ent parts of the deposit have been registered also and they corre-late with geological data in a good way. Thus solution of direct problem in lab has allowed to solve a "converse" problem: "to re-construct" a scheme of natural influence on anatase and rutile structures by analysis of "AnI". Therefore the changing of sorp tion properties after T-influence is one of the reasons of coexis-tence of gold and other noble metals with TiO_2.

PS-08.04.37
COPPER PHOSPHATES: LIBETHEN-ITE $Cu_2(PO_4)(OH)$ AND $Cu_{2.5}Mn(PO_4)_2(OH)$-SYNTHESIS AND CRYSTAL STRUCTURES.

By O. V. Yakubovich*, Lomonosov State University and O. K. Melnikov, Inst. of Crystallography, Moscow, Russia

Crystals of two copper phosphates have been prepared by the hy-drothermal method and characterized by complete X-ray single crystal structure determination:

libethenite $Cu_2(PO_4)(OH)$, a = 8.071(2), b = 8.403(4), c = 5.898(3) Å, Pnnm, Z = 4, ρ_{calc} = 3.97g/cm³, R = 0.0397, R_w = 0.0358, s = 1.28, 814 refl.

$Cu_{2.5}Mn(PO_4)_2(OH)$, a = 8.883(3), b = 7.556(3), c = 5.334 (1) Å, α = 101.33(3), β = 95.80(3), γ = 108.62(3)°, P$\bar{1}$, Z = 2, ρ_{calc} = 4.27g/cm³, R = 0.0310, R_w = 0.0327, s = 1.26, 1720 refl.

A new compound $Cu_{2.5}Mn(PO_4)_2(OH)$ with Cu^{2+}-and Mn^{2+}-cations in the same crystal were received for the first time.

The basis of both structures is formed by a framework of octahe-dra and five-vertex polyhedra of Cu and (Mn). All vertices of PO_4-- tetrahedra are shared with the framework polyhedra. Pe-culiarities of Cu^{2+}-- polyhedron geometry are analized. The po-sitions of the hydrogen atoms are located.

A refinement of the hydrogen position in libethenite allowed to confirm a bifurcated hydrogen bond suggested earlier (Cordsen A. Canad. Mineral., 1978. 16. 153-157). It is shown that li-bethenite is a member of structures with triangular nets in the projection along the axis of 3n Å.

PS-08.04.38 THE MODULAR INTERPRETA-TION OF OXYBORATE STRUCTURES. By B. B. Zvyagin* and G. A. Sydorenko. Inst. of Ore Mineralogy (IGEM), Rus. Ac. Sc.* and Inst. of Mineral Resources, 109017 Moscow, Russia.

The structural variations of oxyborates M_3BO_5 (M = Mg, Mn, Fe) considered by Bovin et al. (Acta Cryst., 1981, A37, 28-35) according to slip and twinning mechanisms may be complete-ly explained by the OD nature of two alternating kinds of layer building modules (BM) (Fig. 1) parallel to the slip and twin planes and having symmetries Pm 2/m (2) and P1 2/m ($\bar{1}$). λ-operations 2 or 2m transforming a BM into itself are relating ad-jacent BM_1 unambiguously while BM_2 may be in two opposite orientations. The BMs may be denoted as H and N (11). BM-pairs NH = b, HN = q, NH = d, H11 = p are symmetrically and, hence, energetically equivalent (Dornberger-Schiff, Grundzüge einer OD Theorie, Berlin, 1964), and slight fluctuations in crystallization conditions and media composition may change the

BM sequence order and cause stacking faults. BM sequences may be described by sequences of BM- or BM-pair symbols. Numbers of consecutive equal letters N, 11, b, d, p or q com-pose numerical symbols like those of Zdanov. These symbols di-rectly correspond to the zig-zag chains of light spots imaging B-positions in HREM patterns. Symbols 2 and 2m of the λ-opera-tions acting in H-BMs when used in structure notations are at-tributed to the intervals between equal or mirrorly equal letters (e. g. as for bb, dd or bd). Therefore they paly the same role as letters h and c for close packings. According to the distribution of these operations, there are only two MDO (simple) struc-tures satisfying the homogeneity condition; those of pinakillite (P), ..2.2.2.. and ludwigite (L), ..2m.2m.2m... The other periodic structures listed by Bovin et al. (1981) are inhomoge-neous (complex) as mixtures of P and L. The ratio P/L being e-qual to the ratio of the numbers of 2 and 2m operations is 1 : 2, 1 : 1 and 2 : 1 for the hypothetical structure (HS) in Fig. 8 of (Bovin et al., 1981), orthopinakiolite (OP) and takeuchiite (T) respectively. The modular system is considered with common axes $a_0 \sim 12.5$, $b_0 \sim 3.0$, $c_0 \sim 4.6$ Å (c being the thickness of a layer pair). For periodic structures $\vec{a} = \vec{a}_0$, $\vec{b} = \vec{b}_0$, $\vec{c} = (m/5)\vec{a}_0 + n\vec{c}_0$. In reciprocal space $\vec{a}^* = \vec{a}_0^* - (m/5n)\vec{c}_0^*$, $\vec{c}^* = \vec{c}_0^*/n$ defining the diffractional features. The m, n values are ±1, 1; 0, 2; ±1, 3; 0, 4; 0, 6 for P, L, HS, OP and T respectively. A single slip corresponds to an operation sequence ..2.2.2.2m.2m.2.2.2.., a single twinning- to ..2.2.2m.2.2... Two planes border-ing a N (11) layer or an H layer may serve as slip or twin planes respectively. Their choice is thus ambiguous, the corresponding mechanisms are not convincing and may have no direct relation to reality.
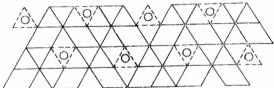

Fig. 1. Scheme of a BM quadruple NH11H. The octahedra are projecting into rhombi, circles indicate B-atoms.

PS-08.04.39 CRYSTALLOGRAPHIC STUDY ON A SERIES OF POLYMETALLATE OXYGEN CLUSTERS. By M.C.Shao,* G.Q. Huang, S.W. Zhang, Y.G. Wei & Y.Q. Tang, Department of Chemistry, Peking University, Beijing, 100871, P.R. China

Polyoxoanions are important for elucidating the biological and catalytic functions of metal chalcogenide clusters; a special type of chemistry seems to be related to reduced and mixed valence clusters.

If molybdate(VI) and tungstate(VI) are reduced in acidic solution under N_2 atmosphere, the resultant solution will be oxidized after exposition to air, and leads to the formation of novel and remarkable anions.

With that we call Red-Ox Reconstructing (ROR) method, we have successfully synthesized a serie of different types of heteropolyanions including three new type of high-nuclearity of clusters. The types and characteristics of these structures are:

(I) Keggin-type anions: (1) $[VMo_{12}O_{40}]^{3-}$, space group F-m$\bar{3}$m, a= 22.334(2)Å, V=11140Å³, Z=8, R factor is 0.055; (2) $[VW_{12}O_{40}]^{3-}$, space group P-$\bar{4}$3m, a=11.027(5)Å, V=1340(11)Å³, Z=1, R factor is 0.054.