Bragg Institute Neutron Beam Instrument Proposal

ID	**P2597**
Title	**Structure, magnetism and oxide ionic conduction mechanisms in vacancy-ordered perovskite ferrites**
Round	**2012-2 Neutron**

Schedule

The experiment has been scheduled using the following equipment and scientists.

Equipment	Start Date	End Date	Length
Koala	02/04/2012	02/04/2012	1
Koala	02/07/2012	05/07/2012	4
Koala	27/09/2012	29/09/2012	3
Wombat	28/09/2012	29/09/2012	2
Wombat	07/10/2012	09/10/2012	3

Researchers

Name	Role
Chris Ling (Uni Sydney)	Principal Scientist
Josie Auckett (Uni Sydney)	Co-proposer
Andrew Studer (ANSTO - BI)	Co-proposer

Proposed Research (PDF)

The next 2 pages have been uploaded as part of the proposal.

Solid-state materials with high oxide ionic conductivity at "intermediate" temperatures (~600–800 ºC) are of great interest as potential electrolytes in a new generation of solid-oxide fuel cells (SOFCs). Reducing the operating temperature of SOFCs below 1000 ºC would increase efficiency and lifetime, and reduce cost by allowing the use of cheaper materials for other critical components such as casings, seals and interconnects. [1] While many candidate materials are being actively investigated, only two structure types are known to support reversible oxygen intercalation/ deintercalation right down to room temperature: K_2NiF_4 (*eg*, La_2MO_4, M = Co, Ni, Cu) [2] and the Brownmillerite-type oxygen-deficient perovskites $Sr_2M_2O_5$, M = Fe, Co. [3–5] Experimental and theoretical studies that can shed light on the oxygen diffusion processes in these unique compounds are therefore of considerable interest to the materials science community.

We recently grew the first ever large single crystal of $Sr_2Fe_2O_5$ by the floating-zone method, and collected single-crystal neutron diffraction data on Wombat. The crystal was found to be twinned on a microscopic scale with respect to the unit cell of the disordered oxygen-deficient perovskite from which it forms, but this twinning was not complete or equivalent in all directions. The Wombat data revealed a supercell with a doubled *a* axis, compared to the conventional *Icmm* model containing disordered left- and right-handed tetrahedral chains. This corresponds to the $\beta = 0$, $\gamma = ½$ case of the $I2/m(0\beta\gamma)0s$ chain-ordering modulation proposed by D'Hondt *et al*. [6] on the basis of electron microscopy and electron diffraction evidence. We reported its first observation by neutron diffraction, [7] proving that the tetrahedral chains are long-range ordered at room temperature, in a more complex manner than the *Ibm*2 model previously assumed to describe local chain order. The superstructure peaks disappear at 540 °C in a pseudo-first order manner (Figure 1), an observation that we have combined with the results of a single-crystal QENS experiment (IN5@ILL) and *ab initio* molecular dynamics calculations, to propose a new model for the oxide ionic diffusion mechanism (paper in preparation).

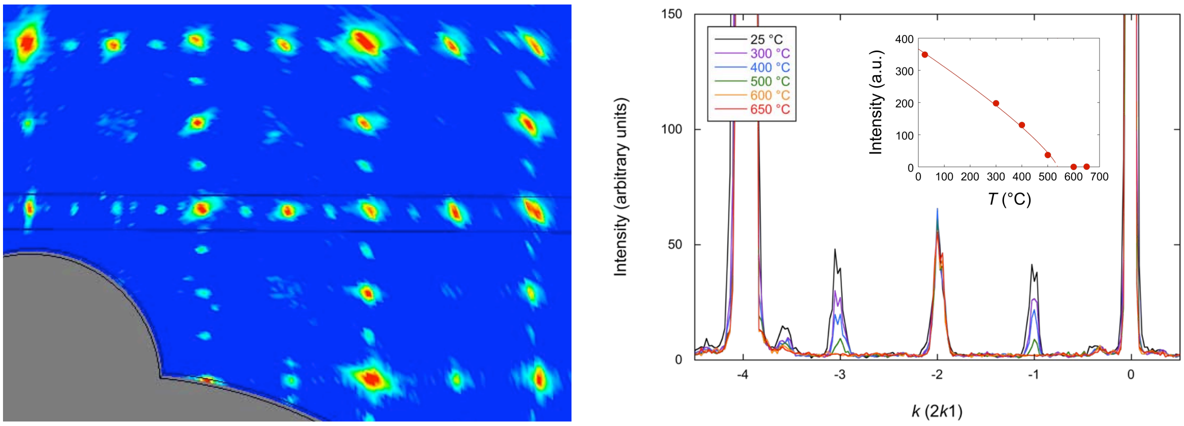

Figure 1. (Left) Reconstructed precession image of the zeroeth-order Laue zone of $Sr_2Fe_2O_5$ from Wombat data at room temperature. (Right) Integrated intensities along the line indicated by the black box on the left-hand figure, showing the disappearance of the superstructure peaks at 540 °C.

We subsequently grew a large crystal of the related brownmillerite $Ca_2Fe_2O_5$ by the same method. Single-crystal neutron Laue (Koala) images of the entire boule (Figure 2) show that it is untwinned, and data collected from a small fragment could be used to refine not only the crystal structure but also the ordered magnetic structure in unprecedented detail, including a weak ferromagnetic (FM) canting of the G-type antiferromagnetic (AFM) state, which had been proposed on the basis of physical property measurements [8] and symmetry arguments [9] but never before refined against diffraction data. While this is a significant result in its own right, we intend to delay publication until after we have conducted the further experiments proposed below. The quality of this $Ca_2Fe_2O_5$ crystal means that we can use it to resolve a number of other outstanding questions concerning this compound, which collectively will have significantly higher impact.

(1) Tetrahedral chains in $Ca_2Fe_2O_5$ display simple long-range order up to 963 K, above which temperature the structure becomes incommensurately modulated in a similar manner to $Sr_2Fe_2O_5$ at room temperature. [10] A series of high-temperature monochromatic single-crystal diffraction experiments on Wombat, along the same lines as our work on the Sr analogue [7] where incommensurate order at room temperature gives way to interchain disorder in the ionic conducting regime, will provide valuable insight into why the Ca compound is a poorer ionic conductor and how it could be modified to ameliorate that. The result is expected to be 'cleaner' and easier to interpret in this case due to the absence of twinning in our $Ca_2Fe_2O_5$ crystal.

(2) A substantial magnetic susceptibility anomaly in the range $40\ K < T < 140\ K$ has been attributed to a reorientation of the AFM easy axis from [001] to [100]. [11] However, when we carried out magnetic structure

refinements against low-temperature single-crystal neutron Laue (Koala) data collected from our crystal we found no evidence for such a reorientation. The effect must therefore be due to a more subtle change in the balance between competing AFM and FM interactions, possibly giving rise to frustrated and/or low-dimensional spin ordering. Monochromatic single-crystal neutron diffraction data are required to search for evidence of the magnetic diffuse scattering that should accompany and help us to elucidate these features.

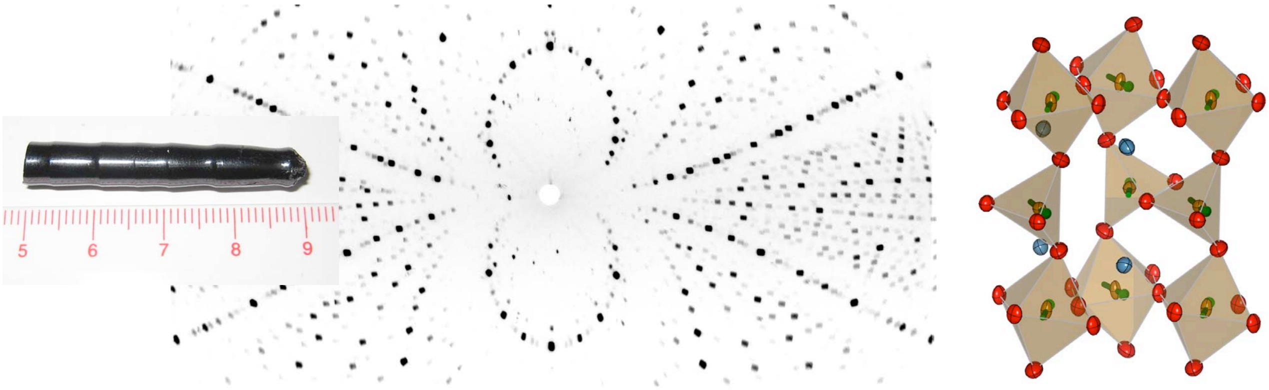

Figure 2. Our floating-zone grown crystal boule of $Ca_2Fe_2O_5$ (scale bar is in cm) superimposed on a neutron Laue diffractogram (Koala) taken from the whole boule. The crystal and magnetic (canted AFM) structure on the right was refined against Koala data taken from a smaller fragment.

(3) The reduction of $Ca_2Fe_2O_5$ and $Sr_2Fe_2O_5$ with CaH_2 at 550 K was recently found to produce $A$$FeO_2$ oxides with an unprecedented infinite-layered structure consisting of corner-connected square-planar FeO_4 units that recall the topology of the superconducting layered cuprates. [12,13] It has been shown that perfectly oriented thin films of (Sr,Ca)FeO_2 can be obtained by epitaxial reduction of brownmillerite precursor films, [13,14] which means that we should be able to convert fragments of our single crystals using the same method. Because the reduction process is diffusion limited, we are attempting these experiments on fragments at the lower size limit for collection of neutron Laue data on Koala (~0.1 mm^3). We have sealed a range of different-sized crystals (and some reference powder) in quartz tubes for reduction by CaH_2 over the next 2 months. The structures of these oxides have never been investigated with single-crystal diffraction data; and, surprisingly, the temperature dependence of their low-temperature magnetic structures has not been investigated in detail.

This work is the first part of the PhD project of Josie Auckett (due for completion in 2015).

Experimental details

We wish to collect single crystal neutron diffraction data on Wombat for $Ca_2Fe_2O_5$ (a) in the cryocooler at low temperatures (10, 100, 200, 300, 400 K) to probe magnetic order and (b) in the vacuum furnace at high temperatures (500, 600, 700, 800, 900 K) to probe structural (interchain) order. The Eulerian cradle will be used to align the crystal initially at room temperature. 10 days are requested based on 1 day *per* temperature.

We wish to collect single crystal neutron Laue data in the cryofurnace on Koala for $SrFeO_2$ and $CaFeO_2$. We will require 1 day for crystal testing and sorting (some prior testing will be performed with x-rays, but this will not be possible for the larger crystals due to absorption), and 2 days data collection for each of $CaFeO_2$ and $SrFeO_2$ (10, 100, 200, 300 K @ 12h *per* data set, based on 9 exposures of 90 minutes each) = 5 days total.

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