Experimental report

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Proposal: 7-03-169 **Council:** 4/2018

Title: Dynamics of the formamidinium organic cation in mixed hybrid inorganic-organic perovskites

Research area: Materials

This proposal is a new proposal

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Samples: MA1-xFAxPbI3

Instrument	Requested days	Allocated days	From	To
D7	2	0		
IN6-SHARP	5	5	13/09/2018	18/09/2018
IN16B	6	0		
IN5	2	2	18/09/2018	20/09/2018

Abstract:

The proposed research focuses on a detailed characterisation of the dynamics of the formamidinium organic cation in a class of novel mixed hybrid inorganic-organic perovskites, i.e. MA1-xFAxPbI3 (MA = methylammonium, CH3NH3; FA = formamidinium, CH(NH2)2+; x = 0, 0.25, 0.50, 0.75 and 1.0), with a view towards their application in perovskite solar cells. To capture the different types of dynamics of the formamidinium organic cation over a large temperature range, we will employ several complementary spectrometers (IN16b, IN6 and IN5), as well as D7 to check the possible presence of ferroelectric or antiferroelectric domains, which should affect considerably the functional properties of these technologically important materials. The proposed studies are embedded in a larger research program focused on the characterisation and development of hybrid inorganic-organic perovskites, by means of several complementary techniques, such as X-ray and neutron diffraction etc.

Dynamics of the formamidinium organic cation in mixed hybrid inorganic-organic perovskites (exp. 7-03-169)

1 Scientific background

Hybrid inorganic-organic perovskites have attracted an enormous interest recently due to their promising applications as absorbers in photovoltaic devices [1,2]. One of the most promising materials has the chemical formula $MA_{1-x}FA_xPbI_3$, where MA is methylammonium, CH_3NH_3, and FA is formamidinium, $CH(NH_2)_2^+$. An important question with respect to $MA_{1-x}FA_xPbI_3$ concerns the role the organic cation (MA and FA) has on the performance of the perovskite solar cell. The organic cation has been hypothesized to affect several properties including, e.g., the formation of microscopic (anti)ferroelectric domains, which helps to separate charge carriers by the electric field and therefore results in longer carrier diffusion lengths [3], and a giant modulation of the dielectric function which, in turn, lowers the exciton binding energy [4]. Still, these effects are currently under debate and some studies are contradictory to each other. It is therefore important to gain a full understanding of the dynamics of the organic cation at the atomic scale. A well-suited method for this is quasielastic neutron scattering (QENS), since hydrogen has a very large incoherent cross section for neutrons; therefore, the QENS signal will be dominated by contributions from the hydrogen atoms in the MA or FA molecule, and the organic cation dynamics can be probed. As the majority of previous studies have focused on $MAPbI_3$ [3,4], we aimed to elucidate the dynamics of the FA organic cation in the mixed hybrid inorganic-organic perovskites $MA_{1-x}FA_xPbI_3$ by employing QENS.

2 Experimental details

The QENS measurements were performed on the time-of-flight spectrometers IN5 and IN6. The $Fa_xMa_{1-x}PbI_3$ powder samples were filled inside rectangular Al cans with volume $30\times40\times0.2$ mm^3 which were sealed by Pb wire. At IN6, five stoichiometries were investigated, namely x =0, 0.25, 0.4, 0.75 and 1.0. All five samples were investigated at the temperatures 2, 50, 100, 150, 200, 250, 300, and 350 K and with an incident neutron wavelength of 5.1 Å. Measurements were also performed on IN5, using 2.5 Å wavelength neutrons, which allowed to probe the structure factor at higher Q-values, up to 4 $Å^{-1}$. These measurements were performed on $x = 0, 0.4$, and 1.0 samples and at T = 2, 50, 100, 200, and 300 K. Additionally, we performed measurements with 1.7 Å neutrons at 2 K to obtain a larger energy window and study the inelastic spectrum in more detail. In addition, the mixed $x = 0.4$ sample was investigated with 5 Å neutrons at temperatures 50, 75, 100, 125, and 150 K to more carefully study the onset of dynamics. Data reduction was performed in LAMP and comprised normalizing to a vanadium standard, subtraction of empty can counts, and correction for energy-dependent efficiency of the detectors.

3 Preliminary results

Fig. 1 (a) shows a representative $S(Q, E)$ for MAPI measured at 250 K on IN6. The spectrum can be adequately fitted by a delta function, two Lorentzian functions, describing the quasielastic scattering, and a sloping background, convoluted by the instrumental resolution which we measured on the same sample at 2 K. For temperatures above 150 K, two Lorentzian functions were needed to describe the quasielastic scattering. Based on previous studies [3,4], we interpret the wider Lorentzian to describe the C_3 rotation of the methyl and/or ammonia groups around the C-N axis of MA, whereas the narrower Lorentzian most likely describes the C_4 reorientations of the C-N axis itself which is activated above 170 K [4]. Fig. 1 (b) shows the extracted elastic incoherent structure factor (EISF) from the lineshape fitting for 150 K and 250 K. The data is compared to different jump models describing C_3 rotation of the methyl and/or ammonia groups around the C-N axis, C_4 reorientations of the C-N axis, and a coupled $C_3 \otimes C_4$ rotation.

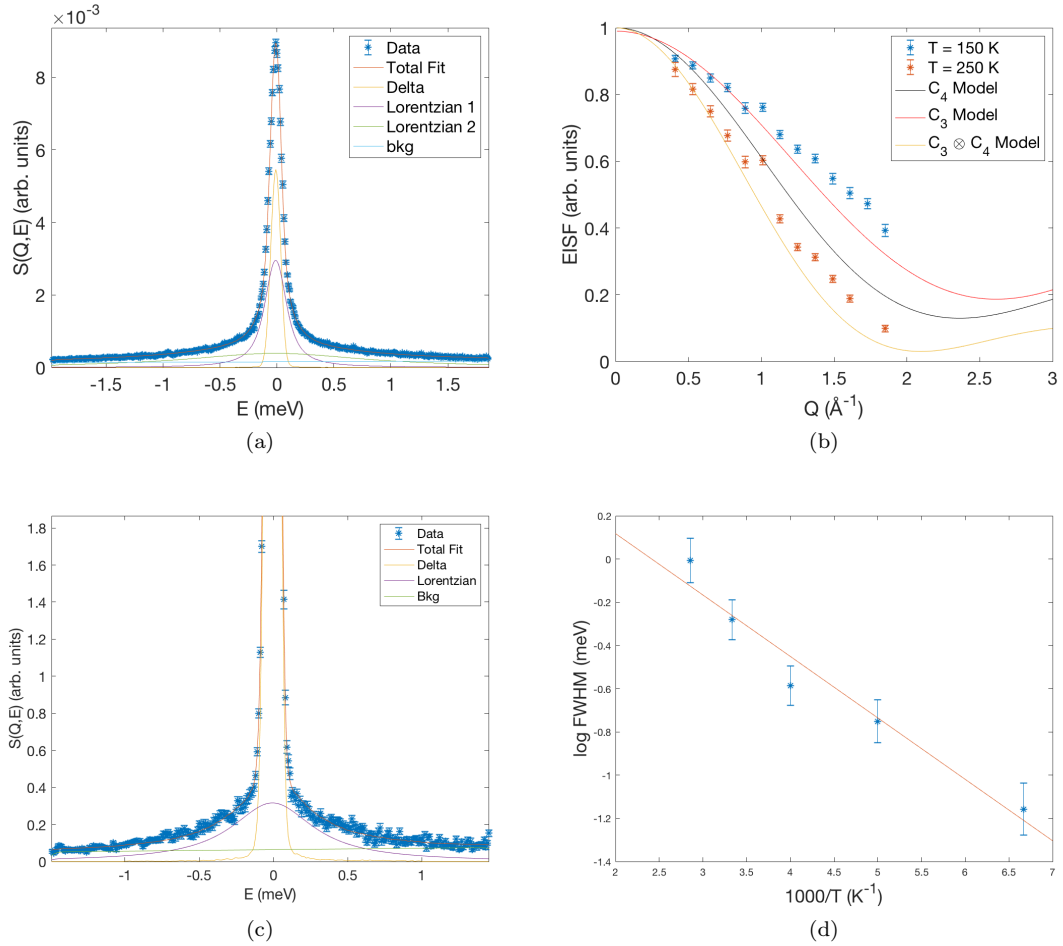

Figure 1: (a) Fitting of the quasielastic lineshape for MAPI at $T = 250$ K and $Q = 1.61$ Å^{-1}. (b) EISF of MAPI at $T = 150$ K and $T = 250$ K, togheter with jump diffusion models describing localized motions. (c) Fitting of the quasielastic lineshape for FAPI at $T = 350$ K and $Q = 0.7$ Å^{-1}. (d) Arrenius plot of the FWHM of the fitted Lorentzian for FAPI.

Fig. 1 (c) shows a a representative $S(Q, E)$ for FAPI measured at 350 K on IN6. For FAPI, the quasielastic part could be described by a single Lorentzian for all temperatures. Fig. 1 (d) shows an Arrenius plot of the extracted full width at half maximum (FWHM) of the quasielastic component for FAPI. From this, an activation energy of ~ 24 meV for FA reorientations on $FAPbI_3$ was extracted.

Further analysis of the QENS data, including, e.g., the evaluation of different jump diffusion models for describing FA reorientations, and the comparison to computer simulations and inelastic neutron scattering and Raman spectroscopy measurements, are ongoing. Unfortunately, the QENS data for FAPI is featured by a large uncertainty due to a small sample volume (~ 10 times less than the other compositions), meaning that these spectra must be re-measured.

(1) W. S. Yang, N. J. J. Jun Hong Noh, *et al.*, *Science* **348** (2015) 2013–2017.
(2) J. P. Correa-Baena, A. Abate *et al.*, *Energy Environ. Sci.* **10** (2017) 710–727.
(3) A. M. Leguy, J. M. Frost, *et al.*, *Nat. Commun.* **6** (2015).
(4) T. Chen, B. J. Foley, *et al.*, *Phys. Chem. Chem. Phys.* **17** (2015) 31278–31286.