

**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  $F(h)$  occur at reciprocal space points  $h = g + k_m$  where  $g$  is a Bragg reflection of the parent structure and the limited number of  $k_m$  are multiples of an even smaller number of base vectors. When substructures exist  $h = g + g'$  and the  $k_m$  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  $k_m$  makes a dominant contribution to data where  $h = g + k_m$ . A hierarchical approach to refinement can then be developed based on the relative intensities of reflections with different  $k_m$ . The number of different irreducible representations to be used at any  $k_m$  is determined by the number of  $k_m$  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>1,3</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  $\text{Di}$ - $\text{CaCoSi}_2\text{O}_6(\text{CaCoPx})$  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  $\text{Cd}_2\text{Nb}_2\text{O}_7$

K. Lukaszewicz, A. Pietraszko and J. Stepien-Damm, Institute of Low Temperature and Structure Research, Polish Academy of Sciences, 50-950 Wrocław P.O. Box 937, Poland, and N.N. Kolpakova, Ioffe Physico-Technical Institute, Acad. of Sci., 194021, St. Petersburg, Russia

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