Experimental Report

26/02/2014

Proposal: **5-31-2230** **Council:** 4/2012

Title: Nuclear and Magnetic structure of the FeSO4(OD,F) Solid Solution

This proposal is a new proposal

Researh Area: Materials

Main proposer: **ROUSSE Gwenaelle**

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Samples:
FeSO4F
FeSO4(OH)
FeSO4(OH/F)

Instrument	Req. Days	All. Days	From	To
D2B	2	2	21/11/2012	23/11/2012

Abstract:

We propose to study the nuclear and magnetic structure of a solid solution of the FeSO4(F,OH) in which we have precise control over the content of F and OH anionic groups. Preliminary temperature-dependent magnetic susceptibility measurements show that long-range magnetic order is established at 100K in the fully fluorinated FeSO$_4$F sample. In contrast, the FeSO$_4$OH sample actually demonstrates an ordering temperature of 115K as determined by close examination of the derivative of the susceptibility with respect to temperature. An intermediate composition FeSO$_{4}$(OH)$_{0:45}$F$_{0:55}$ shows an ordering temperature very similar to the FeSO$_4$F end member. We will use low-temperature neutron diffraction to accurately determine the orientation of both the proton as well as the magnetic moments at low temperatures and use this information to rationalize the observed magnetic behavior.

Proposal 5-31-2230 – D2B – Experimental Report

Experiment carried out by : Marine Reynaud, Josh Kurzman, Jean-Noel Chotard, Gwenaëlle Rousse

Local contact: Thomas Hansen

Our group was awarded two days on the D2B diffractometer to measure some materials designed for the positive electrode of Li-ion batteries. The study of such compounds often requires the use of high-flux and high-resolution neutron powder diffraction, as available on the D2B diffractometer, since these samples are based on relatively heavy transition metals together with more lighter elements (in particular Li, H, O, N), which poorly scatter X-rays. Please refer to the proposal for more details about the scientific context.

The experiment, performed on November 2012, was a success as we could carefully measure four samples, and the corresponding results lead to three publications in peer-reviewed international scientific journals[1–3] (including one with Juan Rodríguez-Carvajal as ILL co-author), and were also included in a thesis dissertation[4].

We first measured a sample of $Li_1Fe(SO_4)_2$, which is the compound obtained after the charge of the electrode material $Li_2Fe(SO_4)_2$. The unit cell of $Li_1Fe(SO_4)_2$ had been predicted from X-ray diffraction[5], but the quality of the laboratory XRD data did not allow to accurately refine the structure. The refinement of the NPD pattern obtained at D2B enabled us to (i) refine precisely the structure of $Li_1Fe(SO_4)_2$, which is built on a similar framework of FeO_6 octahedra and SO_4 tetrahedra as its mother phase, and (ii) determine the position of the Li atoms within the channels of the structural framework. To locate the Li atoms within the structure, we used calculations of Fourier differential maps. The details of the refinement and the results are presented in references [1] and [4]. These results (**Figure 1**) were of high importance to understand the mechanism of insertion/deinsertion of Li into the electrode material $Li_2Fe(SO_4)_2$, and were also used for a theoretical study of this system, whose results will be published soon[6].

Second, we measured two samples of the new layered hydroxysulfates $LiMSO_4OH$ (M = Mn, Fe), which can be used as positive electrode material for Li-ion batteries as well. The NPD patterns recorded at D2B enabled to first confirm the structure that we previously determined from laboratory X-ray diffraction, but more important, they permitted to determine the accurate position of the lithium and hydrogen atoms. The Rietveld refinement of the D2B data and the resulting structural model were published in reference [2], and are illustrated in **Figure 2**.

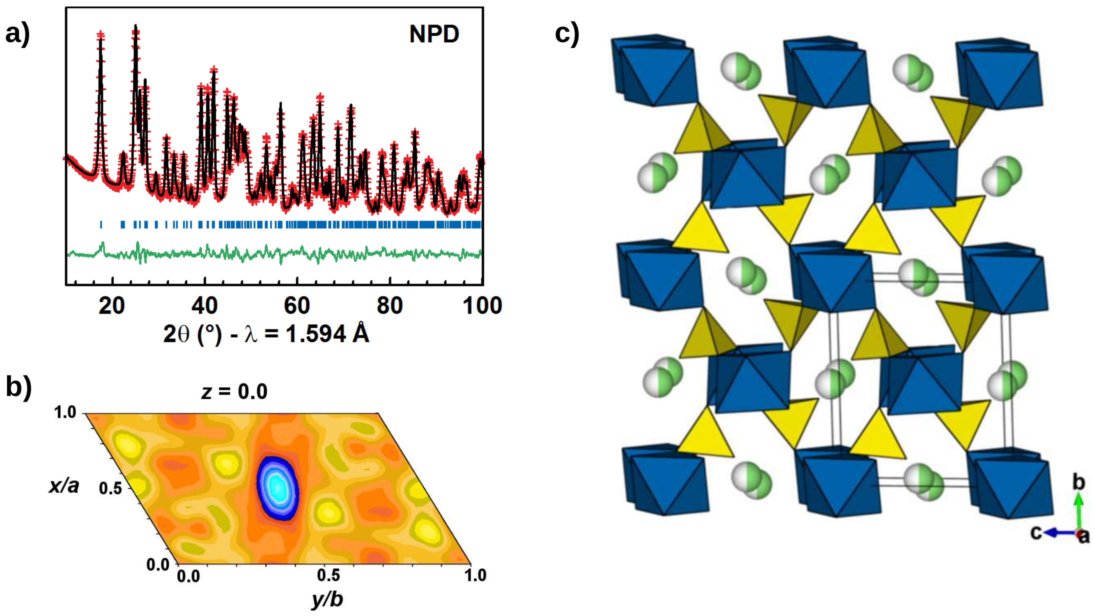

Figure 1: (a) Final Rietveld refinement of the $Li_1Fe(SO_4)_2$ structure against the NPD pattern measured at D2B. (b) Section of the Fourrier difference maps obtained from the refinement of the NPD pattern of $Li_1Fe(SO_4)_2$ against the FeO_6 octahedra and SO_4 tetrahedra framework pertaining to $Li_2Fe(SO_4)_2$ structure; the blue ellipsoid shows the position of the missing Li atom. (c) Resulting structural model for $Li_1Fe(SO_4)_2$, with the lithium atoms (half-colored green balls) sitting in the middle of the channels running along the a-axis.

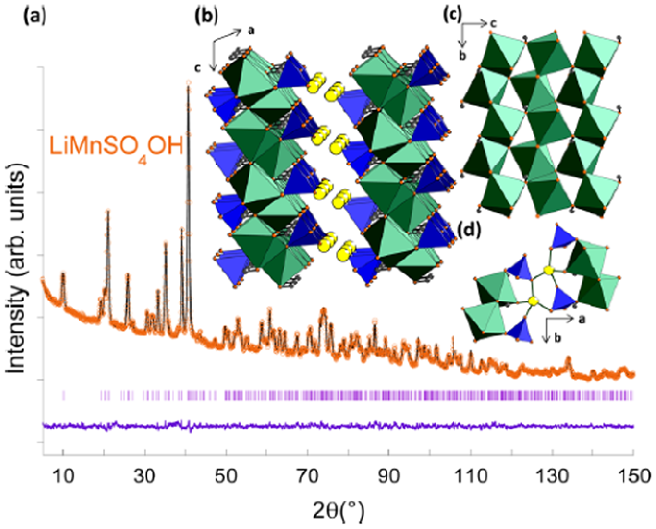

Figure 2: (a) Rietveld refinement of the NPD pattern of $LiMn(SO_4)OH$. (b, c, d) Views of the layered structure of $LiMn(SO_4)OH$; Mn atoms are in the center of the green octahedra, SO_4 tetrahedra are blue, O is orange, Li is yellow and H is represented as small black spheres. Adapted from ref. [2].

Finally, we measured a sample of the new nitrogen-susbtituted polyoxoanion compound Li_3SO_3N, which is of interest for the preparation of new 3d transition metal-based nitrogen-susbtituted polyoxoanion compounds that could be used as high energy-capacity positive electrode materials for Li-ion batteries. Here, D2B data have been useful to: (i) confirm the structural model determined from X-ray diffraction, and (ii) distinguish between the oxygen and nitrogen atoms, which was not possible with X-rays. Thus, we could determine the arrangement between O and N, with the nitrogen being partially disordered over the O sites (**Figure 3**).

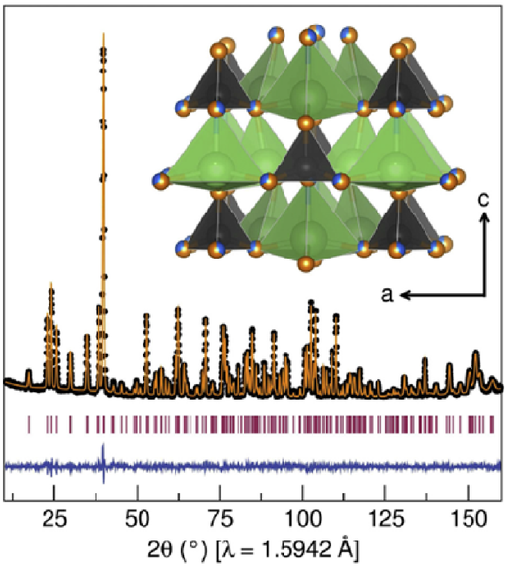

Figure 3: Rietveld refinement of the NPD pattern of Li_3SO_3N, whose structure is shown in inset: dark tetrahedra are SO_3N, light ones are LiO_3N, bicolored anions are the positions partially occupied by O and N.

References

(1) Reynaud, M.; Rousse, G.; Chotard, J.-N.; Rodríguez-Carvajal, J.; Tarascon, J.-M. *Inorg. Chem.* **2013**, *52*, 10456.

(2) Subban, C. V.; Ati, M.; Rousse, G.; Abakumov, A. M.; Van Tendeloo, G.; Janot, R.; Tarascon, J.-M. *J. Am. Chem. Soc.* **2013**, *135*, 3653.

(3) Kurzman, J. A.; Jouan, G.; Courty, M.; Palacín, M. R.; Armand, M.; Recham, N. *Solid State Sci.* **2013**, *25*, 28.

(4) Reynaud, M. Design of new sulfate-based positive electrode materials for Li- and Na-ion batteries / Elaboration de nouveaux matériaux à base de sulfates pour l'électrode positive des batteries à ions Li et Na. Ph.D. dissertation, Université de Picardie Jules Verne: Amiens (France), 2013.

(5) Reynaud, M.; Ati, M.; Melot, B. C.; Sougrati, M. T.; Rousse, G.; Chotard, J.-N.; Tarascon, J.-M. *Electrochem. Commun.* **2012**, *21*, 77.

(6) Clark, J.; Eames, C.; Reynaud, M.; Rousse, G.; Chotard, J.-N.; Tarascon, J.-M.; Islam, M. S. *J. Mater. Chem. A* **submitted**.