Experimental report

13/02/2019

Proposal:	**7-02-175**	**Council:**	4/2018
Title:	Study of the lattice and spin dynamics in the Metal-Organic Framework(CH3NH3)Co(COOH)3		
Research area:	Physics		

This proposal is a new proposal

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Samples: CH3NH3Co(COOH)3

Instrument	Requested days	Allocated days	From	To
IN12	8	7	25/09/2018	02/10/2018

Abstract:

Magnetic hybrid organic-inorganic Perovskites have attracted much attention lately as they potentially show a magneto-electric coupling, thanks to the strong interaction between the framework and the molecular host. In particular, a diffraction study at zero-field of CH3NH3Co(COOH)3 shows a structural transition around 90 K concomitant with an antiferroelectric behaviour and a magnetic order below 15 K.

Under applied field, magnetisation and polarisation measurements highlight a coupling between the magnetic and electric order. We would like to investigate the lattice and spin dynamics at zero-field in this system, in order to better understand the interplay between the magnetic framework and the molecular host, which leads to these field-induced properties. We hence request 8 days on IN12.

Study of the lattice and spin dynamics in the Metal-Organic Framework $[CH_3NH_3][Co(COOH)_3]$

$MACo(COOH)_3$ (MA = CH_3NH_3) is an example of metal-organic framework (MOF) magnet displaying a perovskite-like structure, which can be described as the well-known ABX_3 structure. In this compound, the B site is occupied by a magnetic ion (Co^{2+}) and the X_3 positions are occupied by formate molecules acting as bridges between the B sites, so that the $Co(COOH)_6$ units form a framework with cavities filled with methylammonium cations (CH_3NH_3).

We have performed a neutron inelastic study of the acoustic phonons in the (H 0 L) plane, using the cold triple-axis spectrometer IN12. As shown on fig. 1a), the transverse acoustic phonon modes associated to the framework, measured near the (2 2 0) Bragg position and in the [2-q 0 2+q] direction, could be identified on top of a broad scattering arising from the hydrogen incoherent contribution at low energy. These constant-Q cuts measured at several points of the Brillouin zone also show a high damping of the phonon branch when going towards the zone boundary. This broadening has been studied and reported in another hybrid perovskite compounds and was attributed to the molecular disorder, affecting the framework dynamics through strong hydrogen bonding [1]. In particular, the temperature dependence of the molecular dynamics was carried out at the zone boundaries through the structural transition. Fig. 1b) displays the temperature dependence of the broad quasielastic scattering associated to the molecule measured at the (0.5 0 1.5) zone boundary. Interestingly, the data shows a clear change in the quasielastic linewidth when increasing the temperature, which may indicate a change in the molecular dynamics when going through the structural transition, as was reported in other organic-inorganic compounds [2,3]. Although these features have been observed at the zone boundary, our previous study on the hybrid compound $MAPbCl_3$ shows that the ordering and distortions of the molecule also affect the phonon branch near the zone center [1] through the hydrogen bonding. These results are evidence for a strong coupling between the framework and the A-site molecular cation. Therefore, in $MACo(COOH)_3$, the molecular dynamics and its distortions as function of temperature may thus affect the octahedral environment and the magnetic properties of the B-site (in this case, Co^{2+}) thanks to this coupling.

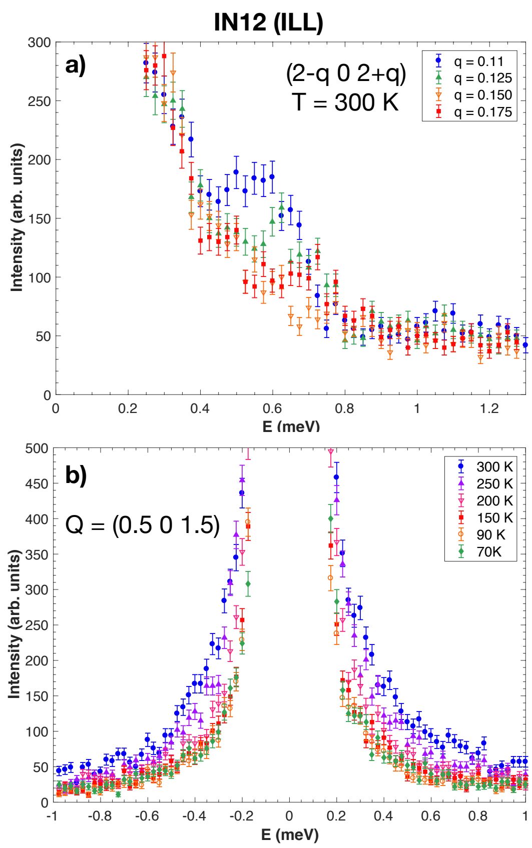

Fig.1 a) Constant-Q scans in the (2-q 0 2+q) direction at 300K. b) Inelastic scans at the Q = (0.5 0 1.5) zone boundary for several temperatures. The data was measured on IN12 (ILL, France).

[1] M. Songvilay et al., *Phys. Rev. Materials* 2, 123601 (2018)
[2] I. P. Swainson et al., *Phys. Rev. B,* 92, 100303(R) (2015)
[3] K. L. Brown et al., *Phys. Rev. B* 96, 1744111 (2017)