

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 10⁻⁵ 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 σ 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 γ -, γ' -, δ -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:

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

where $\parallel\parallel\parallel\parallel, \uparrow, \emptyset, \pm, 0$ 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_{σ}^{3d} and $m_{\sigma}^T = g/2x m_{\sigma}^{3d}$. From the