Experimental Report

Proposal: **5-31-2266** **Council:** 10/2012

Title: Magnetic characterisation of mixed-cation low-dimensional chain structures

This proposal is a new proposal

Researh Area: Chemistry

Main proposer: **GREAVES Colin**

Experimental Team: GREAVES Colin

Local Contact: RITTER Clemens

Samples: CoxMn(1-x)Sb2O4

Instrument	Req. Days	All. Days	From	To
D2B	2	2	24/07/2013	26/07/2013

Abstract:

Schafarzikite (FeSb2O4) is tetragonal with 1-D chains of FeO6 octahedra along [001]. We have previously shown that mixed Fe/Co cations within the chains lead to a change in magnetically ordered structure, consistent with the FeSb2O4 and CoSb2O4 parent phases. This experiment plans to determine the nuclear and magnetic structures of mixed Mn/Co analogues. Here, the strong spin-orbit coupling and magnetic interactions of Co are expected to dominate those of Mn, leading to a fundamentally different groundstate even for low cobalt content. Associated with this is the effect of Co on the antiferromagnetic transition, which is very gradual in MnSb2O4 but sharp in CoSb2O4.

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Both $MnSb_2O_4$ and $CoSb_2O_4$ adopt the Schafarzikite (MX_2O_4) structure-type, characterised by pseudo-1D chains of edge-sharing [MO_6] octahedra aligned along (001). In this study, $Mn_xCo_{1-x}Sb_2O_4$ has been synthesised for $x = 0.2$, 0.4, 0.5, 0.6 and 0.8 by solid-state reaction within sealed quartz ampoules. NPD data (D2B) have been collected at 298 K and 5 K for the entire composition range, and at a selection of intermediate temperatures for $x = 0.2$. Data have been refined using the GSAS package.

Room temperature results show a linear increase in unit cell parameters with increasing x, and a gradual change in atomic coordination from $CoSb_2O_4$-like to $MnSb_2O_4$-like. The $O2_{ax}$ position shows a large thermal displacement parameter for all compositions; refinement of an anisotropic model shows displacement mainly in the *ab*-plane. This indicates local rotation of the [MO_6] octahedra, consistent with the different bonding requirements of Co^{2+} and Mn^{2+}. On cooling, the displacement parameter for M in $Mn_{0.2}Co_{0.8}Sb_2O_4$ shows a dramatic increase below 60 K. A number of refinement models have been tested, suggesting that the increase is related to a local displacement of the [MO_6] octahedra, occurring over a similar temperature range as the magnetic ordering transitions.

The magnetic structures of $Mn_xCo_{1-x}Sb_2O_4$ show a gradual change from C_z-type (ferromagnetic (FM) chains, antiferromagnetic (AFM) planes) to A_x-type (AFM chains, FM planes) with increasing x (figure 1). Small amounts of Co^{2+} within the $MnSb_2O_4$ structure do not cause a significant change in magnetic ground-state as anticipated, although the observed behaviour is very similar to that seen in $Fe_xCo_{1-x}Sb_2O_4$. The refined magnetic moments show a reduced magnitude to the expected values, connected with the disruption of magnetic interaction on cation mixing.

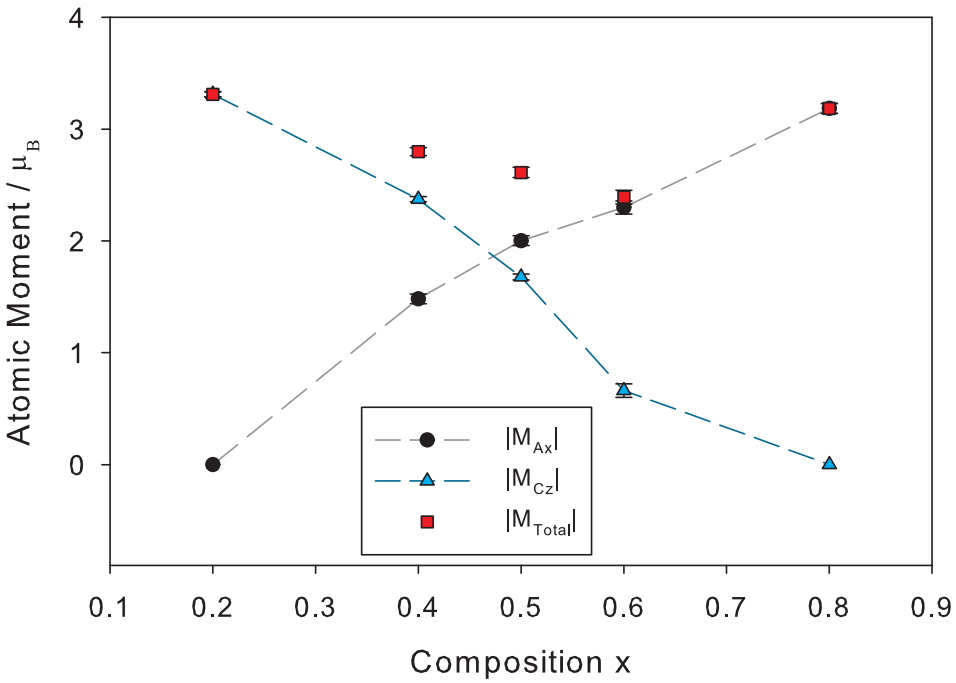

Figure 1: Refined magnetic moments from 5 K NPD data for $Mn_xCo_{1-x}Sb_2O_4$.

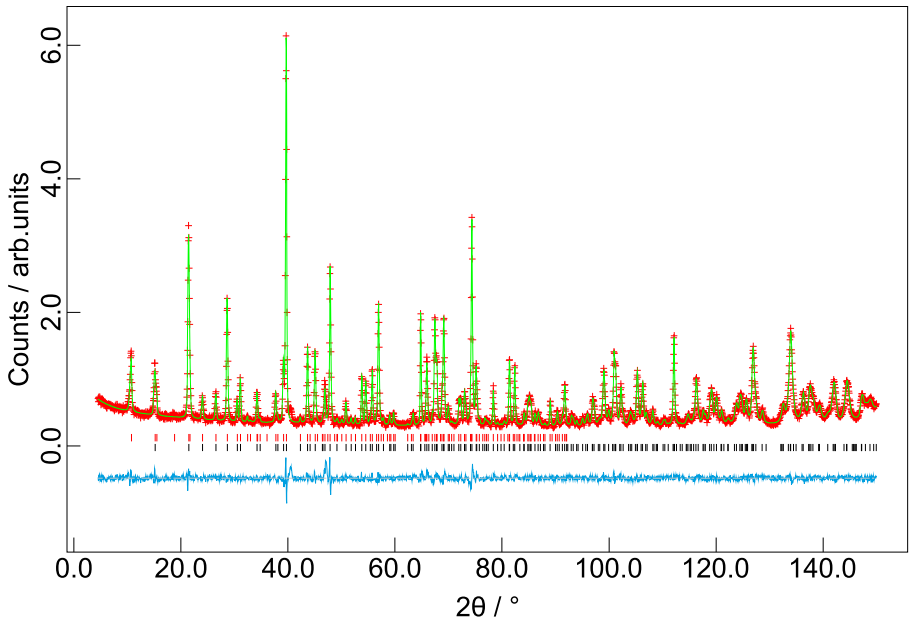

Figure 2: NPD fitted profiles for $Mn_{0.5}Co_{0.5}Sb_2O_4$ at 5 K. Black tickmarks-nuclear reflections; red tickmarks-magnetic reflections.