

This research group seeks to understand and exploit the factors (strain, composition, electronic band structure etc.) that determine structure and function in the crystalline solid state. Our interest is in the balance between local crystal chemistry and longer range order in a wide range of compositionally and/or displacively flexible crystalline solids. The principal experimental research tools used are synthesis, transmission electron microscopy and scanning electron microscopy in combination with powder and single crystal X-ray diffraction. Systems investigated include wide range non-stoichiometric solid solutions, displacively flexible framework structures, ferroic phases, solid electrolytes, and incommensurately modulated structures. Achievements over recent years include the first coherent view of the crystal chemistry underlying the phenomenon of ferroelectricity within the Aurivillius family of displacive ferroelectrics, the use of compositely modulated structure formalism to describe, refine, and interpret "infinitely adaptive", non-stoichiometric solid solution fields, and the discovery and subsequent modelling of displacive flexibility and its consequences in a range of flexible framework structures.



Ordering Phenomena in Doped $\text{Ni}_{1+x}\text{M}_y\text{Te}_2$ ($\text{M} = \text{Ag}, \text{Cu}, \text{In}$)

A detailed TEM and XRD study has been carried out on B8 related ternary solid solution phases in the $\text{Ni}_{1+x}\text{M}_y\text{Te}_2$ ($\text{M} = \text{Ag}, \text{Cu}, \text{In}$) systems. Despite previous reports of large B8 ternary compositional homogeneity ranges in the $\text{Ni}_{1+x}\text{M}_y\text{Te}_2$ ($\text{M} = \text{Ag}, \text{Cu}$) systems, no evidence for incorporation of Ag into $\text{Ni}_{1+x}\text{Te}_2$ could be found while Cu could be incorporated but only if the Cu content was at much lower concentrations than previously suggested. In the case of $\text{M} = \text{In}$, two roughly determined solid solution fields were observed, an expected one based on the $\text{Ni}_{1+x}\text{Te}_2$ solid solution (SS1) and a second unexpected, quite distinct and compositionally broad solid solution (SS2) centred on the nominal composition $\text{Ni}_{2.80}\text{In}_{0.80}\text{Te}_2$. The latter SS2 solid solution was shown to be incommensurately modulated with a composition-dependent primary modulation wavevector. The origin of the incommensurate modulation in the case of the SS2 solid solution is attributed to the regular alternation of In-rich and Te-rich layers along the c direction. (with F. Brink, L. Norén, and H. Rundlof [U. Uppsala, Sweden])

Flexible Microporous Framework Structures

The inherent displacive flexibility of many framework structures plays a crucial role in many of their useful physical properties (low thermal expansion, easy ion exchange, catalytic activity, ..) and arises as a result of the existence of essentially zero frequency, Rigid Unit Modes (RUM's) entailing rotations but not distortions of their constituent polyhedral units. Such materials are frequently polymorphic and often undergo several displacive structural phase transitions, due to the condensation of RUM modes, as a function of temperature, pressure etc. A program has begun to systematically investigate a range of flexible, microporous framework structures in order to identify the appropriate RUM modes (via temperature-dependent electron diffraction), to analyze the displacive structural phase transitions therein, and to understand the physical properties associated with this inherent displacive flexibility. (with Y. Liu, L. Norén, Li Ying, and T.J. White [Inst. Environmental Science and Engineering, Nanyang Tech. U. Singapore])

Modulated Structures in Metal Oxyfluoride Systems

The compositional range of existence of the simultaneously ferroelectric and ferroelastic $A_2BM^VI O_3F_3$ ($A, B =$ alkali metal, $M^VI = Mo, W$) family of elpasolite-related oxyfluoride phases has been widened by the successful synthesis of elpasolite-related $Tl_3MoO_3F_3$. DSC showed two major polymorphic phase transitions at $42^\circ C$ and $130^\circ C$, respectively. Electron diffraction and XRD studies of the complex room temperature polymorphic form of this material has revealed a long period monoclinic superstructure coexisting with a highly structured, three-dimensional, continuous diffuse intensity distribution (arising from local O/F ordering and associated structural relaxation). (with F. Brink, L. Norén)

The Effects of Local Strain on the Crystal Chemistry of Solid Solutions

Planning for an ARC funded project to characterize substitutional strain in several wide range non-stoichiometric solid solution systems is under way. Several different but complementary techniques (vibrational spectral line broadening, diffuse intensity measurement and modelling and charge density analysis) will be used to investigate if it is possible to obtain direct measures of the enthalpy of mixing in such systems. It is planned to investigate Fe/Zn ordering in sphalerites, A/B ordering in AB_2S_4 thiospinels and oxygen/vacancy ordering and coupled cation ordering in anion-deficient "defect perovskites". (with T.R. Welberry, and A. Pring [South Australian Museum], N. Ishizawa [Tokyo Inst. Tech., Japan])

The Refinement of Partially Overlapped Reflections from Twinned Crystals

Automatic procedures often result in the identification of a unit cell for just the major of two twin related components of an X-ray diffraction pattern. We have developed a technique to cope with such data collected on our Nonius CAD4 CCD diffractometer by modifying the twin parameters a_i in the model $Y(h) = \sum_i a_i |F(h_i)|^2$ to become $a_i p_i$, where the integer j defines the refinable process used for evaluating p_i . This procedure has now been applied to a number of structures with considerable success. (with A.D. Rae, A.J. Edwards, A.C. Willis)

Polytypic Behaviour in Crystals in Terms of 1:1 Disordered Parent Structures

The 1:1 disordered parent structure is the Fourier transform of reflections of a particular index condition. Ordering the structure necessarily removes some symmetry elements and the choice of these symmetry elements is not necessarily unique. In the last year we have found four different crystal systems where different orderings correspond to options that include different space groups as well as different orientations of the same structure. We have studied two polymorphs of 9,10-phenanthrene quinone, both showing polytypic behaviour. The low temperature form has a 1:1 disordered $P21/c$ parent structure and ordering requires the doubling of the a and b axes to form layers of $C-1$ symmetry. Stacking layers $c/2$ apart results in either Cc or $F-1$ symmetry. We found and refined twinned crystals of each space group. Stacking faults were a feature of both. We also found and refined a crystal that could only be described in terms of the coexistence of uncorrelated blocks with different space groups. The averaging of intensities from different mosaic blocks with different stacking fault populations affords a workable model. (with A.D. Rae, A.C. Willis)

<http://www.rsc.anu.edu.au/withers.html>