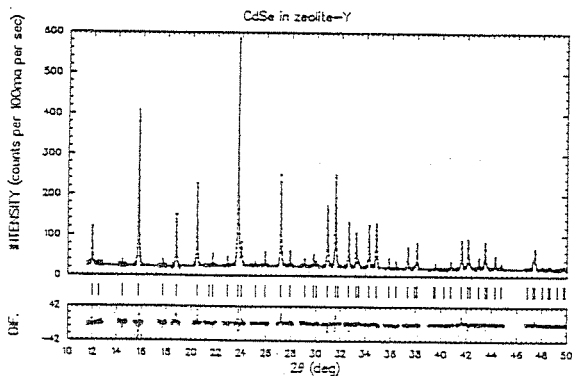


07.7-2 A STUDY OF SEMICONDUCTOR INTERCALATION IN ZEOLITE-Y USING POWDER SYNCHROTRON X-RAY DIFFRACTION. By M.M. Eddy, G.D. Stucky, J.E. MacDougall, Dept. of Chemistry, U.C.S.B., Santa Barbara, CA 93106, D.E. Cox, Department of Physics, Brookhaven National Lab., Upton, Long Island, New York 11973, and N. Herron, Experimental Station, E.I. du Pont de Nemours and Co., Wilmington, DE 19898.

High resolution x-ray powder diffraction data were collected for a series of CdS and CdSe intercalates in a host zeolite-Y framework. The measurements were made on beam line X13a at the National Synchrotron Light Source, Brookhaven National Laboratory. Each diffractogram was analysed using the profile fitting technique originally devised by Rietveld (H.M. Rietveld, J. Appl. Cryst., (1969), 2, 65), and the extra-framework material was located using standard Fourier methods. Four samples, with different concentrations of Cd, S and Se, were investigated and an example of the excellent agreement between observed (solid line) and calculated (dotted line) profiles for CdSe in zeolite-Y is given in Fig. 1. Also shown is the difference between these two curves.

In all cases Cd prefers to occupy a site within the sodalite unit, capping the double-6-ring, coordinated to three framework oxygens. Also associated with this particular Cd is an oxygen of a hydroxyl group or water molecule which results from inadequate dehydration and gives an octahedral arrangement around the cation. As the concentration of Cd is increased occupation of the 12-ring occurs. These results provide a possible explanation for the interesting results found from U.V. spectroscopy, which show that above a critical loading the intercalate acts like a semiconductor. Within the sodalite unit of zeolite-Y there exist cubes of cadmium and sulphur. These are discrete entities at low semiconductor loadings. However as the concentration is increased a network is set up which is modulated by the host framework.

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07.7-3 NEW CRYSTAL CHEMISTRY, NON-STOICHIOMETRIC AND GLASSY COMPOUNDS IN THE As - V - O SYSTEM.

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A thorough investigation of the As - V - O system allowed to synthesize new compounds or new polymorphs containing  $As^{5+}-V^{5+}$ ,  $As^{5+}-V^{4+}$  or mixed valences of vanadium  $As^{5+}-V^{5+}-V^{4+}$ . Crystal structures of the double oxides  $\beta-AsVO_5$ ,  $AsV_3O_9$  and  $As_2V_4O_{13}$  were determined giving a new insight in the general chemical system As - V - O and its potentialities in the field of intercalation chemistry, catalysis and conduction properties of alkaline doped glassy families  $As_2^{5+}V_{2x}^{5+}V_{4-4x}^{4+}O_{13+x}$  and  $As_2^{5+}As_{2y}^{3+}V_{4-4y}^{4+}O_{13+3y}$  (with  $x \leq 1$  and  $y \leq 1$ ).

$\beta-AsVO_5$  crystallizes in the monoclinic system, space group  $P2_1/n$ . The crystal structure is rather different from  $\alpha-AsVO_5$  previously structurally investigated by N. G. Chernorukov et al. (Russian J. of Inorg. Chem., 1978, 23, 10, 1475-1481) and its intercalation potentialities reported by J. W. Johnson et al. (Inorg. Chem., 1982, 21, 3820-3825).  $\beta-AsVO_5$  is a layer structure built up from square pyramids  $VO_5$  associated in pairs by edge sharing, these blocks being corner shared to  $AsO_4$  tetrahedra.

$AsV_3O_9$ , orthorhombic system, space group  $Pbca$ , contains infinite double strings of octahedra  $(V_2O_8)_n$  sharing edges and corners, running parallel to [100] and via interconnected  $(As_2O_7)$  groups. Structurally, this compound localized on the pseudo-system  $As_2V_2O_9-V_4O_9$ , shows similarities with  $\beta-AsVO_5$ .

$As_2V_4O_{13}$  is triclinic, exhibiting a rather complex cation distribution in a cubic close packed array of oxygen atoms (R. E. Enjalbert et al., Acta Cryst., 1986, C 42, 1465-1467).

Structural investigation of the amorphous compounds mentioned above has been performed using both LAXS and EXAFS techniques.

On the base of these structural informations intercalation chemistry has been developed using organic molecules or metal complexes. The aim of this contribution is to discuss these subsequent results which are directly related too with the P - V - O system widely explored (E. Bordes et al., J. Chem. Soc. Chem. Comm., 1985, 294-296, ...).