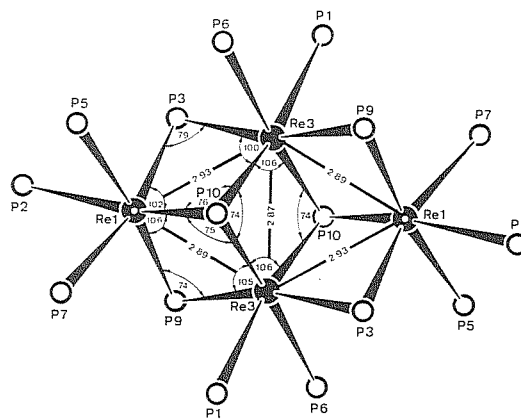


Fig. 1. Re-Re bonding within one group of four condensed ReP_6 octahedra.