

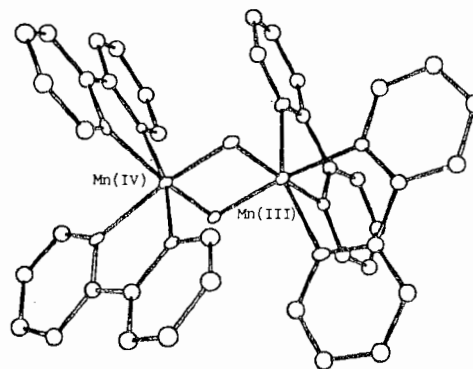
crystal structure (Ye, Z.G., Kolpakova, N.N., Rivera, J.-P. and Schmid, H., *Ferroelectrics*, 1991, 144, 275-280). The crystal structure has been redetermined at RT, 350K and 440K. Precise crystal structure analysis proved considerable anisotropy of cadmium temperature factors. In good agreement with x-ray diffraction data, this anisotropy can be explained by assuming the crystal structure of cadmium niobate with dynamic disorder of cadmium atoms displaced at random by about 0.1 Å along twofold axes, in a plane perpendicular to the threefold symmetry axis in the lattice cell with space group  $Fd\bar{3}m$ . In the high temperature paraelectric phase of  $Cd_2Nb_2O_7$  each cadmium atom occupies at random one of six positions in the corners of a small hexahedron. On lowering of temperature, a local symmetry breaking takes place with different kinds of ordering, resulting in consecutive phase transitions. At room temperature, due to fine twinning, the diffraction pattern is very similar to that observed at elevated temperatures.

**MS-08.01.06 VALENCE CONTRAST STUDIES ON MIXED-VALENCE INORGANIC AND METALO-ORGANIC SOLIDS**  
P. Coppens\*, Y. Gao, M.R. Pressprich and A. Frost-Jensen  
Chemistry Department, State University of New York at Buffalo, Buffalo, NY 14214 and SUNY X3 beamline at Brookhaven National Laboratory, Upton, NY 11973, USA

Since the position of the absorption edge differs for atoms of the same element in different chemical environments, resonance scattering can be used to study valency and the effect of site coordination on the electron-binding energy. This *valence-specific diffraction* combines crystallography with spectroscopy and gives unique, site-specific, information on electronic structure. We have applied valence-contrast diffraction at seven different wavelengths to single crystals of the mixed valence low-dimensional conducting material  $NbSe_3$ , and have found the absorption edge of Nb(II) to be shifted by about +4 eV, relative to that of the other Nb atoms, indicating Nb(II) to be more positive, thus resolving a controversy in the literature (Y. Gao, M.R. Pressprich and P. Coppens, *Acta Cryst. A*, In Press). A second study on a di- $\mu$ -oxo-bridged dimanganese complex (see figure), a model compound for enzymes involved in the oxygen-producing hydrolysis of water, shows the absorption edge of the Mn(IV) atom to be shifted to higher energies by several eV relative to that of Mn(III), in almost quantitative agreement with parallel theoretical calculations (Y. Gao, A. Frost-Jensen, M.R. Pressprich, P. Coppens, A. Marquez and M. Dupuis, *J. Am. Chem. Soc.*, 1992, 114, 9214-9215).

By measuring the intensity variation of Bragg peaks as a function of wavelength (H. Stragier, J.O. Cross, J.J. Rehr and L.B. Sorensen, *Phys. Rev. Letters*, 1992, 69, 3064) in scans at different angles of rotation around the scattering vector, additional information can be obtained. Following absorption correction, inverse Kramers-Kronig transformation leads to the *site-specific, anisotropic* K-shell atomic absorption spectrum. We have done a series of measurements of this type on the mixed-valence manganese compound, and will discuss their interpretation.

Support of the work by the Department of Energy (DEFG0291ER45231) and the National Science Foundation (CHE9021069) is gratefully acknowledged.



**MS-08.01.07 A MULTI-DISCIPLINARY APPROACH TO THE SOLUTION OF POLYCRYSTALLINE MINERAL STRUCTURES**

R J Cernik, SERC Daresbury Laboratory, Warrington, UK

The growing success of structure solution from powder data has significant implications for the study of minerals. This is because many natural samples and synthetic analogues occur only as microcrystals or powders. However, powder diffraction alone is not always enough to solve a crystal structure *ab initio*, especially if there are impurities or multiple phases present. Other techniques such as electron diffraction and microscopy, NMR, and microcrystal diffraction are extremely valuable aids to the structure solution of these complex materials. The power of a multi-disciplinary approach will be illustrated with respect to the solution of two previously unknown structures. These are the important catalyst precursor material aurichalcite (Cernik R J, Harding M M, Kariuki B, Cressey G and Bell A M T to be submitted to *Acta B* 1993), and the hydrothermally synthesized Mg Leucite which is an analogue of naturally occurring substituted framework feldspathoid structures (Bell A M T, Henderson C M B, Cernik R J, Champness P E, Fitch A N, Kohn, and Redfeam S A T submitted to *Acta B* 1993). Both materials are of considerable importance for both geological and technical reasons in the fields of catalysis, molecular filters and ion exchange. In the case of aurichalcite the starting structure was obtained by extracting a single microcrystal from the bulk material and performing a single crystal data collection on station 9.6 of the Daresbury Synchrotron (Harding et al poster *ibid*). The powder data were then refined by the method of Rietveld in order to determine the bulk structure. In the case of the Mg Leucite sample the unit cell was determined by electron diffraction,  $^{29}Si$  NMR indicated the presence of 12 separate tetrahedral sites. A distorted form of the known related cubic structure was used as the starting point for the refinement of the powder data, the outcome of which was in full agreement with the NMR results. The third example of this multi-disciplinary approach is the analysis of structural variations in chrysotile asbestos. High resolution synchrotron X-ray diffraction on station 9.1 of the SRS at Daresbury revealed the presence of a 7.2 Å layer spacing in addition to the usual 7.3 Å spacing for chrysotile. Electron microscopy suggests that there are substantial quantities of a flat layered variety of serpentine having a range of d values from 7.2 to 7.233 Å. The EM also indicates the morphology of the material showing flat plates at the centre of the fibres which are also shown to possess five fold symmetry (Cressey B A, Cressey G, and Cernik R J submitted to *Can Min* 1993).