

**08.2-46** THE CRYSTAL STRUCTURE OF VACUUM-DEHYDRATED FULLY AMMONIUM-EXCHANGED ZEOLITE A. L.B. McCusker, Institut für Kristallographie und Petrographie, ETH, Zürich, and K. Seff, Department of Chemistry, University of Hawaii, Honolulu.

The crystal structure of fully ammonium-exchanged zeolite A dehydrated at 25°C and 10<sup>-5</sup> Torr has been determined by single-crystal x-ray diffraction techniques in the space group  $Fm\bar{3}c$  ( $a = 24.568(2)\text{Å}$ ). The structure was refined to a final  $R$  (weighted) index of 0.040.

The 95.0 (idealized occupancy, 96)  $NH_4^+$  ions per unit cell are distributed over 4 sites: 69.4 (68) are associated with 6-oxygen rings - 25.8(6) (24) recessed into sodalite units and 43.6(3) (44) extending into large cavities, 21.6(4) (24) are associated with 8-oxygen rings, and 4.0(4) (4) are opposite 4-oxygen rings. Since there are only 64 6-oxygen rings per unit cell to accommodate the 69.4 (68) threefold-axis cations, 5.4 (4) must have two  $NH_4^+$  ions associated with them. This appears to be one of two relatively unsatisfactory sites adopted by the 8 cations per unit cell which cannot be accommodated by the 64 6-oxygen-ring and 24 8-oxygen-ring sites. The second is that opposite a 4-oxygen ring. The geometry at this position is ill-suited for an  $NH_4^+$  ion to hydrogen bond to framework oxygens.

Of the 107 observed (at the 2 $\sigma$  level)  $b$  reflections (all odd Miller indices), 30 are inconsistent with the  $c$ -glide condition of  $Fm\bar{3}c$ . Apparently, the  $NH_4^+$  ions are not completely disordered in one or more of their  $Fm\bar{3}c$  equipoints; that ordering results in violations of the  $c$ -glide symmetry.

**08.2-47** A COMPARISON OF THE -SNSS STRUCTURAL UNIT IN  $Ph_4As^+S_4N^-$ ,  $(Ph_3P)_2N^+S_4N^-$ ,  $Ph_3PS_3N_2$ , AND  $C_{11}H_{20}N_2O_2S_3$ .

By A. W. Cordes and P. N. Swepston, University of Arkansas, U.S.A.; T. Chivers and R. T. Oakley, University of Calgary, Canada.

The -SNSS structural unit has now been observed in a number of X-ray crystal structures. In two neutral acyclic compounds and in the acyclic  $S_4N^-$  anion, the

X-SNSS groups have been found to be essentially planar and to exist in "sickle-shaped" *cis-trans* configurations ( $X = Ph_3PN-$  (Chivers, T., et.al. J. Chem. Soc., Chem.

Commun. 1980, 35.);  $X = C_{11}H_{20}O_2N-$  (Tamura, C., et.al.

Acta Cryst. 1977, B33, 3918.);  $X = S^-$  in  $(Ph_3P)_2N^+S_4N^-$

(Chivers, T., et.al. J. Amer. Chem. Soc. 1980, 102,

4517.);  $X = S^-$  in  $Ph_4As^+S_4N^-$ ). The prominent bonding

features of this structural unit include a short terminal SS bond suggestive of multiple bond character (mean value of 1.91 Å), a nonbonded sulfur-sulfur contact significantly shorter than the van der Waals separation (mean value of 3.16 Å), and a mean SN distance which is fairly constant between the four structures (mean value of 1.60 Å) but individual SN distances which vary considerably between structures. The published structure

of  $(Ph_3P)_2N^+S_4N^-$  has been re-refined using a disordered anion model.

**08.2-48** LATTICE IMAGING AND CRYSTAL STRUCTURE DETERMINATION OF 6H AND 12H MAGNESIUM SIALONS. By G. Singh\*, P. Korgul, D.P. Thompson and A. Hendry, Wolfson Research Group for High-Strength Materials, Crystallography Laboratory, University of Newcastle upon Tyne, England.

6H and 12H are polytypoid phases which have 6M:7X compositions ( $M = Mg, Si, Al$ ;  $X = O, N$ ) in the Mg-Si-Al-O-N system. Both phases have ranges of homogeneity with 6H containing a larger amount of magnesium and oxygen than 12H. The unit-cell dimensions (6H:  $a, 3.06 c, 16.33\text{Å}$ ; 12H:  $a, 3.07 c, 32.65\text{Å}$ ) correspond to cell contents of 6M + 7X and 12M + 14X respectively and the crystal structures, determined by X-ray powder methods, show that 6H consists of two layers of octahedra and five layers of tetrahedra whereas 12H consists of one layer of octahedra and 6 layers of tetrahedra repeated twice per cell; in both structures certain of the tetrahedral sites are partially vacant to give the observed 6M:7X composition.

Confirmation of the structures is shown by the good agreement obtained between high-resolution electron microscope lattice images of 6H and 12H and images calculated using the X-ray structural parameters.

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**08.2-49** ANALYSIS OF VALENCE-ELECTRON STRUCTURE OF SOLIDS DIRECTLY FROM THEIR CRYSTALLINE STRUCTURES: VALENCE-ELECTRON STRUCTURES AND MAGNETIC-MOMENT STRUCTURES OF  $\gamma$ -,  $\gamma'$ -,  $\delta$ -Fe,  $Fe_3Si$ ,  $Fe_4N$ ,  $FeP$ ,  $FeO$  and  $FeAl$ . By S.H. Yü, Department of Physics, Jilin University, Changchun, Jilin, China.

An analysis of the valence-electron structure of most solids is possible, to a first-order approximation, directly from their crystalline structures. This is based on an empirical electron theory of solids and molecules, and knowledge of the fine structures of atomic valences of 78 elements in the form of discrete levels of hybridization states as derived from the study of more than a thousand crystal and molecular structures. For illustration, analyses of the title compounds are presented, based on the B-type hybridization states of Fe:

$$\begin{array}{l} \text{h state: } \left( \begin{array}{cc} \overline{3d} & 4s & \overline{4p} \\ \uparrow\uparrow\uparrow\uparrow & \emptyset & \pm 00 \\ \uparrow\uparrow\uparrow\uparrow & \emptyset & \pm 00 \end{array} \right) & 1, m, n, \tau = 2, 1, 2, 0 \\ \text{t state: } \left( \begin{array}{cc} \parallel & \pm \\ \dots & \pm 00 \end{array} \right) & 1', m', n', \tau = 1, 1, 3, 1 \end{array}$$

where  $\parallel = \uparrow, \uparrow, \uparrow, \uparrow, \emptyset, \dots, \pm, 0$  represent dumb pair, magnetic, lattice, covalent, equivalent s-p covalent electron and empty orbit, respectively; and  $\tau = 0$  or 1 according to the presence or absence of lattice electrons (S.H. Yü, Kexue Tongbac (1978) 23, 214-222 and Yü (1981), in press).

According to the present electron theory, 18 hybridization levels with relative fractions  $C_{t\sigma}$  and  $C_{h\sigma} = 1 - C_{t\sigma}$  of t and h states possess their own number of covalent and lattice electrons  $n_{c\sigma}$ ,  $n_{l\sigma}$  and  $n_{t\sigma} = n_{c\sigma} + n_{l\sigma}$  as calculated from the values of 1, m, n,  $\tau$ , 1', m', n',  $\tau'$  and also possess their own  $R_{\sigma}(1)$  as calculated from  $R_h(1)$  and  $R_t(1)$  which are obtained for Fe from an empirical formula in the pre-mentioned reference. In addition, they possess their own magnetic moment  $m_{\sigma}^{3d}$  and  $m_{\sigma}^T = g/2x m_{\sigma}^{3d}$ . From the

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  $n_\sigma$  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:

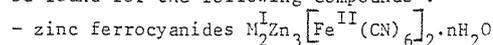
Structure	Fe <sub>940</sub>	γ-Fe	γ'-Fe	δ-Fe	Fe <sub>I</sub> Si(Fe <sub>II</sub> ) <sub>2</sub>	Fe <sup>C</sup> N(Fe <sup>F</sup> ) <sub>3</sub>	FeP	FeAl		
σ of Fe	Fe	Fe	Fe	Fe	Fe <sub>I</sub>	Fe <sub>II</sub>	Fe	Fe		
$C_{t\sigma}$	0	.334	.334	.334	.334	.571	.095	.413	.874	1
$D(n_A)$ Å	2.139	2.556	2.556	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		
$m_\sigma^T$ 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,

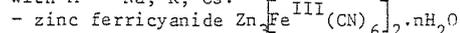
E. Garnier and A. Hardy, Laboratoire de Cristalochimie Minérale, Université de Poitiers, 40, Av. du Recteur Pineau, 86022 Poitiers, France.

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:



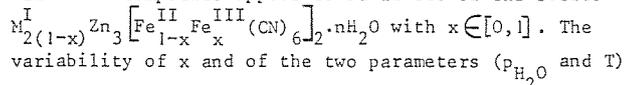
Structural studies have been done for compounds

with  $M^I = Na, K, Cs$ .



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



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  $Mn_3[PO_4][B(OH)_4](OH)_2$ .