Experimental report

01/09/2017

Proposal:	**5-31-2461**	**Council:**	4/2016

Title: Investigating the origin of the magnetic switching in Sr2-xCaxCrSbO6.

Research area: Chemistry

This proposal is a new proposal

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Samples: Sr_2CrSbO_6
Ca_2CrSbO_6
$Sr_{1.75}Ca_{0.25}CrSbO_6$
$Sr_{1.5}Ca_{0.5}CrSbO_6$
$SrCaCrSbO_6$
$Sr_{0.5}Ca_{1.5}CrSbO_6$

Instrument	Requested days	Allocated days	From	To
D1B	0	2	20/06/2016	22/06/2016
D2B	4	2	26/09/2016	28/09/2016

Abstract:

Sr_2CrSbO_6 and Ca_2CrSbO_6 are both double perovskites with a high degree of cation ordering however Sr_2CrSbO_6 is an antiferromagnet while Ca_2CrSbO_6 is a ferromagnet. To investigate this switching of the magnetic properties by simply changing the diamagnetic cation we synthesised the series $Sr_{2-x}Ca_xCrSbO_6$ and found that, surprisingly, there is an intermediate paramagnetic state rather than a spin-glass state between the antiferromagnetic and ferromagnetic states. We wish to investigate whether the change in the magnetic properties across the series can be correlated to the degree of octahedral tilting and confirm whether, as suggested from powder x-ray diffraction, there is a structural phase transition from the I2/m to the $P2_1/n$ space group between x=0.25 and x=0.5. To do this we propose to collect powder neutron diffraction data on six compounds in the series on instrument D2b at room temperature and at 2 K using a wavelength of 1.59 Å and at 2 K using a wavelength of 2.40 Å to refine the crystal structures and to look for magnetic Bragg peaks. Thus 18 data collections are required, which we estimate will require four days of beamtime on instrument D2b.

Experimental report: Investigating the origin of the magnetic switching in $Sr_{2-x}Ca_xCrSbO_6$

We requested four days on D2b to study the nuclear and magnetic structure of six compounds in the $Sr_{2-x}Ca_xCrSbO_6$ series (x=0, 0.25, 0.5, 1.0, 1.5, 2.0). We were granted 2 days on D1b (20/06/16-22/06/16) followed by 2 days on D2b (26/09/16-28/09/16). A wavelength of 2.52 Å was used on D1b and data were collected on all six compounds in 1 K steps from 2 K to typically 20 K. This was to enable us to study the evolution of the magnetic structure of all six compounds. The x=0, 0.5 and 1.0 compositions were selected for further study on D2b on which data were collected using a wavelength of 1.594 Å at room temperature, 25 K and 2 K. Low temperature measurements were conducted in the cryofurnace and room temperature measurements were carried out on the rotating sample table whilst waiting for the cryofurnace to change temperature. This allowed us to maximise the time spent collecting data. Below is a summary of the main results of the proposal, which are currently being written up for publication.

Sr_2CrSbO_6

The I2/m and P2$_1$/n space groups have been previously suggested for Sr_2CrSbO_6 [1][2] and from x-ray diffraction data alone we thought that the I2/m model was appropriate. However in the neutron diffraction data the symmetry needed to be lowered to $I\bar{1}$ to account for all of the peak splitting observed in the high-resolution D2b data. This gave lattice parameters at room temperature of a=5.55664(8) Å, b=5.57821(8) Å, c=7.84771(10) Å, α=89.9979(32)°, β=89.9668(24)° and γ=89.9374(11)° and the distorted away from monoclinic symmetry was even more pronounced at 2 K with the refinement yielding lattice parameters of a=5.53808(22) Å, b=5.53662(23)Å, c=7.89660(14) Å, α=90.1931(27)°, β=89.8548(30)° and γ=90.0665(13)°. The full refinement at 2 K is shown in Figure 1. The structural model refined at 2 K was input into the D1b data and the wavelength was refined with the lattice parameter fixed to normalise the two data sets. From this we found that the magnetic structure was similar to that published previously but with $m_{x1}=-m_{x2}$; $m_y=0$ and $m_{z1}=-m_{z2}$, rather than $m_{y1}=m_{y2}$. This alteration as well as the change in the structural model from P2$_1$/n to $I\bar{1}$ gave a more realistic refined Cr(III) moment of 2.368(11) μ_B rather than the reported 1.64 μ_B [2].

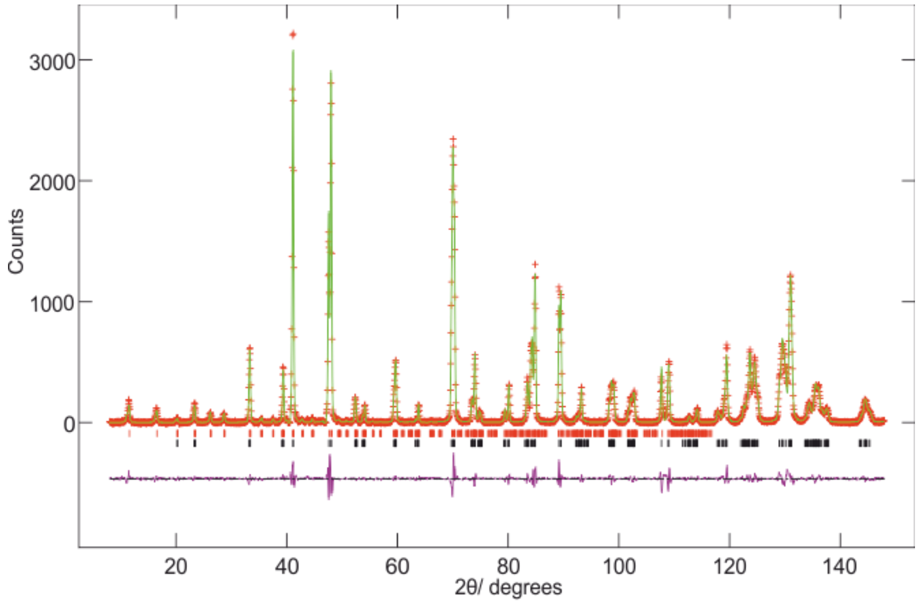

Figure 1 - Observed (red crosses) and calculated (green line) neutron powder diffraction profiles recorded on D2b at 2 K (λ=2.52 Å) for Sr_2CrSbO_6 using the $I\bar{1}$ space group model. Reflection markers are shown for magnetic (top) and structural (bottom) Sr_2CrSbO_6.

$Sr_{1.75}Ca_{0.25}CrSbO_6$ and $Sr_{1.50}Ca_{0.50}CrSbO_6$

From magnetometry data both of these compounds appeared to be paramagnetic down to 2 K. However, from the D1b data, small magnetic Bragg peaks corresponding to the same magnetic structure as Sr_2CrSbO_6 were staring to appear below 5 K in $Sr_{1.75}Ca_{0.25}CrSbO_6$ (see figure 4). Weak additional reflections corresponding to a (ooe) tilt were also apparent, suggesting that the space group had changed to $P2_1/n$ upon introducing Ca. At 2 K magnetic reflections corresponding to the Sr_2CrSbO_6 magnetic structure are just about visible in $Sr_{1.50}Ca_{0.50}CrSbO_6$ as well suggesting that the magnetic structure switches from antiferromagnetic to ferromagnetic without going through a paramagnetic intermediate. Close inspection of the D2b data collected on $Sr_{1.50}Ca_{0.50}CrSbO_6$, particularly of the high-angle region as shown in Figure 2, shows that this composition is phase separated into two perovskite phases, both of space group $P2_1/n$. The phase with the smaller volume unit cell has been shown from the neutron refinement to be more Ca-rich and this corresponds to a smaller average B-O-B tilt angle of 162.38˚ rather than 165.07˚ in the more Sr-rich phase.

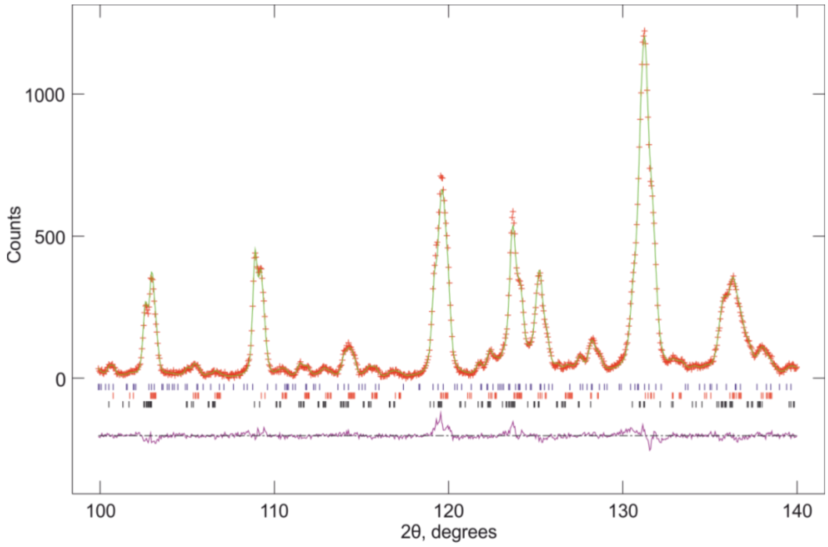

Figure 2 – Close-up of observed (red crosses) and calculated (green line) neutron powder diffraction profiles recorded between 100˚ and 140˚ on D2b at RT (λ=2.52 Å) for nominal $Sr_{1.5}Ca_{0.5}CrSbO_6$ using a two-phase model. Reflection markers are shown top to bottom for $Sr_{0.61}Ca_{1.39}Sb_2O_7$, $Sr_{1.53}Ca_{0.47}Cr_{1.02}Sb_{0.98}O_6$ ($P2_1/n$) and $Sr_{1.74}Ca_{0.26}Cr_{1.02}Sb_{0.98}O_6$ ($P2_1/n$).

$SrCaCrSbO_6$, $Sr_{0.5}Ca_{1.5}CrSbO_6$ and Ca_2CrSbO_6

All of these three compounds crystallise in the $P2_1/n$ space group but the *a* and *b* lattice parameters diverge (especially $1.5 \leq x \leq 2.0$) and the (ooe) tilts increase as more Ca is introduced. Compared to $Sr_{1.50}Ca_{0.50}CrSbO_6$, the average B-O-B bond angle of $SrCaCrSbO_6$ has further decreased to 160.22˚ at 300 K. Although there was unfortunately insufficient time to collect neutron diffraction data on D2b on $Sr_{0.5}Ca_{1.5}CrSbO_6$ and Ca_2CrSbO_6, previous neutron diffraction work on Ca_2CrSbO_6 gives a room temperature average B-O-B bond angle of 152.5˚[2], which is close to the value of 152.1˚ we refined for the same composition from synchrotron x-ray diffraction data. The average B-O-B bond angle we refined for $Sr_{1.50}Ca_{0.50}CrSbO_6$ from x-ray synchrotron data of 156.0˚ is approximately equidistant between the bond B-O-B bond angles of the x=1.0 and x=2.0 compositions, thus there is a clear trend that the B-O-B bond angles decrease substantially as the Ca composition increases.

From the SQUID data all compositions above x=0.5 are ferromagnetic with T_C increasing with increasing Ca content. This ferromagnetic transition is also evident in the D1b data and the spins were found to co-aligned in the *xy* plane. The refined moment of the Cr(III) ion as a function of temperature for all compositions bar x=0.5 is shown in Figure 3 and shows the onset of magnetic ordering increasing from 7 K for $SrCaCrSbO_6$ to 14 K for Ca_2CrSbO_6. The onset of magnetic order can also be followed in the contour plots in Figure 4. The refined moment of Cr(III) in Ca_2CrSbO_6 at 2 K was found to be 2.564(28) μ_B, which is within error of the value of 2.6(2) μ_B reported in the literature.

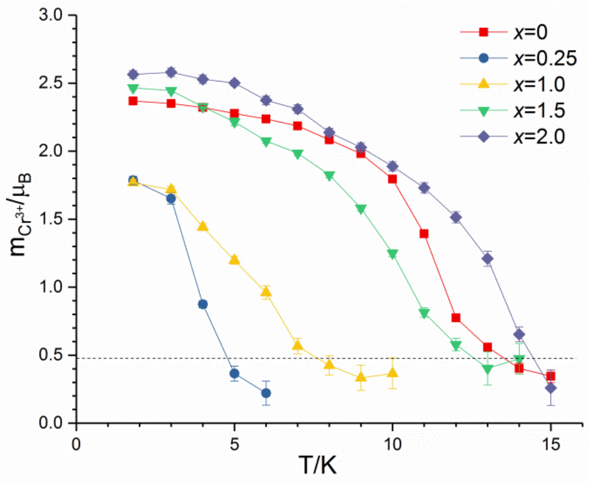

Figure 3 – Refined Cr(III) moment as a function of temperature for compositions with x=0, 0.25, 1.0, 1.5 and 2.0. The dashed line is an estimate of the background level.

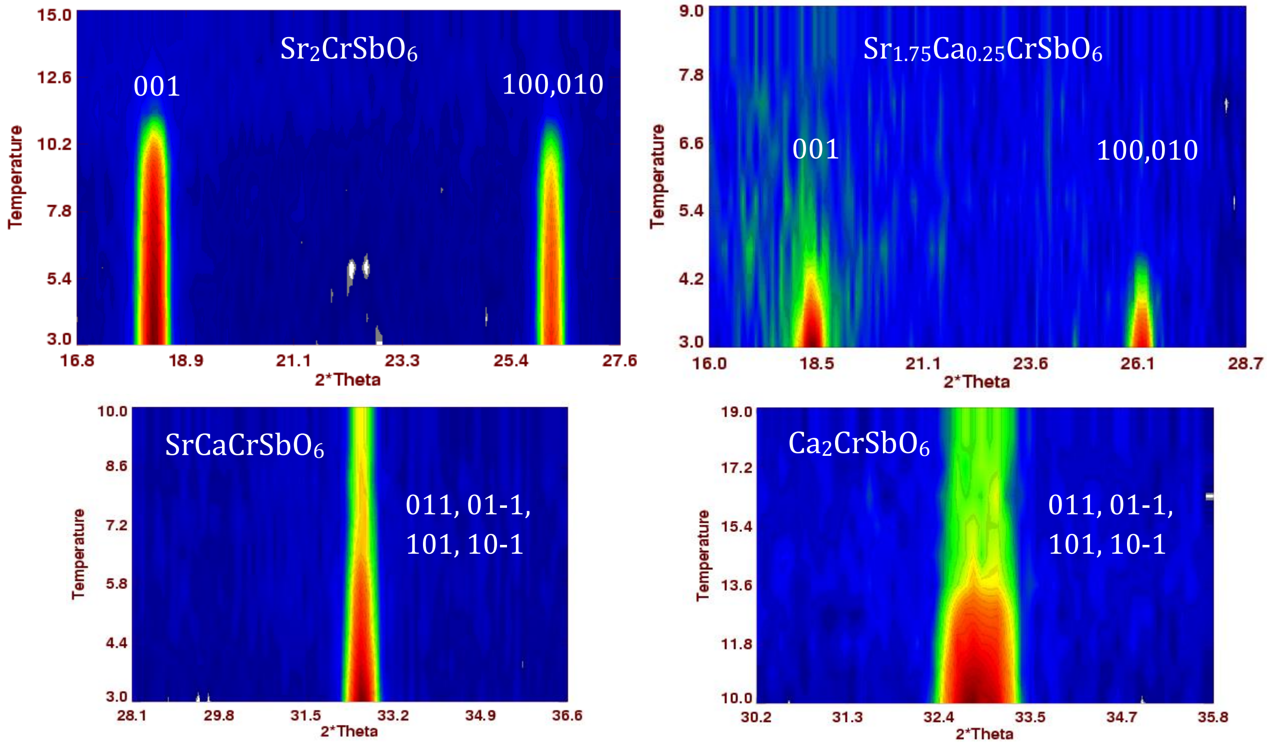

Figure 4 – 2D contour plots created using neutron diffraction data collected on D1b showing the intensity of select magnetic Bragg peaks as a function of temperature for Sr_2CrSbO_6, $Sr_{1.75}Ca_{0.25}CrSbO_6$, $SrCaCrSbO_6$ and Ca_2CrSbO_6.

[1] A.Faik, J. M. Igartua, M. Gateshki and G. J. Cuello, *J. Solid State Chem.* **182**, 1717 (2009) **[2]** M. Retuerto, M. García-Hernández, M. J. Martinez-Lope, M. T. Fernández-Díaz, J. P. Attfield and J. A. Alonso, *J. Mater. Chem.* **17**, 3555 (2007)