Experimental Report

26/02/2015

Proposal:	**5-31-2308**	**Council:**	4/2014

Title: Study of the influence of the organic group in the magnetic interaction mechanisms of MILs based on imidazolium tetrahalureferrates family.

This proposal is a new proposal

Researh Area: Materials

Main proposer: **DE PEDRO DEL VALLE Manuel**

Experimental Team: GARCIA SAIZ Abel
DE PEDRO DEL VALLE Manuel

Local Contact: FABELO ROSA Oscar Ramon
FERNANDEZ DIAZ Maria Teresa

Samples: 1-ethyl-2,3-dimethylimidazolium FeX4 (X= Cl and Br)

Instrument	Req. Days	All. Days	From	To
D1B	2	2	22/11/2014	24/11/2014
D2B	2	2	24/11/2014	26/11/2014

Abstract:

The study of Magnetic Ionic Liquids (MILs) has been a new and emergent field since 2005. These materials allow physicochemical properties (viscosity, melting point, chemical stability, high ion conductivity, etc.) to be controlled by external magnetic fields [1]. During these last few years the synthesis, study and application of these smart materials has increased exponentially [2], being necessary to provide a complete picture of their crystal structure and main magnetic interactions in play. It was generally assumed that magnetic interactions were negligible in MILs, so they were not expected to exhibit 3D ordering [3]. However, we have found that it is possible to synthetize MILs with three-dimensional ordering, which opens up new fields of understanding and improving the magnetic couplings within MILs in their condensed phases [4]. Thus, the question about cooperative magnetic effects, complex anion interaction, and magnetostructural correlation is quite important and it is actually in focus of materials science. These aspects could be explained connecting experimental studies (magnetic and X-Ray and neutron powder diffraction) and first-principle based theoretical methods.

Experimental report 5-31-2308

Magnetic ionic liquid (MILs) based on imidazolium cation and tetrahaloferrate ion present several non-covalent interactions such as hydrogen bonds, halogen-halogen (between the nearest metal complex anions) or anion-π (between the anion and cation) interactions. These materials can show several phase transitions from room temperature and interesting magnetic phenomena at low temperatures like a three-dimensional (3D) magnetic ordering. Furthermore, a complete picture of its magnetic behaviour is still missing being extremely sensitive to temperature cooling rate effect. Therefore, using suitable rates of cooling from room temperature solid state, different ordered crystalline phases can be obtained with different magnetic behaviours. In this experiment we plan to study the crystal and magnetic structure of new MILs with 3D antiferromagnetic ordering, 1-ethyl-2,3-dimethylimidazolium tetrahalureferrates, Edimim[FeX_4] (X=Cl and Br), with neutron diffraction experiments.

Initially high flux neutron diffraction on D1B were performed. About 3 g of both samples was milled and placed in a cylindrical vanadium container at room temperature. The sample was placed inside the cryostat at 100 K. We collected data each 5 minutes in a sweep mode in the cooling process from 100 K to 2 K. The magnetic ordering of these compounds appear near of 3 and 9 K for chloride and bromide, respectively. The presence of H atoms in the cation part (H= 13) predicted low statistic in the neutron diffraction pattern. Therefore, we measured above and below the magnetic transition 3 hours per spectra. From 2 K to above the magnetic transition we collected data each 0.1 K (Cl) and 0.3 K (Br) during 14 hours (see Figure 1 and 2). In addition to this, these compounds present a solid-solid transition above 230 K. Magnetic measurements show that if you maintain these MILs at 240 K for 30 min before quenching at 100 K, the magnetic curve displays a small displacement of ordering temperature and different shape with respect to the quenching phase. These facts indicate that the magnetic coupling is modified with the cooling rate process. So we programmed a new sequence after the last measurement above the magnetic transition, trying to reproduce this experiment. We warmed at 240 K and wait 30 min. Then, a fast cooling process down to 10 and 2 K and collect data. No significant difference between the first and second experiment was detected.

The crystalline structure of Edimim[FeX_4] (X=Cl and Br) were also studied from high resolution neutron powder diffraction patterns (D2B) with $\lambda = 1.5938$ Å at 300, 100 y 10 K. Longer data collection time allowed us to increase the signal-noise ratio. The data collection time was extended up to 5 hours per scan (Figure 3). In addition, we programmed a sequence for Dimim[$FeCl_4$] consisting in quenching the sample at 100 K, then going to 10 K and 2 K and collect spectra (6 h) [phase 1(b)]. After that, we warmed at 240 K and wait 30 min. Then, a fast cooling process down to 10 K and 2 K and collect data (6 h) [phase 1(a)]. A comparative view of the nuclear pattern (10 K) as difference from the magnetic ones (2 K) (Figure 4) reveals significant difference between the first and second process, in good agreement with D1B data. We will combine these results with ssynchrotron X-Ray powder diffraction measurements obtained in ALBA (Barcelona). The promising results obtained in these experiments would lead us to obtain the crystal and magnetic structure in these compounds and allow us to give further insight in the origin of the different magnetic behaviours at low temperatures by cooling rate effect.

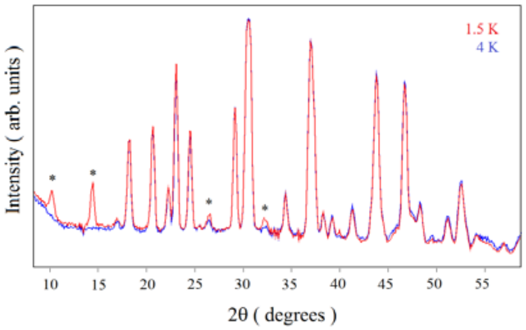

Fig. 1 (a). Neutron diffraction patterns at 10 and 2 K on D1B for Edimim[$FeCl_4$].

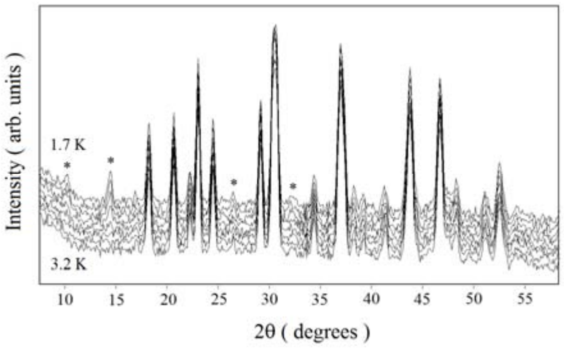

Fig. 1 (b). Neutron diffraction patterns between 1.7 and 3.2 K on D1B for Edimim[$FeCl_4$].

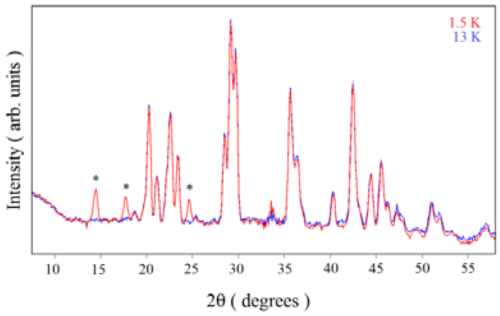

Fig. 2 (a). Neutron diffraction patterns at 10 and 2 K on D1B for Edimim[$FeBr_4$].

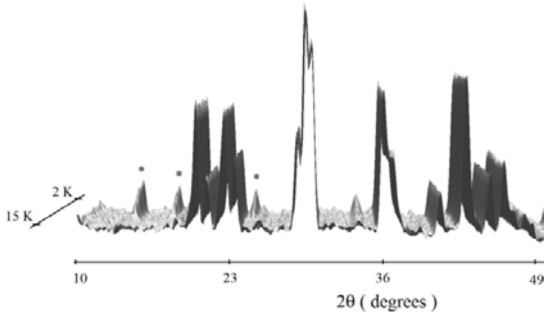

Fig. 2 (b). Neutron diffraction patterns between 2 and 15 K on D1B for Edimim[$FeBr_4$].

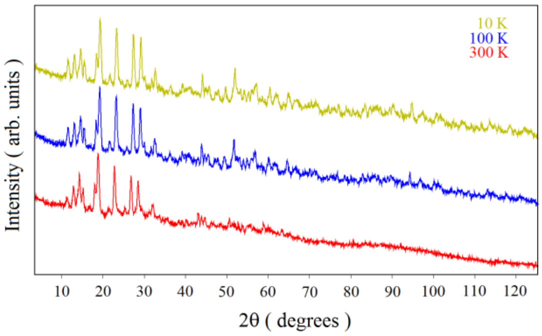

Fig. 3 (a) Neutron diffraction patterns at 300 and 100 and 10 K on D2B for Edimim[$FeCl_4$].

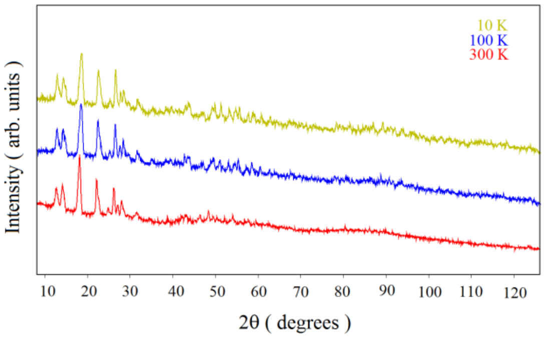

Fig. 3 (a) Neutron diffraction patterns at 300 and 100 and 10 K on D2B for Edimim[$FeBr_4$].

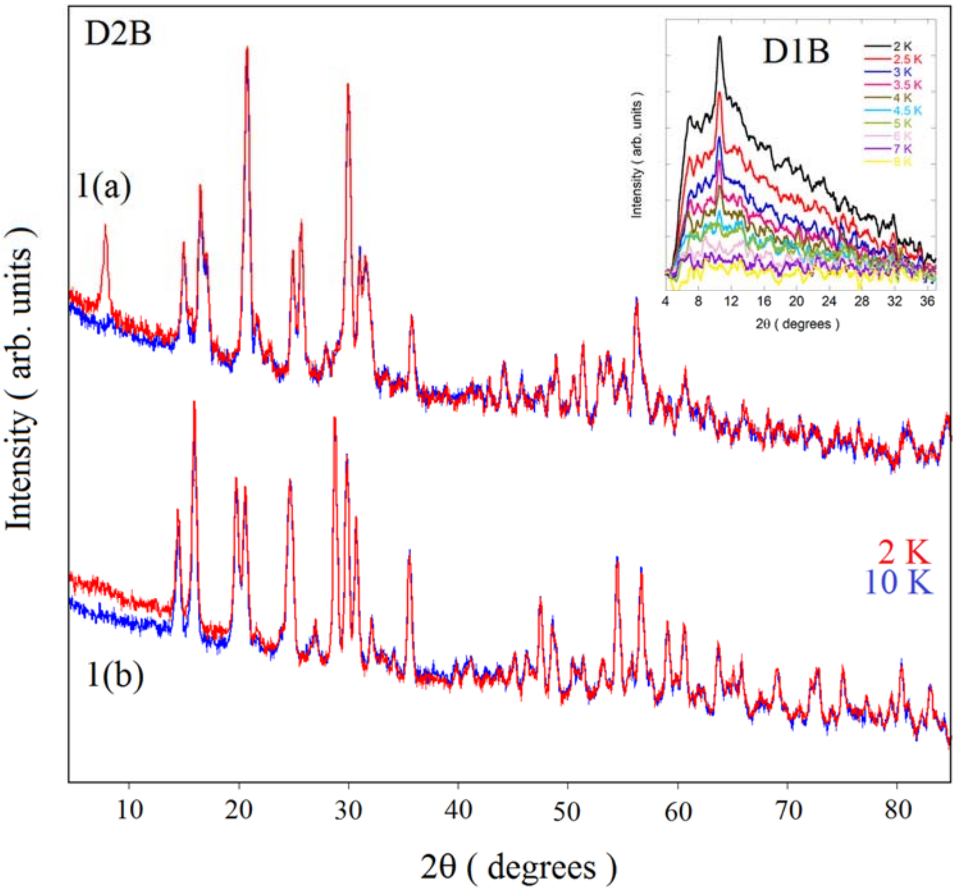

Fig. 4. Neutron patterns at 10 and 2 K for relaxed 1(a) and quenched 1(b) phase of Dimim[$FeCl_4$]. The inset shows the temperature dependence of the difference diagrams of D1B patterns obtained by subtracting the nuclear contribution of quenched phase.