ESRF	**Experiment title:** Correlation of structures and properties of layered oxide chalcogenides $Sr_2CoO_2Cu_{2-delta}S_2$ and $Sr_2NiO_2Cu_2Se_2$	**Experiment number:** CH-4997
Beamline: ID22	**Date of experiment:** from: 25 FEB 2017 to: 27 FEB 2017	**Date of report:** 4 SEP 2017
Shifts: 6	**Local contact(s):** Dr A N Fitch	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Mr Jack Blandy*, Dr Simon Cassidy*, Prof Simon Clarke

Report:

The aim of the experiment was to probe the changes in structure accompanying deintercalation of Cu from $Sr_2CoO_2Cu_{2-\delta}S_2$, in particular the orthorhombic distortion [1] and also to explore the structural changes that accompany the magnetic transition at about 50 K in $Sr_2NiO_2Cu_2Se_2$ in order to make compariosn with the sulfide analogue [2]. This experiment has been accompanied by a complementary powder neutron diffraction experiment at the ISIS facility to probe the evolution of the magnetic ordering.

Figure 1 shows the refinement at room temperature for $Sr_2NiO_2Cu_2Se_2$. The structure is modelled in *I4/mmm* according to the normal structure found for related compounds.

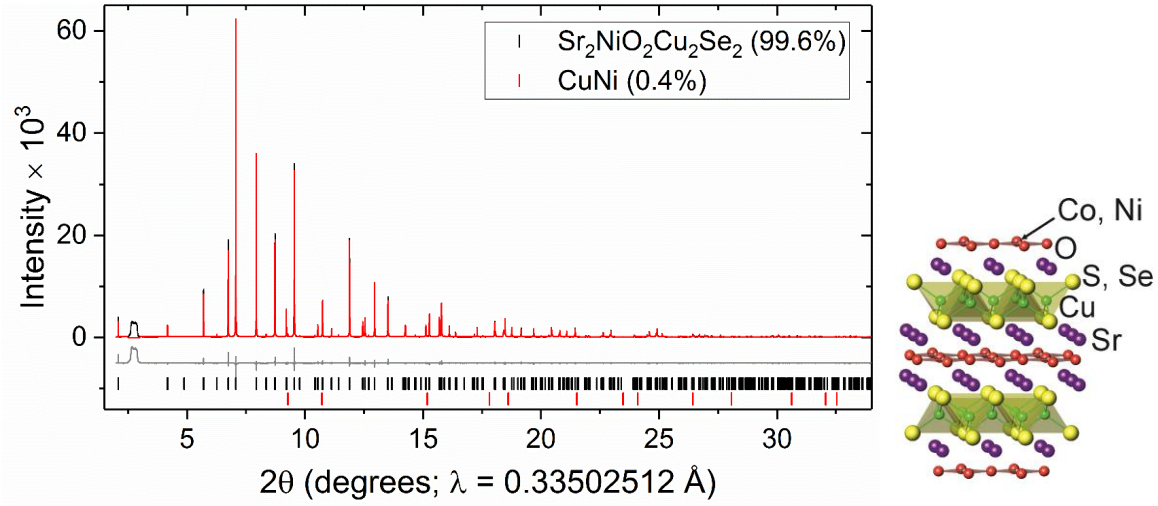

Figure 1. Rietveld refinement of $Sr_2NiO_2Cu_2Se_2$ at room temperature.

Figure 2 shows the behaviour of the 017 reflection of the same $Sr_2NiO_2Cu_2Se_2$ sample measured on warming from 5 K to 140 K. This shows an unexpected broadening of the reflection on warming which coincides with exposure to the hard X-rays of ID22. Attempts to model the data in the region around 60K, which coincides with the magnetic transition, as a

distortion, or as multiple phases failed to give satisfactory fits. The broadening found on ID22 was not evident on the neutron diffractometer HRPD at 60 K, nor on the I11 diffractometer at Diamond at 100 K, even though both instruments should have been able to resolve it. It is possible that the sample undergoes an X-ray-induced electronic transition. and this needs to be probed by carrying out further measurements on ID22 using different wavelengths and using different sample histories (e.g. to investigate whether the broadening depends on the duration of the exposure to X-rays). This investigation will be the subject of a further experiment proposal.

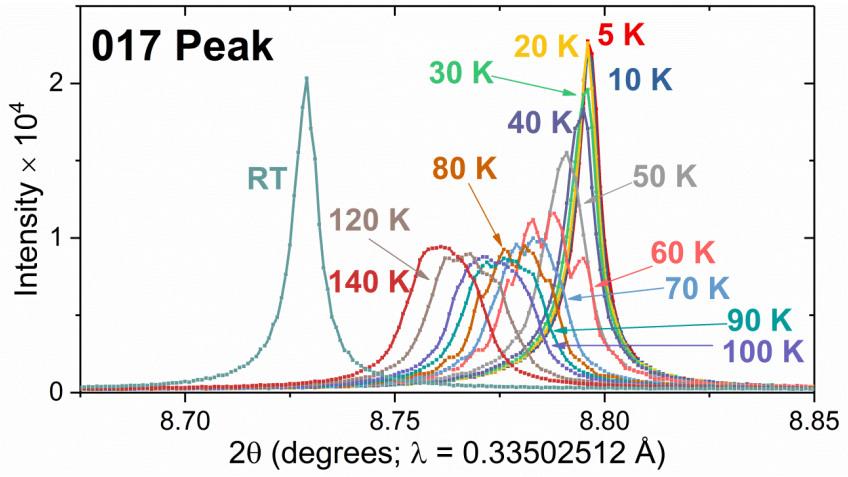

Figure 2. Raw PXRD patterns of $Sr_2NiO_2Cu_2Se_2$ measured at various temperatures using ID22 diffractometer, the 017 peak is emphasised

In the case of $Sr_2CoO_2Cu_{2-\delta}S_2$ Figure 3 shows the behaviour of the orthorhombic distortion which increases with the oxidation of the system and which is barely resolved in the parent ($\delta = 0$) sample (JNB051), but well-resolved for JNB087 ($\delta = 0.18(1)$) and JNB086 ($\delta = 0.24(1)$). The origin of this increase in the distortion is now unclear. The explanation that it is driven by the size of the orbital contribution to the ordered magnetic moment through a magneto-elastic coupling [1] may be in doubt because the oxidation also reduces the size of the ordered moment [1]. Analysis of these data are still ongoing and other experiments are planned or in progress using complementary techniques and computation.

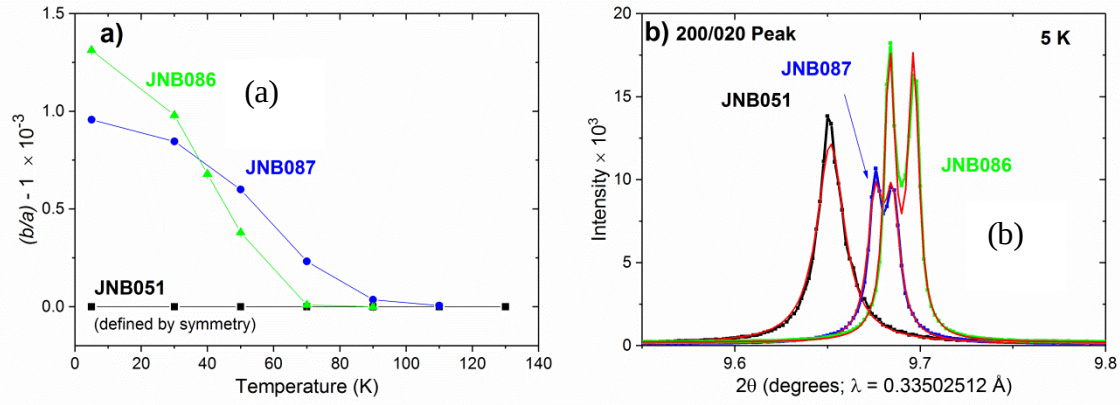

Figure 3 (a). Orthorhombic distortion of three samples of $Sr_2CoO_2Cu_{2-d}S_2$ as a function of temperature (the lines are guides to the eye); b) the splitting of the 200/020 peak at 5 K for the same three samples

[1] Smura, C. F. *et al. J. Am. Chem Soc.* **2011**, *133*, 2691-2705.
[2] Clarke, S. J. *et al. Inorg. Chem.* **2008**, *47*, 8473–8486.