Personal Statement for Consideration for the Physical Crystallography Thesis Prize

Mark S. Senn

University of Edinburgh

My Ph. D. thesis details, through crystallographic methods, the structural study of several metal oxides which exhibit complex structural and magnetic phase transitions. To achieve this I have performed single crystal and powder x-ray diffraction experiments using both laboratory sources and those at central facilities. Neutron powder diffraction studies have also been utilised to study both structural and magnetic ordering. Crystal structures have been studied both as a function of temperature and pressure.

The bulk of my thesis is centred on the solution of a long standing problem in physical crystallography, that of the Verwey (low temperature) structure of magnetite which has remained unsolved for over 70 years since its discovery. The solution is presented in my thesis through a detailed micro-crystal diffraction study. I have illustrated how conventional problems that prohibit the solution of the structure such as twinning and multiple scattering may be overcome experimentally, and how any residual twinning may be correctly modelled through symmetry analysis. The resulting crystal structure (506 parameters) whose distortions from their high symmetry positions are subtle, requires critical analysis of the significance and robustness of the refined parameters, and this is also given in my thesis.

Throughout the thesis, particular attention has been paid not only just to the solution of the structures but also to the physical interpretation of resulting structures. In particular, the crystal structures have been analysed using empirical bond valence sum calculations, local mode distortions of coordination environments and lattice (distortion) mode analysis. Additionally, for magnetite, the coordinates have been used as the basis of electronic structure (DFT+U) calculations in order to understand the role of the electron distributions in the Verwey phase. Attempts have also been made to rationalise experimental observations of physical properties such as the observed polarisation which develops below the transition.

Both temperature and pressure dependent powder diffraction data have been collected for the 6H perovskites of the type $Ba_3ARu_2O_9$ which form the second part of my thesis. Here attention has been paid not only to the evolution of the average structure with temperature, but diffraction profiles have been carefully modelled to extract microstrains which have been correlated with phase transitions. The solution of several magnetic structures is also presented and, here again, representation (symmetry mode) analysis has been made use of. How the evolution of this magnetic ordering affects both micro and macrostrain of the structures is also investigated. In the case of $Ba_3NdRu_2O_9$, the correlation of macrostrain with order parameters for the magnetic phase transitions suggests a possible explanation for the complex spin reorientation transition which is observed.

In my thesis I have made use of recent developments in instrumentation and methodology to study subtle phase transitions which arise as a result of electronic ordering phenomena in the solid state. I have illustrated how now, more than ever, crystallography should be at the forefront of understanding the relationship between structure, electronic structure and physical properties.