Experimental Report

Proposal: **5-31-2289** **Council:** 10/2012

Title: Crystallographic and magnetic study of new potassium-based fluorosulfates for Li-ion batteries

This proposal is a new proposal

Researh Area: Chemistry

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Samples: KFeSO4F, KCoSO4F, FeSO4F, LiFESO4F, NaFeSO4F with KTP structure

Instrument	Req. Days	All. Days	From	To
D20	3	3	05/04/2013	08/04/2013

Abstract:

We have recently discovered a new family of positive electrode material for Li-ion batteries: iron fluorosulfates. Among them KFeSO4F crystallises in the KTiOPO4 (KTP) structure, and one can remove K electrochemically and chemically, leading to KTP-like FeSO4F, into which we could further re-insert some other alkaline ions (Na, Li) at an attractive redox potential. We would like to measure this sample, the colbalt analog and the iron K-depleted one, plus the Na and Li reinserted samples to precisely locate the alkaline ions within the framework. Moreover, our previous Synchrotron experiments indicate that two space groups are possible : Pna21 and Pnna, and we are confident that NPD can solve this issue. Secondly, these samples are antiferromagnetic and Squid measurements indicate a long range magnetic order below 25K. We would like to study the magnetic structures of all these new compounds in order to get a detailed view on the iono-covalency of these compounds, which dictates both the redox potential of the battery and the magnetic structure which develops at low temperature.

Proposal 5-31-2289 – D20 – Experimental Report

Experiment carried out by : Marine Reynaud, Chinmayee Subban, Jean-Noël Chotard, Gwenaëlle Rousse

Local contact: Thomas Hansen

Our group was awarded three days on the D20 diffractometer to measure some materials designed for the positive electrode of Li-ion batteries, and determine their magnetic structure at low temperature. The study of the magnetic structure of such battery materials is of high interest since these structures are used for theoretical calculations on these compounds, but also because we have recently remarked that the electrochemical properties of these compounds might be related to their magnetic ones, and more data on different phases are required to fully confirm this conjecture[1]. Please refer to the proposal for more details about the scientific context.

The experiment was carried out on April 2013, and resulted to be a success since we could measure 13 samples at different temperatures and obtained high-quality data. The results of the analysis and treatment of these data have been published in one PhD dissertation[2], two peer-reviewed international scientific journals (with Juan Rodriguez-Carvajal as ILL co-author)[3,4], and other two articles are currently being written.

During this experiment, we measured, among others, samples of the new series of compounds having for general formula $Li_xM(SO_4)_2$ (x =1 or 2 and M = Fe, Co, Mn, Ni), which crystallize either in a monoclinic structure (M = Fe, Co, Mn) or in an orthorhombic structure (M = Ni). Preliminary magnetic measurements had suggested that these phases ordered antiferromagnetically at low temperature (between 50K and 4K depending on the nature of the transition metal), and we proposed to employ the high-flux configuration offered by the D20 diffractometer to get high quality data and determine their magnetic structures. While cooling the samples, we could observe magnetic peaks growing for all the samples. We were able to solve the magnetic structures of all these compounds using symmetry analysis (**Figure 1** and **Figure 2**).

Both the monoclinic and orthorhombic structures adopted by these compounds present particular arrangements of MO_6 octahedra and SO_4 tetrahedra that solely allows super-super-exchange interactions, so that these compounds can be seen as model cases to probe the Goodenough-Kanamori-Anderson rules.[2–4] Moreover, the magnetic structure that we determined for the orthorhombic nickel disulfate $Li_2Ni(SO_4)_2$ shows the inversion center associated with time inversion, so this compound should be a linear magnetoelectric.[4]

The results obtained from this experiment and published in references [2], [3] and [4] have already been employed for theoretical investigations of the monoclinic phases $Li_2M^{II}(SO_4)_2$ (M = Fe, Co, Mn) and $Li_1Fe^{III}(SO_4)_2$, which provided good estimations of the open circuit voltages for these compounds [5].

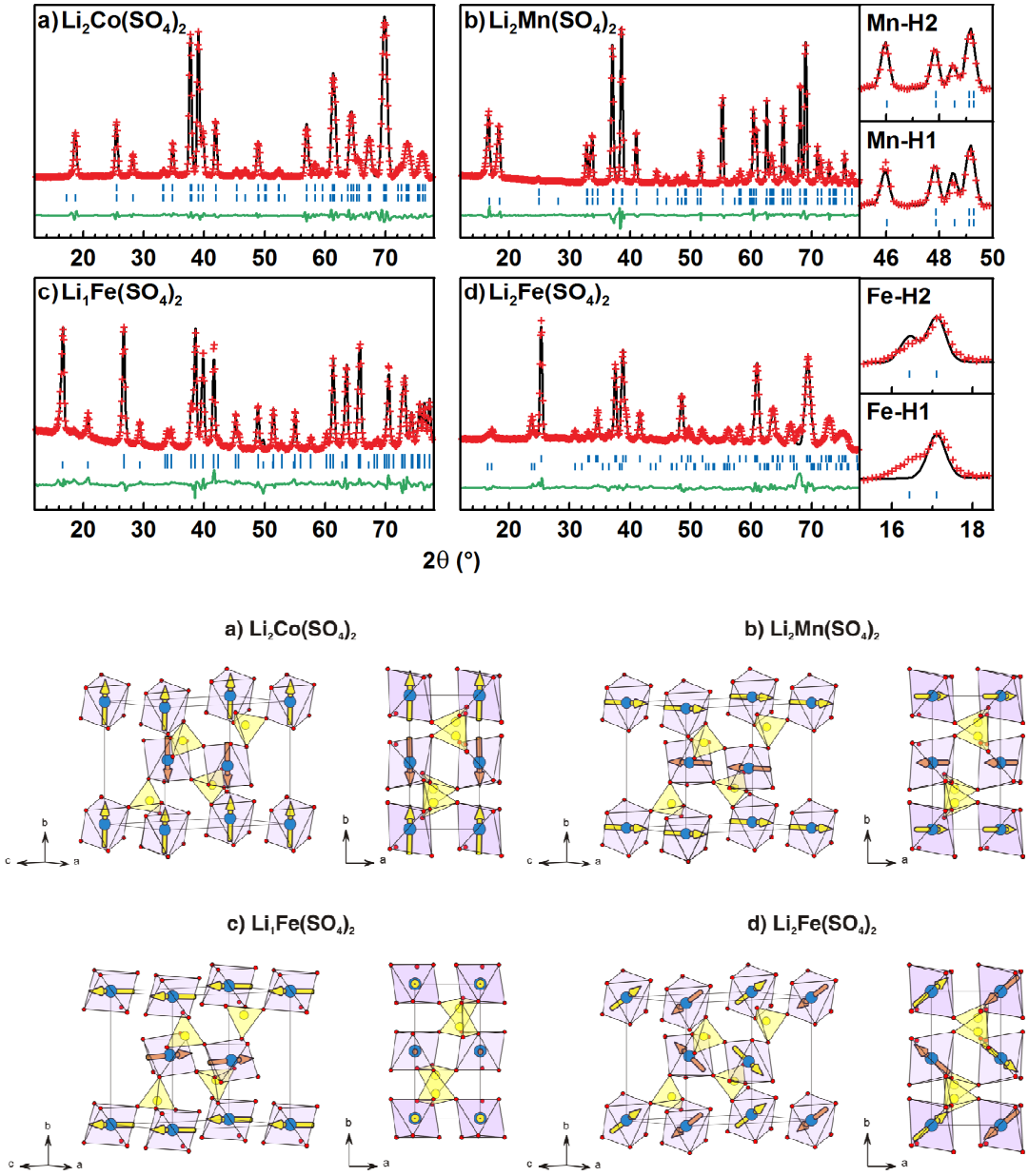

Figure 1: At the top: Refinement of the nuclear and magnetic parts of the NPD patterns measured at 1.85K for (a) $Li_2Co(SO_4)_2$ (λ = 2.418 Å), (b) $Li_2Mn(SO_4)_2$ (λ = 2.416 Å), (c) $Li_1Fe(SO_4)_2$ (λ = 2.416 Å) and (d) $Li_2Fe(SO_4)_2$ (λ = 2.418 Å). At the bottom: Drawings of the nuclear and magnetic structures of the same compounds. Magnetic moments are represented by a vector through the 3d metal atoms. Yellow vectors stand for positive moments, while the orange ones stand for negative moments. For clarity, Li atoms are omitted.

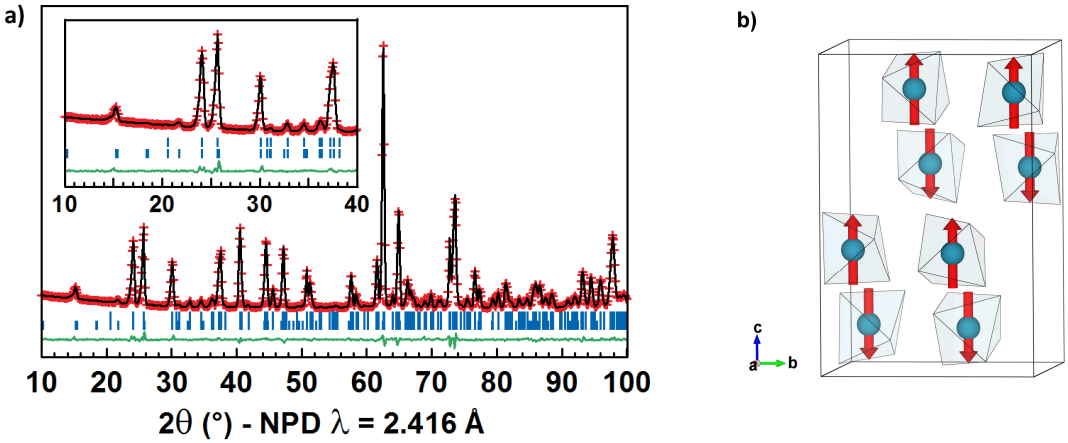

Figure 2: (a) Rietveld refinement of the NPD pattern of $Li_2Ni^{II}(SO_4)_2$ measured at 1.85 K. (b) Magnetic structure of $Li_2Ni(SO_4)_2$. The blue balls shown the position of the Ni atoms within the unit cell, and red vectors represent their magnetic moments. For the sake of clarity, all other atoms (Li, S, O) are omitted.

Analyses of the other samples that we measured during this experiment (Li*M*SO_4OH and K*M*SO4F, with M = transition metal) are still underway, and reports are being written.

References

(1) Rousse, G.; Tarascon, J.-M. Sulfate-Based Polyanionic Compounds for Li-Ion Batteries: Synthesis, Crystal Chemistry and Electrochemistry Aspects. *Chem. Mater.* **2013**.

(2) 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.

(3) Reynaud, M.; Rousse, G.; Chotard, J.-N.; Rodríguez-Carvajal, J.; Tarascon, J.-M. Marinite $Li_2M(SO_4)_2$ (M = Co, Fe, Mn) and $Li_1Fe(SO_4)_2$: Model Compounds for Super−super Exchange Magnetic Interactions. *Inorg. Chem.* **2013**, *52*, 10456–10466.

(4) Reynaud, M.; Rodríguez-Carvajal, J.; Chotard, J.-N.; Tarascon, J.-M.; Rousse, G. Magnetic Structure and Properties of Orthorhombic $Li_2Ni(SO_4)_2$: A Possible Magnetoelectric Material. *Phys. Rev. B* **2014**, *in press*.

(5) Clark, J.; Eames, C.; Reynaud, M.; Rousse, G.; Chotard, J.-N.; Tarascon, J.-M.; Islam, M. S. High-Voltage Sulphate Cathodes $Li_2M(SO_4)_2$ (M = Fe, Mn, Co): Atomic-Scale Studies of Structures, Lithium Diffusion and Voltage Trends. *J. Mater. Chem. A* **submitted**.