Experimental report

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Proposal: 5-13-273 **Council:** 4/2017

Title: Molecular dynamics in CH3NH3PbCl3

Research area: Physics

This proposal is a new proposal

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Samples: CH3NH3PbCl3

Instrument	Requested days	Allocated days	From	To
D9	0	6	15/03/2018	21/03/2018
D10	6	0		
D7	7	5	06/04/2018	11/04/2018

Abstract:

The organic-inorganic perovskites (CH3NH3Pb(Br,Cl,I)3) have been identified as efficient photovoltaic materials. Recent neutron scattering results on powder has shown a strong coupling between the organic molecules and the inorganic framework. Here we propose a single crystal neutron diffraction study on CH3NH3PbCl3 to measure the diffuse scattering related to the organic molecular dynamics in this compound. Polarized neutrons on D7 are necessary to separate the incoherent signal coming from the hydrogen atoms from the coherent diffuse scattering we would like to study. We would also like to check any additional contribution on Bragg peaks as the organic molecules lock at low temperature and record data to refine the thermal factors related to the hydrogen displacements on D10.

Study of the molecular dynamics in the hybrid perovskite $CH_3NH_3PbCl_3$ by means of neutron diffraction

$MAPbCl_3$ is an organic-inorganic hybrid perovskite, consisting of an inorganic perovskite host framework composed of corner-bonded $PbCl_3$ octahedra, with an organic molecular cation (MA is methylammonium CH_3NH_3) occupying the interstitial space. This compound displays three structural transitions from cubic to tetragonal to orthorhombic phase as temperature is decreased. These transitions are driven by the rotation and distortion of the $PbCl_3$ octahedra and associated rotation of the MA cation.
Our group has recently investigated the inorganic framework dynamics by means of neutron inelastic scattering on IN12 (M. Songvilay et al., *Phys. Rev. Materials* 2, 123601 (2018)) and completed this work with single crystal diffraction in order to collect additional information on the molecular dynamics throughout the structural transitions.

The single crystal diffraction experiment was carried out on the D9 diffractometer in order to measure the thermal coefficient associated to the molecule, the lead and the halide atoms as function of temperature. Interestingly, the results showed that the thermal coefficient was the largest for the halide atoms in the cubic phase, which corresponds to the molecular disordered phase. An anisotropic model was used to refine the data.

In parallel, we performed a polarized neutron diffraction experiment on D7 in order to observed the Q dependence of diffuse scattering associated to the molecular dynamics. The use of a polarized beam allowed to separate the coherent scattering from the incoherent scattering of hydrogen. Hence this method allowed to study the Q dependence of the nuclear diffuse scattering hidden in the incoherent part coming for the hydrogen.
Interestingly, a broad signal could be observed near the M symmetry point, even in the cubic phase at high temperature, while superlattice peak at this position, associated to the structural change from the cubic to orthorhombic phase, only appears below 170K. Fig. 1 shows a colormap in the (HK0) plane obtained on D7 and a colormap obtained on LET (ISIS, UK) for E = 0 meV (middle and right panels). The broad features seen on D7 are absent from the LET data, thus indicating that they correspond to diffuse scattering in energy (and not momentum). This diffuse scattering may be evidence for relaxational dynamics precursor of the ordering of the methylammonium molecules, and allows to characterize collective motions of the organic cation. A detailed temperature dependence of this diffuse scattering using polarized neutrons would thus allow us to capture the critical behavior of this signal.

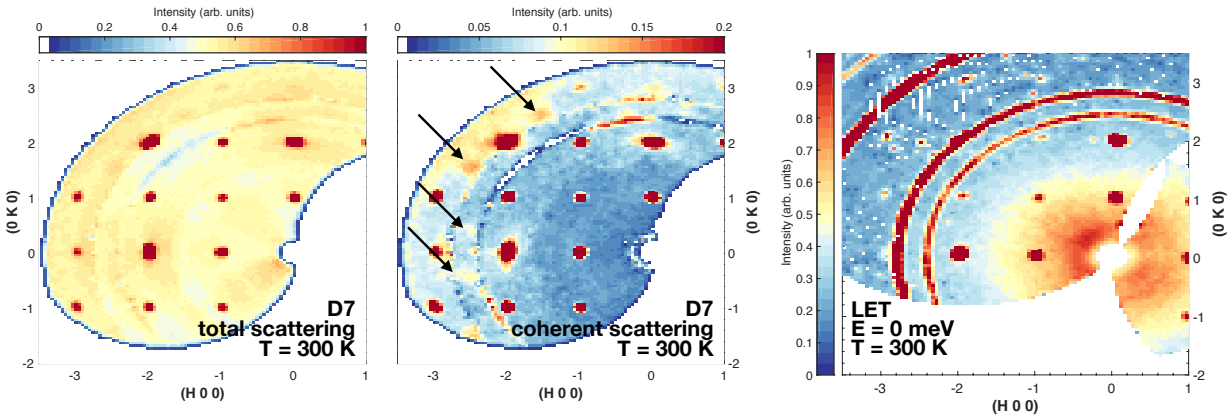

Figure 1: left and middle panels: Colormap representing the total scattering (left) and coherent scattering (middle), corrected from the background, measured on the D7 diffractometer at 300 K on a single crystal of $CH_3NH_3PbCl_3$. right: Constant E = 0 meV slice measured on LET (ISIS) at 300 K on the same crystal.