Experimental report

20/01/2022

Proposal:	**CRG-2783**	**Council:**	4/2020
Title:	Nuclear and magnetic structures ofLi2Mn2(SO4)3		
Research area:			

This proposal is a new proposal

Main proposer:	**Marine REYNAUD**
Experimental team:	Marcus FEHSE
Local contacts:	Oscar Ramon FABELO ROSA

Samples: Li2Mn2(SO4)3

Instrument	Requested days	Allocated days	From	To
D1B	1	1	21/09/2020	22/09/2020

Abstract:

Proposal CRG-D1B-20-381 Experimental report: Nuclear and Magnetic structures of $Li_2Mn_2(SO_4)_3$

Main proposer: Marine Reynaud, Co-proposers: Iciar Monterrubio, Marcus Fehse.

Local contact: Oscar Fabelo Rosa

Li-ion batteries have played a key role in the development of portable electronic devices for the last twenty years, and are nowadays on the way to be used for developing higher-volume applications, such as electric vehicles or large-scale electrochemical storage for smart-grid electricity management. To achieve these goals, high energy density electrode materials based on low-cost, abundant and environmental benign elements are specifically required. Up to now, the most promising polyanionic material has been the so-called olivine $LiFePO_4$ (3.45 V vs. Li^+/Li^0 and ~150 mAh/g). In an attempt to identify other good contenders displaying higher redox potentials, sulfate-based compounds have been studied, with in particular the disulfates $Li_2M(SO_4)_2$[1–4] (M = Fe, Mn, Ni, Co, Zn, Mg) and the trisulphates $Li_2M_2(SO_4)_3$ (M = Mn, Mg, Fe)[5,6], among which the iron-based compounds present attractive electrochemical properties.

Besides their electrochemical properties, the 3D structure of these polyanionic compounds make them materials of interest for magnetic studies. The peculiar 3D frameworks of the two polymorphs $Li_2M(SO_4)_2$ solely enable super-super-exchange antiferromagnetic interactions, and the magnetic structure of the orthorhombic polymorphs have the inversion center associated with time inversion and could therefore be magnetoelectric[2,4,7]. In the 3D structure of $Li_2Mn_2(SO_4)_3$ published by Isasi *et al.*[5] (Figure 1a), manganese atoms occupy two crystallographically independent octahedral sites, labelled Mn1 and Mn2, where $[Mn2]O_6$ octahedra (in purple in Figure 1a) are organized in pairs sharing one common edge while $[Mn1]O_6$ octahedra (in rose in Figure 1a) are isolated and connected to other MnO_6 octahedra through SO_4 tetrahedra. So far, we have confirmed this structural model from Synchrotron XRD performed at ALBA, as seen in the Rietveld refinement of a sample of $Li_2Mn_2(SO_4)_3$ produced at our lab (Fig. 1b).

Neutron powder diffraction data are also valuable to fully confirm the structural model of $Li_2Mn_2(SO_4)_3$ as this technique will provide a better contrast for Li and O positions than XRD. In the past, the superstructure (related to O positions) of another sulfate-based material - $Na_2Co(SO_4)_2$ - were indeed unveiled by some of our team thanks to its NPD pattern.[8] In addition, preliminary temperature-dependent magnetic susceptibility measurements show that the trisulphates $Li_2M_2(SO_4)_3$ also order antiferromagnetically at around 7.5 K (Figure 1c).

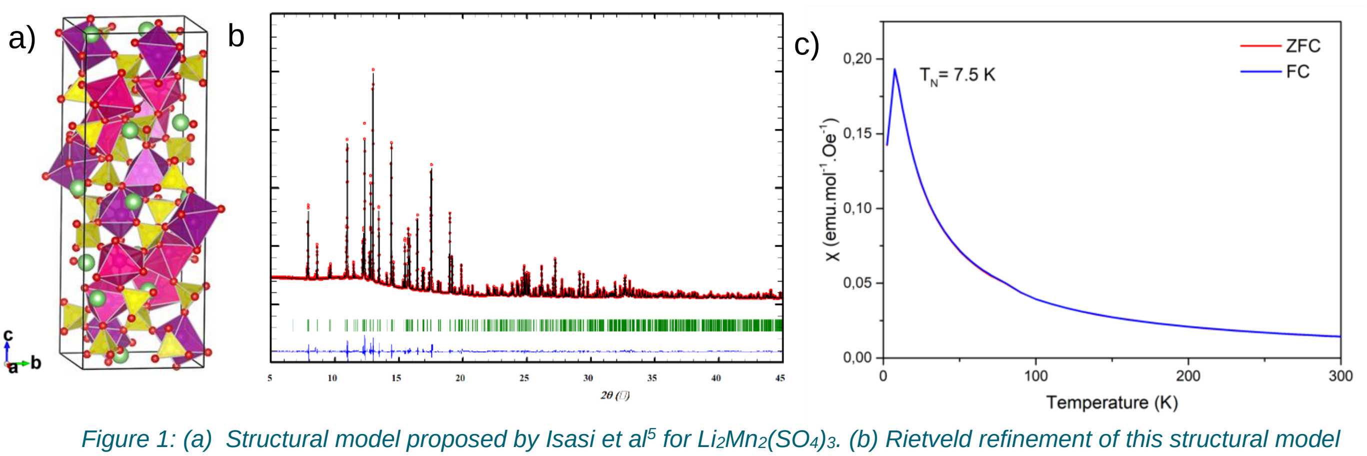

Figure 1: (a) Structural model proposed by Isasi et al[5] for $Li_2Mn_2(SO_4)_3$. (b) Rietveld refinement of this structural model against the Synchrotron XRD pattern of a sample $Li_2Mn_2(SO_4)_3$. (c) Temperature dependent magnetic susceptibility of a sample of $Li_2Mn_2(SO_4)_3$ indicating long-range ordering at 7.5K.

In our 24h of beamtime (18-19/9/20) we measured 3 samples at D1B. Due to Covid restriction, the data acquisition was controlled remotely by the users while the sample change was handled by the local contact. For each sample, we acquired the NPD pattern at room temperature with a wavelength of 1.28 Å to refine the nuclear structures of these compounds. Then, the NPD patterns were acquired at 2.52 Å while cooling down to 1.5K distinguishing the growth of the magnetic peaks (Fig. 2). Then, the samples were measured at 1.5K for a longer acquisition at 2.52 Å obtaining high quality data with high statistics with the aim to determine the magnetic structures and analyze the topology of the magnetic exchange pathways for this family of compounds.

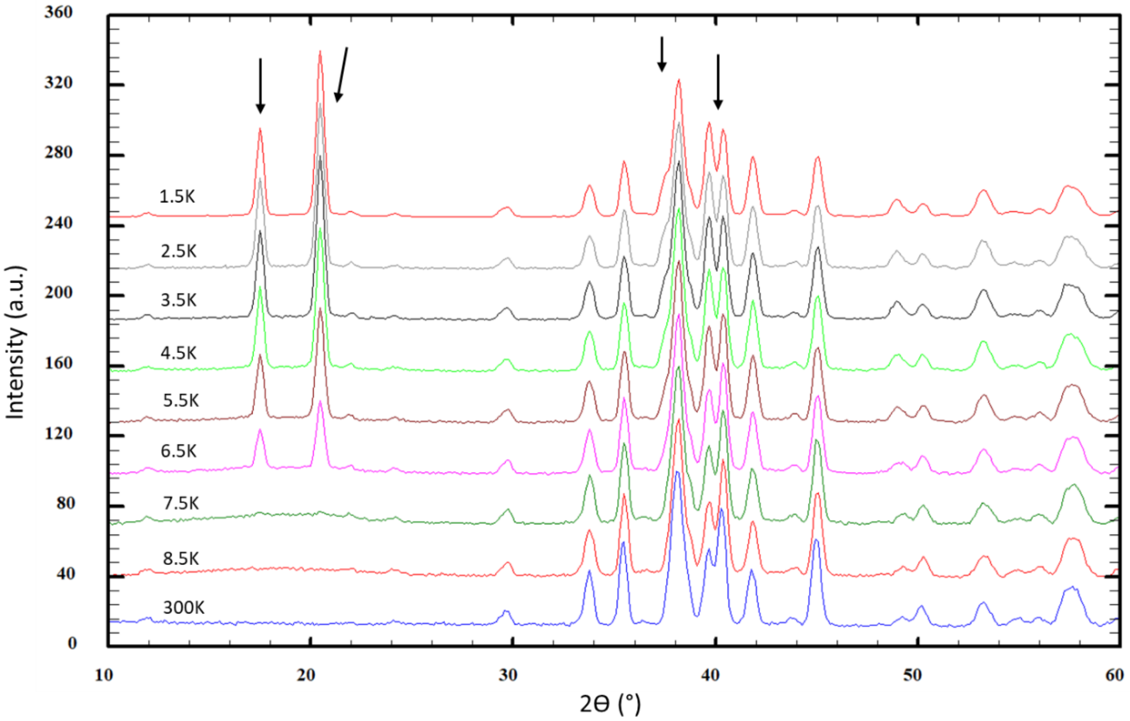

Figure 2: NPD patterns of Li2Mn2(SO4)3 upon heating showing the additional magnetic peaks (black arrows)

In conclusion, this beamtime at D1B diffractometer allowed us to obtain high quality diffraction patterns that will allow us to determine the magnetic structure of $Li_2Mn_2(SO_4)_3$. This will provide better understanding of material properties. Furthermore, the data obtained during the beamline will be published in the following months and, it will also be part of the PhD work of Iciar Monterrubio.

We would like to warmly thank Oscar Fabelo Rosa for his dedication and professional support during our beamtime which greatly contributed to its success.

References:

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