08.3–13 TERNARY LANTHANOID IRON AND COBALT PHOSPHIDES WITH THE NEW YCo_5P_3 TYPE STRUCTURE. By W. Jeitschko and U. Meisen, Anorganisch-Chemisches Institut, Universität Münster, D-4400 Münster, West Germany.

Crystals of the new compound YCo_5P_3 were prepared by the tin flux technique. Their structure was determined from X ray data and refined to a residual of R = 0.051 for 908 unique structure factors and 30 variable parameters.

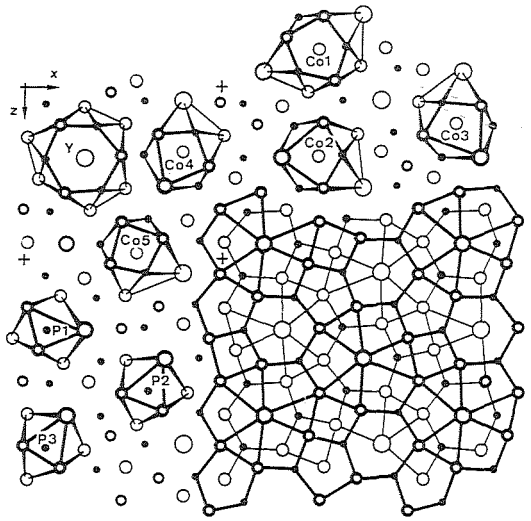

Fig. 1. Crystal structure and near-neighbor coordinations of YCo_5P_3. Atoms connected by thin and thick lines are at y = 1/4 and 3/4 respectively. The coordination polyhedra all have mirror planes perpendicular to the projection direction.

It is of a new type (Fig. 1), space group Pnma, a = 11.820(2) Å, b = 3.666(1) Å, c = 10.336(2) Å, V = 447.9 $Å^3$, Z = 4. The compounds $LnCo_5P_3$ (with Ln = Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu), YFe_5P_3 and $LnFe_5P_3$ (with Ln = Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) are isotypic with YCo_5P_3. The structure of isotypic $GdFe_5P_3$ was also refined from single crystal X ray data: R = 0.063 for 30 variables and 693 F values. The YCo_5P_3 type structure belongs to a large family of structures with trigonal prismatic metal environment of the metalloid atoms (augmented usually by three additional atoms outside the rectangular faces of the prism). In Fig. 2 it is compared to its most closely related structures of $LaCo_5P_3$ (Davydov and Kuz'ma, Dopov. Akad. Nauk. Ukr. RSR Ser. A: Fiz. Mat. Tekh. Nauki (1981) p. 81) and UNi_5Si_3 with YNi_5Si_3 type (Aksel'rud, Yarovets, Bodak, Yarmolyuk and Gladyshevskii, Sov. Phys. Crystallogr. (1976) 21, 210). The similarities are not as great in the coordination polyhedra of the metal atoms. The Y atoms in YCo_5P_3 and YNi_5Si_3 have a coordination number of 18 whereas the La atoms in $LaCo_5P_3$ have coordination number 21.

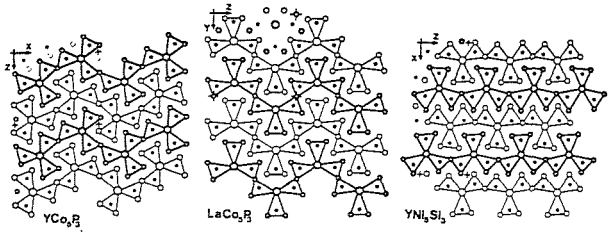

Fig. 2. Similarities of the structures of YCo_5P_3, $LaCo_5P_3$ and YNi_5Si_3 (UNi_5Si_3 type). The trigonal prisms of metal atoms (large and small circles for the rare earth and transition metals respectively) around the metalloid atoms (black dots) are emphasized. Atoms connected by thin and thick lines are separated from each other by half a translation period of the projection direction.

08.3–14 CRYSTAL STRUCTURE OF $LaCo_8P_5$. By U. Meisen and W. Jeitschko, Anorganisch-Chemisches Institut, Universität Münster, D-4400 Münster, West Germany.

Single crystals of the new compound $LaCo_8P_5$ were grown by reaction of the elemental components in a tin flux. They have orthorhombic symmetry: a = 10.501(3) Å, b = 3.596(1) Å, c = 9.343(2) Å, V = 352.8 $Å^3$, space group Pmmn, Z = 2. The structure was determined by direct methods and refined to a residual of R = 0.040 for 49 variable parameters and 927 unique F values. It belongs to a large family of structures of which the ternary equiatomic structures of the Fe_2P and TiNiSi type may be considered as the most simple representatives. These structures are usually characterized by the arrangement of the coordination polyhedra of the metalloid atoms. These polyhedra consist always of trigonal prisms of metal atoms which are augmented by three additional atoms outside the rectangular faces of the prisms. In the structures with a metal:metalloid ratio of 2:1 (e.g. $LaCo_5P_3$) the trigonal prisms share only edges. In $LaCo_8P_5$ with a slightly lower metal content some of the prisms share also faces (Fig. 1). While the compounds with a metal: metalloid ratio of 2:1 have no metalloid--metalloid bonds, the lower metal content (9:5) of $LaCo_8P_5$ results in a short P-P distance of 2.48 Å, which is formed across the common face of the face sharing prisms. The La atoms have a large coordination number: 8 P (3.09 and 3.15 Å), 9 Co (from 3.08 to 3.34 Å) and 2 La at 3.60 Å. There are five different Co sites in the structure. In three of these the Co atoms have a coordination of 8 metal and 4 P atoms. These sites corresponds to the sites of the small transition metal atoms in the ternary Fe_2P and TiNiSi type structures. There it is sometimes called the tetrahedral site, because the four P neighbors form distorted tetrahedra. One Co atom has a coordination of 10 metal and 5 P atoms. The latter form a square pyramid. It corresponds to sites of the larger transition metals in the ternary Fe_2P and TiNiSi type structures. The thermal parameters of the Co atoms correlate with the coordination numbers: large thermal amplitudes are observed for sites with large coordination numbers. This is also the case in related structures as in $Er_2Co_{12}P_7$ and $Er_2Ni_{12}P_7$ (Jeitschko and Jaberg, Z. Anorg. Allg. Chem. (1980) 467, 95) and $Nb_6Ni_6P_9$ (Guérin, Potel, Sergent, J. Less-Common Met. (1981) 78, 177).

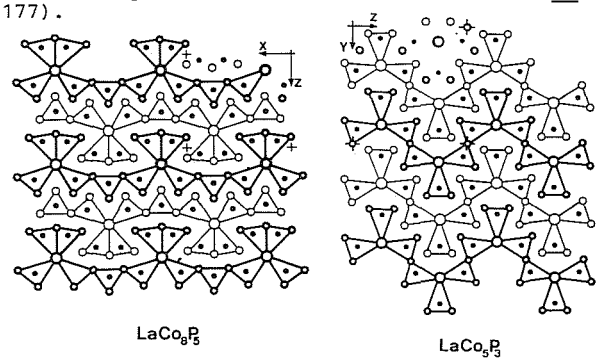

Fig. 1. Comparison of the crystal structures of $LaCo_8P_5$ and $LaCo_5P_3$. The trigonal prisms of metal atoms (large circles:La, small circles:Co) around the P atoms (filled circles) are emphasized. Atoms connected by thin and thick lines are separated from each other by half a translation period of the projection direction.