

**MS-08.01.03** STRUCTURE, SUPERSTRUCTURE AND SUBSTRUCTURE: IMPLICATIONS FOR STRUCTURE ELUCIDATION AND REFINEMENT. By A. David Rae\*, School of Chemistry, University of New South Wales, P.O. Box 1, Kensington, N.S.W. 2033, Australia.

A simple atom based parameterisation is not always the most appropriate description of a structure. Descriptions that link atoms at different crystal sites are to be preferred, especially if structure determination, refinement and analysis of refinement can then be developed on a more logical basis. Of particular interest are those structures which may be described as perturbations of idealised parent structures of higher symmetry. A parent structure may be a composite of substructures, each with its own space group and unit cell. The perturbations may be described using modulation waves and in the composite case each substructure causes a modulation of the other and the symmetries of the modulation waves of one substructure are consistent with the parent symmetry of the other substructure. In such structures reflections  $F(\mathbf{h})$  occur at reciprocal space points  $\mathbf{h} = \mathbf{g} + \mathbf{k}_m$  where  $\mathbf{g}$  is a Bragg reflection of the parent structure and the limited number of  $\mathbf{k}_m$  are multiples of an even smaller number of base vectors. When substructures exist  $\mathbf{h} = \mathbf{g} + \mathbf{g}'$  and the  $\mathbf{k}_m$  correspond to the mismatch in the reciprocal space lattices of the substructures. When modulation waves are commensurate, superstructures result. Difficulties with refinement are common when superstructures are refined using simple atom based parameters. An attempt will be made to classify these difficulties and define modelling descriptions and refinement strategies for their resolution.

Irreducible representation theory applied to the spacegroup of the parent structure or substructure can be used to define appropriate model parameters which are linear combinations of atom parameters on pseudosymmetrically related atoms. A pseudosymmetry operator is an operator of a parent structure that is destroyed by the modulations. A parameter defined using an irreducible representation associated with a particular vector  $\mathbf{k}_m$  makes a dominant contribution to data where  $\mathbf{h} = \mathbf{g} + \mathbf{k}_m$ . A hierarchical approach to refinement can then be developed based on the relative intensities of reflections with different  $\mathbf{k}_m$ . The number of different irreducible representations to be used at any  $\mathbf{k}_m$  is determined by the number of  $\mathbf{k}_m$  that would have been equivalent under the point symmetry of the parent structure. The assumption that phases calculated from initial models are always correct results in structures that are dependent on refinement pathway and comparative refinement procedures must be developed. Diffraction symmetry enhancement and homometry can also occur. Any modulation wave can have errors in overall phase and amplitude as well as in resolution within a wave. Not all phase errors involve simply a choice of orientation, origin or handedness for the crystal. Twinning and disorder models are sometimes necessary. Anomalous dispersion can be used to aid resolution of refinement difficulties, a feature not available with powder neutron diffraction. Chemical and physical requirements, e.g. Apparent Valence are also helpful. Commensurately modulated structures can also be used to sample solid solution crystal phases, especially when a number of large amplitude modulations coexist. Correlation effects which are a result of commensurability can be examined.

**MS-08.01.04** SYNTHETIC CLINOPYROXENES IN THE SYSTEM  $\text{CaMgSi}_2\text{O}_6\text{-CaCoSi}_2\text{O}_6$  WITH Co ATOMS AT THE M(2) SITES. By Y. Tabira<sup>1,2</sup>, N. Isbizawa<sup>2</sup> and F. Marumo<sup>3,4</sup>, <sup>1</sup>R & D Center, RICOH Co. Ltd, Yokohama, Japan, <sup>2</sup>Research Laboratory of Engineering Materials, Tokyo Institute of Technology, Yokohama, Japan, <sup>3</sup>Department of Earth Sciences, Nihon University, Tokyo, Japan.

One of the authors and his coworkers refined the structure of a synthetic clinopyroxene in the system  $\text{CaMgSi}_2\text{O}_6(\text{Di})\text{-CaTiAl}_2\text{O}_6(\text{CaTiPx})$  with a lower CaTiPx content, and found that  $\text{Ti}^{4+}$  ions were at the M(2) sites contrary to the usual site preference of Ti in pyroxene structures. To accumulate further knowledges on transition-metal distributions in pyroxenes, structure refinements were carried out on two synthetic clinopyroxenes of different Co contents in the system  $\text{Di-CaCoSi}_2\text{O}_6(\text{CaCoPx})$  with the single-crystal X-ray diffraction method, and the obtained distributions of Co atoms were checked by the channeling-enhanced microanalysis.

Crystals of the clinopyroxenes were synthesized under the coexisting condition of crystals and melts. Pulverized glasses with CaCoPx contents of 20 and 70 wt% were annealed at 1000°C for 20 h to crystallize. The obtained polycrystalline powders were heated at 1285°C for 158 h and at 1270°C for 144 h, respectively, and then quenched. The crystals thus obtained were confirmed to be clinopyroxenes with the space group C2/c by taking Weissenberg photographs. High residual electron-densities were observed at a position 0.4 Å apart from the M(2) site along the b axis on the difference Fourier map of each crystal synthesized after a refinement based on the diopside model, where all the  $\text{Co}^{2+}$  ions were located at the M(1) site. The residual densities were well explained with the replacement of  $\text{Ca}^{2+}$  by  $\text{Co}^{2+}$  ions at the M(2) sites, which amount to 3.0(4) atm% in the crystal with the lower Co content and 4.9(4) atm% in the other. The replacement at the M(2) sites was qualitatively confirmed by the ALCHEMI method applied under the condition of the 020 planar channeling. The structure refinements gave the chemical formulae  $[\text{Ca}_{0.970}\text{Co}_{0.030}] [\text{Mg}_{0.831}\text{Co}_{0.169}] \text{Si}_2\text{O}_6$  and  $[\text{Ca}_{0.951}\text{Co}_{0.049}] [\text{Mg}_{0.486}\text{Co}_{0.514}] \text{Si}_2\text{O}_6$  for the respective crystals. Determinations of cation distributions are in progress on crystals of diopside solid solutions containing  $\text{Fe}^{2+}$  and  $\text{Ni}^{2+}$  ions.

**MS-08.01.05** DYNAMIC DISORDER OF CADMIUM IN  $\text{Cd}_2\text{Nb}_2\text{O}_7$

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Cadmium niobate undergoes numerous phase transitions with minute or almost non-observable changes of the

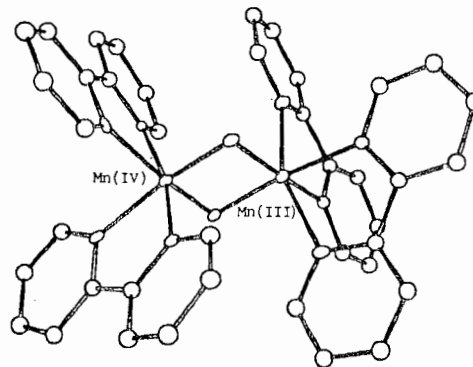
crystal structure (Ye, Z.G., Kolpakova, N.N., Rivera, J.-P. and Schmid, H., *Ferroelectrics*, 1991, 144, 275-280). The crystal structure has been redetermined at RT, 350K and 440K. Precise crystal structure analysis proved considerable anisotropy of cadmium temperature factors. In good agreement with 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**  
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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**

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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).