Experimental report

07/12/2016

Proposal: **7-03-155**

Council: 4/2016

Title: Exploring the unclear dynamics process on a magnetic ionic liquid induced by Solid-to-Solid Phase Transition after Thermal Treatment

Research area: Materials

This proposal is a new proposal

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

Experimental team:
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Local contacts: Michael Marek KOZA

Samples: Dimim[FeCl4] (Dimin: 1 -3-dimethylimidazolium)

Instrument	Requested days	Allocated days	From	To
IN6	4	3	09/09/2016	13/09/2016

Abstract:

The crystal structures of magnetic ionic liquid present a rich dynamical landscape in the ps-ns time scale related with the imidazolium and metal complex groups by temperature effect. In a previous experiments on the IRIS backscattering spectrometer at ISIS and polarized neutron instrument D7 at ILL, we detected an unclear dynamical process. We found a very interesting result; solid-to-solid phase transition in Dimim[FeCl4] (Dimim = 1,3 dimethylimidazolium) phase after thermal treatment show different dynamical process of the CH3 group for the same imidazolium cation below 15 K.

In this new proposal we would like to study this process in detail of the two low-temperature crystalline phases, with the aim of obtaining the relationship between this, the diffraction data and theoretical calculations.

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Title of Experiment:	Exploring the unclear dynamics process on a magnetic ionic liquid induced by Solid to-Solid Phase Transition after Thermal Treatment	**Local Contact:** KOZA Michael Marek
Principal Proposer:	Manuel de Pedro del Valle	**Instrument: IN6**
Experimenta	Manuel de Pedro del Valle/Diego Alba Venero/Oscar Fabelo/ FERNANDEZ DIAZ Maria	**Date of Experiment:**

The crystal structures of magnetic ionic liquid (MILs) based on imidazolium cation and tetrahaloferrate ion are ruled by several non-covalent interactions, like hydrogen bonds, halogen-halogen (between the nearest metal complex anions) or anion-π (between the anion and cation) interactions. Therefore, they present a rich dynamical landscape in the ps-ns time scale related with the imidazolium and metal complex groups by temperature effect. In this experiment on the IN6, we studied the dynamical process in one MIL, 1,3-dimethylimidazolium tetrachloroferrate, Dimim$[FeCl_4]$ and deutered phase by neutron quasielastic spectroscopy (QENS).

Initially about 1 g of Dimim$[FeCl_4]$ were milled and placed in a aluminium container at room temperature. The sample was quenched in liquid nitrogen (LN) and placed in the cryostat at 200 K. The presence of H atoms in the cation part (H = 13) predicted low statistic in the neutron spectroscopy pattern. Therefore, we measured above 8 hours per spectra. At the lowest temperature, a quantum tunneling process of CH_3 groups appears from 1.8 K up to 10 K (see Figure 1, phase I-a). We collected data at 1.5, 5 and 10 K during 24 hours. Crystallographic and magnetic data in D1B and D7 instruments showed that if you keep the compound at 220 K for 30 min after the LN quenching, a new crystal structure appears which has a different magnetic behavior than the previous one (phase Ib). Thus, the dynamical reorientations of the imidazolium cation may be critical to this unexpected crystal and magnetic phase transition, in some way, related with the superexchange interactions that are modified during the heating process. To obtain information of this phenomena we warmed the sample up to 220 K and wait 30 min. Then, a fast cooling process down to 1.5 K and collected data in the same temperature range than in the previous one (1.5, 5 and 10 K during 24 hours). Significant difference between the measurements in the first and second experiments were detected related to quantum tunnelling process and classical rotation of CH_3 groups.

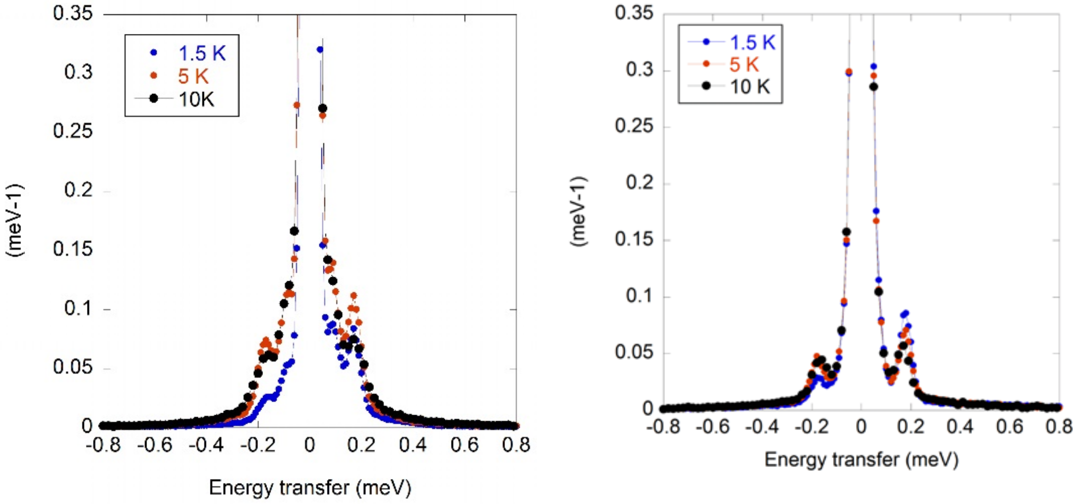

Figure 1. QENS spectra at 1.5, 5 and 10 K for Dimim[$FeCl_4$] before (phase I-a) and after (phase Ib) relaxation process at 220 K.

Finally, we also checked the rotational behaviour of the deutered compound, which has a similar magneto-structual response than the previous one. We repeat the experimental process previously realized. Quenching the sample and take spectra at 1.5, 5 and 10 K. Now, we measured above 5 hours per spectra. We collected data at 1.5, 5 and 10 K during 24 hours. Waiting 30 min at 220 K. A fast cooling process up to 1.5 K and collected data and the same temperatures (35 h). We observed considerable differences between the non-deutered copmpound (see Figure 2) and the two crystallographic phases (phase I-a and I-b).

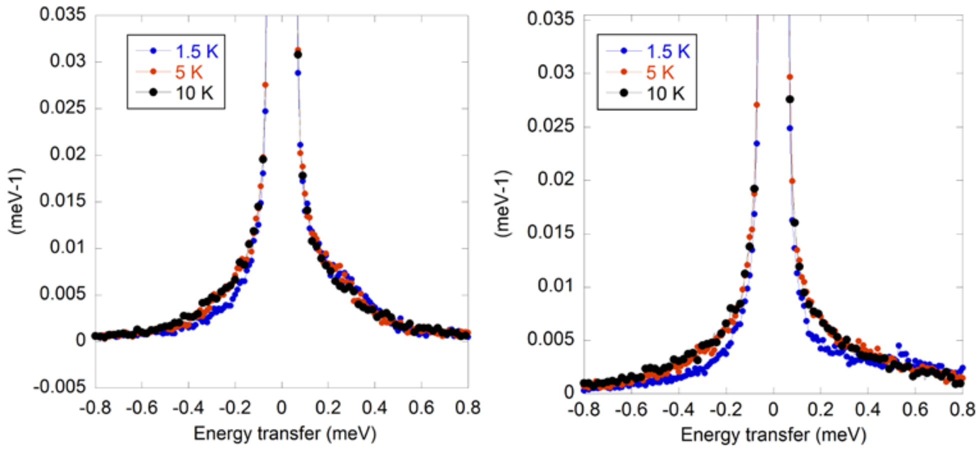

Figure 2. QENS spectra at 5 K for deutered phase of Dimim[$FeCl_4$] before (phase I-a) and after (phase Ib) relaxation process at 220 K.

The promising results obtained in this experiment would allow us to give further insight in the origin of the influence of the hydrogen bonds in the rotational spectrum of the methyl groups and to characterize the CH3 group tunneling.