Experimental report

30/05/2017

Proposal: 5-31-2396 **Council:** 10/2014

Title: Magneto-structural order in "breathing" pyrochlore spinels

Research area: Physics

This proposal is a continuation of 5-31-2275

Main proposer: Goran NILSEN

Experimental team: Hannu MUTKA
Rafal WAWRZYNCZAK
Tom FENNELL
Michel KENZELMANN
Goran NILSEN

Local contacts: Thomas HANSEN

Samples: LiInCr4O8
LiGaCr4O8

Instrument	Requested days	Allocated days	From	To
D20	1	1	28/07/2015	29/07/2015

Abstract:

The spinel oxide family of materials displays a rich variety of physics, from spin frustration to heavy fermion behavior. In this context, we have recently studied the chromium spinels LiGaCr4O8 and LiInCr4O8, where the A-site is populated by two cations. This substitution causes an alternation in the dimensions of the Cr3+ (S=3/2) tetrahedra on the B-site, and leads to a corresponding alternation in the magnetic exchanges. While previous diffraction measurements have shown a two-step magneto-structural ordering in both compounds, the details of the magnetic and nuclear structures have thus far proven elusive. As a first step towards a deeper understanding of the complex low T behavior of these compounds, we propose a magnetic diffraction experiment on the D20 diffractometer.

Magneto-structural order in "breathing" pyrochlores $LiGaCr_4O_8$ and $LiInCr_4O_8$

R. Wawrzynczak,[1] G. Nilsen,[2] Y. Okamoto,[3] and Z. Hiroi[4]

[1] *Institut Laue Langevin, FR-38042 Grenoble, France*
[2] *ISIS Facility, STFC, UK-OX11 0QX Didcot, United Kingdom*
[3] *Department of Applied Physics, Nagoya University, JP-464-8603 Nagoya, Japan*
[4] *Institute for Solid State Physics, University of Tokyo, JP-277-8581 Chiba, Japan*

Using the neutron powder diffractometer D20 (λ=2.41 Å), we have investigated in detail the temperature dependence of the magneto-structural transitions in $LiInCr_4O_8$ and $LiGaCr_4O_8$. In the former material, a structural transition at $T_U \sim 18$ K leads to a coexistence of high-T cubic and low-T tetragonal phases followed by onset of magnetic spin freezing in a short-range ordered pattern at $T_L \sim 12$ K. Diffraction patterns collected on the latter compound suggest a more complicated sequence of structural distortions and magnetic transitions. One of the magnetically ordered phases appears consistent with a collinear $\mathbf{k} = (001)$ *structure, however.*

The $LiGa_{1-x}In_xCr_4O_8$ chromate spinel oxides belong to family of frustrated magnets called "breathing" pyrochlores. The Cr^{3+} cations (S=$\frac{3}{2}$) on the B site are placed on the vertices of corner-sharing tetrahedra forming pyrochlore lattice. Populating the A-site with ions of different sizes leads to an alternation in the sizes of the tetrahedra, thereby also influencing the magnetic interactions in the material.

The macroscopic degeneracy in these systems, caused by antiferromagnetic interactions between the neighbouring Cr^{3+} ions, is lifted by coupling to the lattice, which causes magnetic, structural, and mixed transitions at low temperature. Fig 1. shows the powder thermodiffractogram measured on the $LiInCr_4O_8$ sample, where a transition at $T_U \sim 17$ K results in two phases: cubic ($F4\bar{3}m$) and tetragonal ($I\bar{4}m2$). Magnetic order sets on in the latter at $T_L \sim 12$ K.

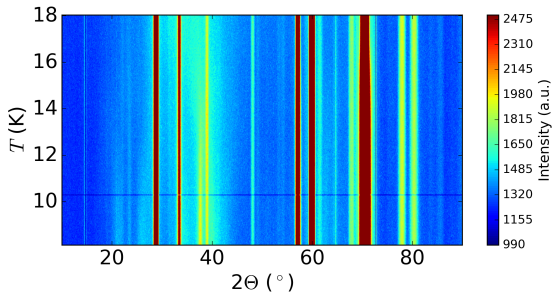

FIG. 1. Thermodiffractogram measured on $LiInCr_4O_8$ around phase transitions.

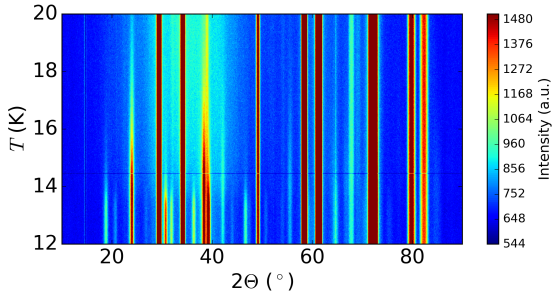

FIG. 2. Thermodiffractogram measured on $LiGaCr_4O_8$ around phase transitions.

A prior high resolution synchrotron X-ray powder diffraction study allowed us to determine that at low temperatures $LiGaCr_4O_8$ hosts a mixture of two lower symmetry phases (either tetragonal or orthorhombic). The first of these arises gradually around $T_U \sim 20$ K, while the latter sets on more abruptly in a first-order transition at $T_L = 13.5$ K. The thermodiffractogram of $LiGaCr_4O_8$ reveals that the structural transitions are in each case accompanied by magnetic order.

Initial refinements of the magnetic structure in the allowed us to identify the magnetic order below T_U as magnetic space group C_A222_1 (Fig. 3), belonging to the mM_5 irreducible representation (Miller-Love notation, parent space group $I\bar{4}m2$, $\mathbf{k} = (001)$), rather than $P_I\bar{4}m2$ (mM_1) (Fig. 4), as proposed in: Saha R., *et al.*, PRB **94**, 064420 (2016).

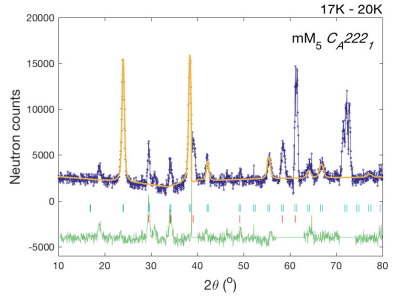

FIG. 3. Rietveld refinement of magnetic structure assuming the C_A222_1 magnetic space group. The unfitted peaks arise from the temperature subtraction, except the peak at 18°, which is a precursor of the low-T ordered structure.

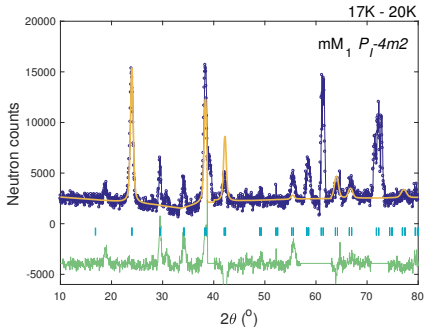

FIG. 4. Rietveld refinement of magnetic structure with assumption of $P_I\bar{4}m2$ magnetic space gorup.