

given crystalline structure, the experimental bond lengths  $D(n_\alpha)$  with  $\alpha=A, B, \dots$  and the number  $I_\alpha$  of equivalent bond lengths can be obtained. Our analysis is based on the bond length differences (BLD)  $D(n_A) - D(n_\alpha)$  and not on  $D(n)$ . We select an appropriate hybridization level of Fe  $\alpha$  to obtain the suitable  $n_{C\sigma}$ ,  $n_{I\sigma}$  and  $R_\sigma(1)$  of Fe and obtain  $n_\alpha$  and  $R(1)$  of Si, N, P, O, Al from crystalline Si and P from the atomic spectroscopic data for  $N_2$ ,  $P_2$ ,  $O_2$  and AlO. Then, by our theory of BLD analysis the covalent bond electron pair numbers  $n$  can be calculated and the theoretical  $D(n_\alpha)$  and  $m_\sigma^{3d}$ ,  $m_\sigma^I$  can be deduced. The results for our eight structures are listed below:

Structure	Fe <sub>940</sub>	γ-Fe	γ'-Fe	δ-Fe	Fe <sub>I</sub> Si(Fe <sub>II</sub> ) <sub>2</sub>	Fe <sup>C</sup> N(Fe <sup>F</sup> ) <sub>3</sub>	FeP	FeAl		
σ of Fe	Fe	Fe	Fe	Fe	Fe <sub>I</sub>	Fe <sub>II</sub>	Fe	Fe		
$C_{t\sigma}$	0	.334	.334	.334	.334	.571	.095	.413	.874	1
$D(n_A)$ Å	2.139	2.556	2.556	2.490	2.469		1.925	2.300		
$D(n_\alpha)$	2.153	2.546	2.537	2.490	2.449		1.894	2.262		
$\Delta D$	-.014	.010	.019	.000	.020		.031	.038		
$m_\sigma^I$ Theor.	3.333	2.168	0.723	2.168	2.168	1.40	1.909	2.948	0.41	0
$m_B$ Exp.	3.3	2.216	0.73	?	2.14	1.46	2	3	0.41	0?
$\Delta m_B$	0.033	.048	-.007		0.03	0.06	0.091	-.052	0	0

The interesting feature is the linear relationship between  $m_B$  (Exp.) &  $C_{t\sigma}$ ; only Fe of FeP is not near the hybridization level. In view of this feature and the smallness of  $\Delta D$  and  $\Delta m_B$  for the ten Fe atoms in the eight structures, the analysis of valence-electron structure appears to be correct to the first order of approximation.

#### 08.2-50 ZINC IRONCYANIDES WITH ZEOLITIC FRAMEWORK OF RHOMBIC TYPE $n[(ZnN_4)_3(FeC_6)_2]$ . By P. Graverreau,

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The new rhombic structural type determined for the zeolitic ironcyanide  $K_2Zn_3[Fe(CN)_6]_2 \cdot nH_2O$  by the present authors (Acta Cryst. (1979). B35.2843) appears to be characteristic of a more important family. This structure, in which  $FeC_6$  octahedra and  $ZnN_4$  tetrahedra are held together by the  $(CN)^-$  ions to constitute a three dimensional frame with large ellipsoidal cavities, can be found for the following compounds:

- zinc ferrocyanides  $M_2^I Zn_3 [Fe^{II}(CN)_6]_2 \cdot nH_2O$

Structural studies have been done for compounds with  $M^I = Na, K, Cs$ .

- zinc ferricyanide  $Zn_3 [Fe^{III}(CN)_6]_2 \cdot nH_2O$

This rhombic phase of zinc ferricyanide is stable under room conditions. Single crystals have been obtained.

All these compounds appear to be limits of the series  $M_2^I(1-x)Zn_3 [Fe_{1-x}^{II}Fe_x^{III}(CN)_6]_2 \cdot nH_2O$  with  $x \in [0, 1]$ . The variability of  $x$  and of the two parameters ( $p_{H_2O}$  and  $T$ )

of the divariant zeolitic equilibrium, together with the ion exchange behavior of these ironcyanides, explain the diversity of results found in literature.

#### 08.2-51 CRYSTAL STRUCTURES OF A SERIES OF SYNTHETIC Fe PHOSPHATES. By O.V. Yakubovich, E.N. Matviyenko, Yu.K. Kabalov, Yu.K. Egorov-Tismenko, M.A. Simonov, N.V. Belov, Department of Geology, Moscow State University, Moscow, USSR.

The crystal structures of Fe phosphates have been studied by X-ray analysis.

Frameworks of Fe octahedra form the basis of the structures of  $Fe_2[PO_4]F$ ,  $Fe^{3+}(Fe^{3+}Fe^{2+}_5)_{18}[PO_4]_{14}$  and  $(Fe_{0.76}Zn_{0.24})_3 \cdot [PO_4]_2$ . In  $Fe_2[PO_4]F$  they are composed of chains composed of four Fe octahedra sharing common edges, while in  $Fe^{3+}(Fe^{3+}_5Fe^{2+}_5)_{18}[PO_4]_{14}(OH)_{24}$  they consist of columns of Fe-octahedra joined by common faces. Similar columns also form a framework of the structure of  $(Fe_{0.76}Zn_{0.24})_3[PO_4]_2$ , but the Fe octahedra, in triplets, are connected not by common faces but by common edges.

In the  $LiFe[PO_4]$  structure these chains are joined into the "chess"-type layers. When the structures of both Li- and Fe polyhedra are present, the  $LiFe[PO_4]$  structure shows the "olivine" strips with chains of Li octahedra encrusted with Fe. In  $Na(Fe_{0.5}Zn_{0.5})[PO_4]Fe$  octahedra are joined together along the edges into infinite columns resembling the "olivine" strip. In  $KFe[PO_4]F$  the Fe octahedra sharing common vertices, form chains intersecting in the (010) projection. The  $Na_2(Fe^{3+}_5Fe^{2+}_{52})Fe^{2+}[PO_4]_3$  structure is made up of chains of Fe octahedra linked together along edges and strengthened by  $PO_4$  tetrahedra. In  $Na_2Fe[PO_4](OH)$ , Fe octahedra joined in pairs along a face are linked together by common vertices and strengthened by  $PO_4$  tetrahedra. The two-row chains of triplets of Fe octahedra, joined together along a face into a column along an edge, are characteristic for  $Na_{2-x}Zn_xFe_3[PO_4]_2(OH)_{2-x}O_x$ .

When the cations of alkali metals are present, they enter the structure of Fe phosphates as single units.

Most of the compounds considered are synthetic modifications of minerals: maricite, sarkopside, zwieselite, lipscombite, triphylite and alluaudite. The compound having an idealized formula  $Na_2Fe_3[PO_4]_2(OH)_2$  is structurally similar to the mineral simanite  $Mn_3[PO_4][B(OH)_4](OH)_2$ .