08.1-10 INTERPRETATION AND DEVELOPMENT OF STRUCTURAL SORTING DIAGRAMS FOR ALL AB TYPE COMPOUNDS USING MOLECULAR ORBITAL IDEAS. By Jeremy K. Burdett and Sarah L. Price, Department of Chemistry, The University of Chicago, Chicago, Illinois 60637.

We consider the incontrovertible global success of the structural sorting maps for solid state AB compounds produced by St. John and Bloch (Phys. Rev. Letts. (1974) 33 1095), Chelikowsky and Phillips (Phys. Rev. B (1978) 17 2453), and Zunger (Phys. Rev. B (1980) 22 5839). These authors construct two dimensional displays, using combinations of atomic parameters from pseudopotential theory, which produce a remarkable topological clustering of AB compounds with the same structure.

We find a justification for this phenomenology in terms of a very simple molecular orbital model for the interactions between atoms A and B. By using a slightly more rigorous molecular orbital treatment, we produce superior structural sorting diagrams for all AB compounds, and hence shed light on the reasons underpinning structural preference, and the tendency to undergo polymorphic phase transitions, in terms of the number of valence electrons, and the relative positions of the energy levels of the constituent atoms.

08.1-11 CATION DISTRIBUTION AND CATION SOLUBILITY STUDIES BASED ON SOLID SOLUTIONS OF THE γ-$Zn_3(PO_4)_2$ STRUCTURE TYPE. By A.G. Nord and T. Stefanidis*, Section of Mineralogy, Swedish Museum of Natural History, S-104 05 Stockholm, and *Dept. of Inorganic and Structural Chemistry, Arrhenius Laboratory, S-106 91 Stockholm, Sweden.

The aim of this study is to correlate solubility, cation radius, unit cell dimensions and cation distribution for $(Me'Me'')_3(PO_4)_2$ orthophosphate solid solutions of the isotypic compounds γ-$Zn_3(PO_4)_2$, $Mg_3(PO_4)_2$, the mineral farringtonite, and $Co_3(PO_4)_2$ (space group $P2_1/n$). This structure type is interesting because two thirds of the cations, M(1), are five-coordinated (distorted trigonal bipyramids) and one third, M(2), are six-coordinated (almost regular octahedra). All solid solutions were equilibrated at ~1070 K. Divalent cations of Mg, Mn, Fe, Co, Ni, Cu, Zn, and Cd were included in the study. The orthophosphates of zinc (γ phase), magnesium and cobalt are almost completely soluble in each other at 1070 K. Fe^{2+} and Mn^{2+} show intermediate solubility, while the solubility of Ni^{2+}, Cu^{2+} and Cd^{2+} in the three base structures is comparatively slight. The observed change of unit cell dimensions is clearly correlated to the incorporated cation's radius. The cation distributions in some $(Mg,Me)_3(PO_4)_2$ solutions have been determined with the Rietveld profile-refinement technique based on X-ray powder data. The M(1) site preference order is $Zn^{2+} >> Co^{2+} > Fe^{2+} > Mg^{2+} > Mn^{2+}$. Mössbauer studies at Uppsala University have confirmed part of these results (H. Annersten, T. Ericsson and A.G. Nord; J. Phys. Chem. Solids (1980) 41, 1235-1240). The cation distribution studies are not yet complete but additional neutron diffraction studies are in progress.

08.1-12 CRYSTAL CHEMISTRY OF POLYPHOSPHIDES WITH COMPOSITION MP_4. By W. Jeitschko and R. Rühl. Lehrstuhl für Anorganische Chemie III, Universität Dortmund, D-4600 Dortmund 50, West Germany.

The thirteen known polyphosphides of the transition and post-transition metals with composition MP_4 crystallize with a total of nine different structure types. The latest additions to this list being 2-MnP_4 (1,2) and 6-MnP_4 (3). In all these compounds the metal atoms have more or less distorted octahedral P coordination. The P atoms are always tetrahedrally coordinated: one half of them by two M and two P atoms, and the other half by one M and three P atoms. In all structure types the P atoms form ten-membered rings which are condensed in different ways, thus forming two-dimensionally infinite sheets, some of which are shown in Figs. 1 and 2. The linkages of the MP_6 octahedra via common corners and edges reflect the arrangements of the P networks. Several of

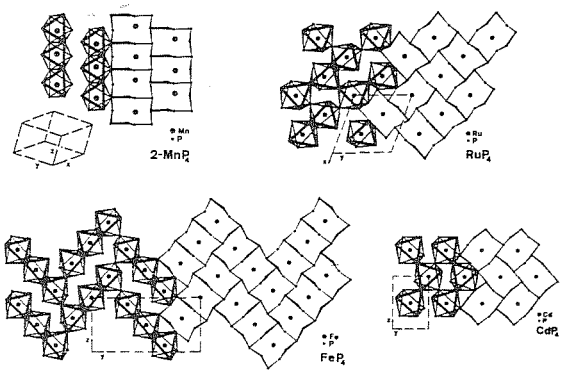

Fig. 1. Crystal structures of 2-MnP_4, RuP_4, α-FeP_4, and CdP_4.

these structure types (e.g. 2-, 6-, and 8-MnP_4) can also be considered as stacking variants. Chemical bonding in these compounds can be rationalized by a simple model where all short near-neighbor interactions are considered as two-electron bonds. In those compounds where the metal atoms obtain a d^6 or d^{10} system no metal-metal bonding exists. In the Mn and Re compounds, where the metal atoms have a d^5 system, the metal atoms form pairs, and in CrP_4 the Cr atoms, with a d^4 system, form infinite zig-zag chains. Accordingly all compounds are diamagnetic.

(1) B.I. Noläng and L.-E. Tergenius, Acta Chem. Scand. A34, 311-312 (1980).
(2) W. Jeitschko, R. Rühl, U. Krieger, and C. Heiden, Mater. Res. Bull. 15, 1755-1762 (1980).
(3) R. Rühl and W. Jeitschko, Acta Crystallogr., in print.

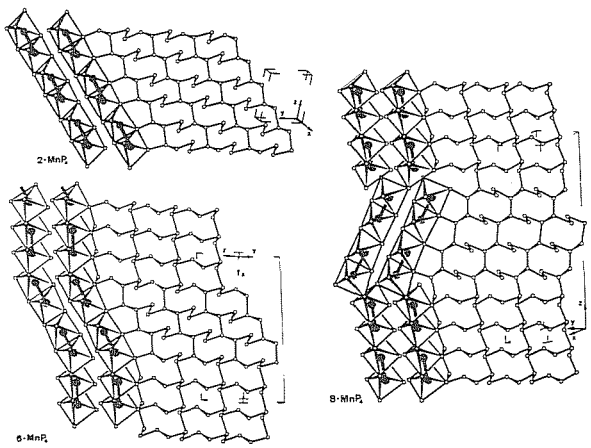

Fig. 2. Crystal structures of three modifications of MnP_4.