Experimental report

23/09/2015

Proposal: 5-53-257 **Council:** 4/2015

Title: Dimim[FeCl4]: A magnetic ionic liquids with unclear magnetic behavior

Research area: Soft condensed matter

This proposal is a new proposal

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

Instrument	Requested days	Allocated days	From	To
D7	7	7	09/09/2015	16/09/2015
D33	2	0		

Abstract:

Dimim[FeCl4] is a magnetic ionic liquid. A complete picture of its magnetic behavior is still missing being extremely sensitive to temperature cooling rate effect. Therefore, using suitable rates of cooling from room temperature solid state, two ordered crystalline phases can be obtained with different magnetic behaviours. One of them display an antiferromagnetic structure whereas the other one exhibits a magnetic phenomena. Therefore, the competition between interactions are modified by this effect being the study of the magneto-structural correlations the major goal of this research. For this objective, we consider that a combination of low angle and polarized neutron diffraction are needed. To accomplish this proposal we apply to 7 and 2 days of beam time at D7 and D33, respectively. Having the experimental knowledge of this magnetic phenomena will allow a direct connection to theoretical models.

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The crystal structures of magnetic ionic liquid (MILs) based on imidazolium cation and tetrahaloferrate ion present several non-covalent interactions, like 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. A complete picture of its magnetic behaviour is still missing being extremely sensitive to temperature cooling rate and history. Therefore, using the appropriate rates of cooling from room temperature, two ordered crystalline phases can be obtained with different magnetic and dynamical behaviours. In this experiment we plan to study the relationship between them in two MILs, 1-ethyl-2,3-dimethylimidazolium tetrahalureferrates, Edimim[FeX_4] (X=Cl and Br), with the diffuse scattering instrument D7 with 3-directional (XYZ) polarization analysis.

Initially about 6 g of Edimim[$FeCl_4$] 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 80 K. The presence of H atoms in the cation part (H = 13) predicted low statistic in the neutron patterns. Therefore, we measured above 6 hours per spectra in order to to increase the signal-noise ratio. Initially, for the quenched phase we collected data at 1.5, 1.8, 2.2, 3, 4, 6, 8, 10 K during 48 hours. The temperature evolution of the D7 patterns shows the appearance of additional elastic intensity at temperatures below to 2 K. In addition, we observed a broad diffuse background in the diffraction patterns below 10 K, also detected in the D1B and D2B experiments [proposal ILL-5-31-2308], which increases in a monotonous way up 10 K. A comparative view of the magnetic and spin incoherent parts obtained from the separation of neutron scattering cross sections (Figure 1), using xyz-polarization analysis, reveals the occurrence of a three-dimensional antiferromagnetic long range magnetic ordering below 2K. In addition, it was unravelled that this diffuse low-angle scattering observed at low temperatures is attributed to the spin incoherent part; not magnetic.

Crystallographic, magnetic and neutron data show that if you keep the compound at 220 K for 30 min after the LN quenching, a new crystal appears which has a different magnetic structure than the previous one. Therefore, in order to follow this process we increase the temperature and collect data at 30, 50, 100, 170 and 220 K during 24 hours. Then, we perform a fast cooling process down to 1.5 K and collect data in the same temperature range than in the previous quenched phase during 48 hours. Significant difference between the measurements in the first and second experiments were detected related to structural, magnetic and incoherent parts (see Figure 2). These facts indicate that the magnetic coupling and dynamical process are modified with the cooling rate process, in good agreement with D2B D1B and QENS data. These promising results obtained would lead us to unravel the unclear magnetic behaviour in these compounds at low temperatures by cooling rate effect.

Finally, we also checked the the bromide compound, which has a similar magneto-structual response. We repeat the experimental process previously realized in the Edimim[FeCl4] during 48 hours. We also observed considerable differences between the two states.

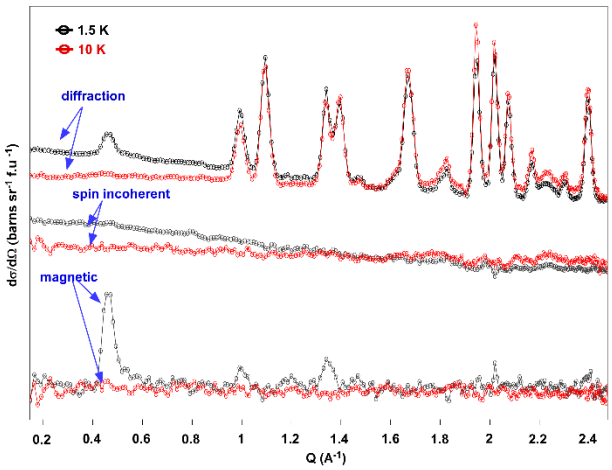

Figure. 1. Separation of neutron scattering cross sections, nuclear and spin incoherent magnetic from a powdered sample of the quenched state of Dimim[$FeCl_4$] measured using xyz-polarization analysis on D7.

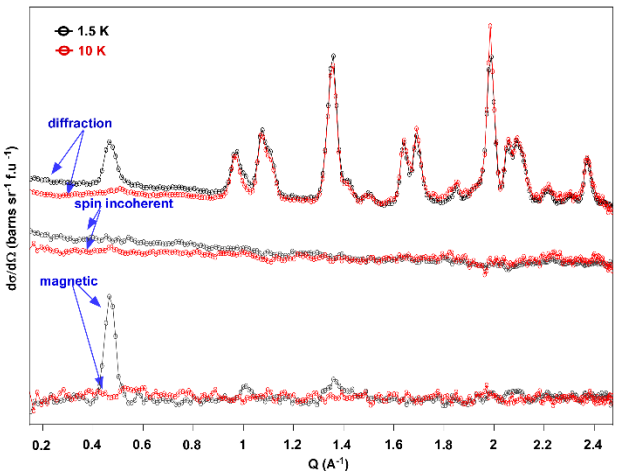

Figure. 2. Separation of neutron scattering cross sections, nuclear and spin incoherent magnetic from a powdered sample of the relaxed state of Dimim[$FeCl_4$] measured using xyz-polarization analysis on D7.