Experimental report

15/06/2017

Proposal: **5-31-2453**

Council: 4/2016

Title: Structural and magnetic structuresof Li3FeN2 at low temperature

Research area: Materials

This proposal is a new proposal

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Experimental team: Nicolas EMERY

Local contacts: Thomas HANSEN

Samples: Li3FeN2
Li2.16FeN2
Li1.97FeN2
Li2.37FeN2
Li3-xyNixN
Li3-2xC0xN
V2O4F2
2H2O

Instrument	Requested days	Allocated days	From	To
D20	1	1	15/07/2016	16/07/2016

Abstract:

Recently, we evidenced a magnetic ordering around 100K through Mössbauer measurements on Li3FeN2. Additional magnetic measurement reveal a broad and unclear antiferomagnetic-like transition. In addition, using several technics (NMR, XRD and Mössbauer), a cationic mixing has been proposed to complete the structural description proposed 25 years ago. The aim of this proposal is first, to confirm the cationic mixing and second, to investigate the nature of the magnetic ordering below the transition. To fulfill these objectives simultaneously, the use of neutron diffraction is best probe due to the magnetic scattering and the higher scattering factor of lithium compared to X-ray.

Structural and magnetic structures of Li_3FeN_2 at low temperature

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Introduction

Nearly 25 years ago it was proposed that Li_3FeN_2 belong to a derivative antifluorite type structure where a quarter of the tetrahedral site are filled by Fe^{3+} ions. It leads to infinite tetrahedral edge-chairing chains filled by Fe^{3+} as display Figure 1 [1]. In addition, a magnetic transition at 10 K was reported and the magnetic moment extracted from paramagnetic state was consistent with a low spin configuration of the Fe^{3+} ions. Very recently we obtained new and intriguing experimental results obtained by various characterization methods on freshly synthesized samples, namely XRD, NMR and Mössbauer spectroscopy. These results paint a slightly different picture in which *the presence of a cationic mixing between lithium and iron sites which can play a major role* on the electronic and magnetic properties of Li_3FeN_2.

Also, our Mössbauer spectra recorded at various temperatures clearly indicate the occurrence of a magnetic ordering below 100K, as shows Figure 2. In particular, a clear Zeeman splitting is evidenced at about 50K, i.e. well above the magnetic transition at 10K reported elsewhere [1]. Complimentary dc magnetization measurements (not shown) suggest the presence of a broad antiferromagnetic-like and weak transition below about 100 K.

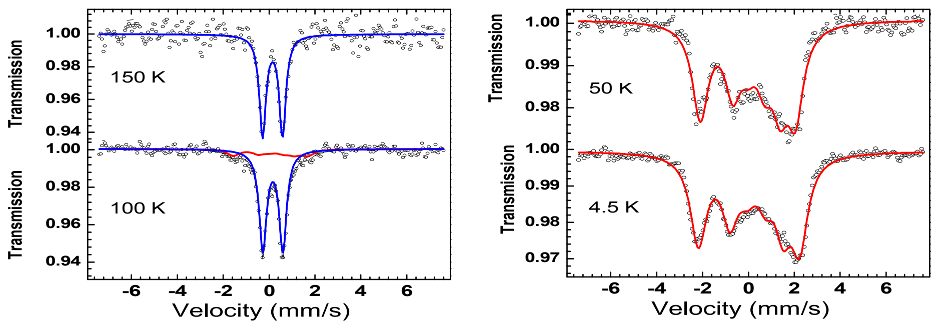

Figure 1: Mössbauer spectra of Li_3FeN_2 recorded at 150, 100, 50 and 4.5K respectively.

The aim of the proposal is to observe the evolution of neutron diffraction patterns versus temperature to the magnetic ordering which occurs below 100K.

Samples and required beam time

During the day of allocated beam time, 2 series of diffraction patterns were recorded in 2 different configurations of the D20 beam line. First, in high flux mode with a wavelength of 2.41 Å and a take-off angle of 42° to follow the evolution of possible magnetic structure and second, using a wavelength of 1.41 Å and a take-off angle of 90° to get structural information.

Figure 2 displays the diffraction pattern recorded at room temperature and 2K. From the structural point of view, both can be well described by the cationic mixed model. However, an impurity, not yet identify, has been detected with its main peak at 26.2°. The reduction of temperature has only a very limited effect on the cell parameter. Indeed, the 3 cell parameters vary from less than 0.1%.

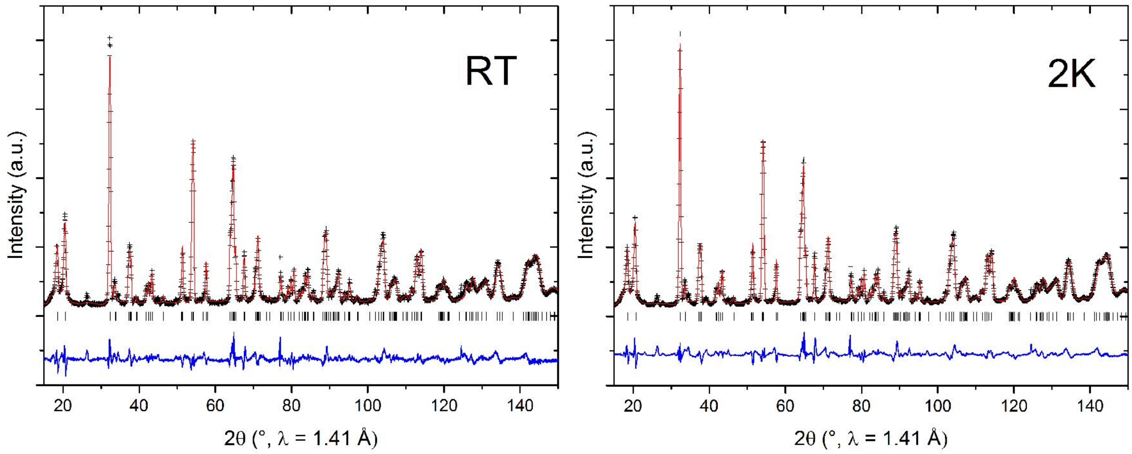

Figure 2: Neutron diffraction pattern of Li_3FeN_2 recorded at room temperature and 2K.

In the high flux configuration, small magnetic reflection were observed as shown in Figure 3 (indicated by arrows). These reflection disappear around 100 K, which is in good agreement with our previous magnetic measurement. Also, Fe^{+3} ions in Li_3FeN_2 are expected to be in the low spin configuration, which can partly explain the low intensity of these magnetic peaks. However, due to the presence of an impurity and the air sensitive nature of Li_3FeN_2, such a small magnetic contribution might also be attributed to the impurity. Further analyses are mandatory to clearly explain the results.

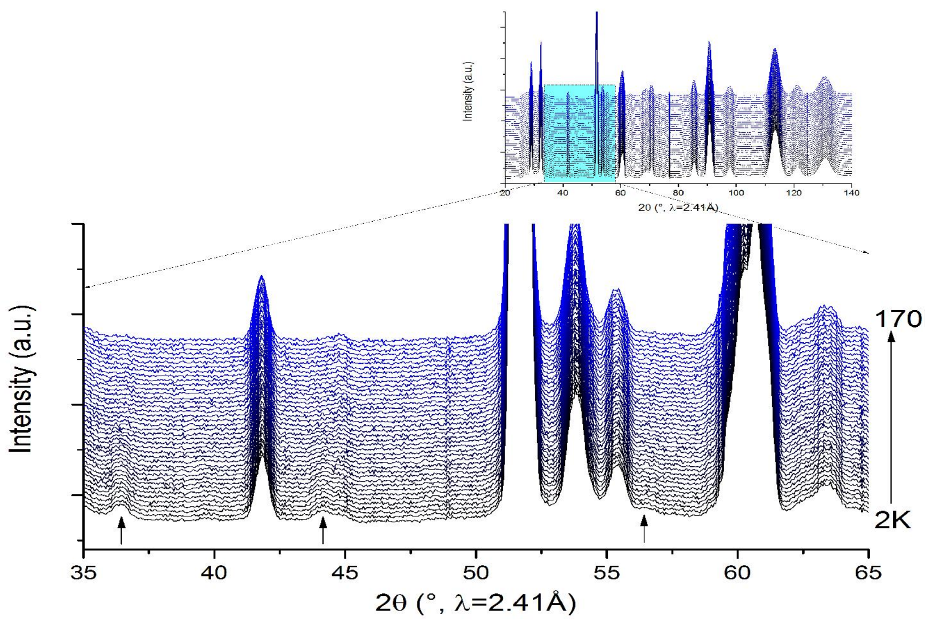

Figure 3: Neutron diffraction patterns recorded from 2K to 170K.

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[1] A. Gudat, R. Kniep, A. Rabenau, W. Bronger, U. Ruschewitz, Li_3FeN_2, a ternary nitride with $[FeN_{4/2}{}^{3-}]$ chains: crystal structure and magnetic properties, *J. Less-Common Met.* 161 (1990) 31-36