Experimental report

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Proposal: 7-04-177 **Council:** 4/2019

Title: Cation Order & Disorder in Photovoltaic Hybrid Perovskites - The Needfor Neutron Spectroscopy under Pressure

Research area: Chemistry

This proposal is a new proposal

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Samples: Methyl ammonium lead iodide

Instrument	Requested days	Allocated days	From	To
IN1 LAG	6	3	20/05/2021	23/05/2021

Abstract:

Since its first use as a sensitizer in 2009, MAPI has become one of the most promising materials for photovoltaics. Notwithstanding the ongoing `race' to develop new solar-energy technologies based on this class of organic-inorganic hybrid materials, access to the phase diagram of MAPI and the underlying structural and dynamical properties has not been a trivial task. Building upon a recent study using the TOSCA spectrometer at ISIS and detailed computational modelling at ambient pressure, this proposal seeks to provide new insights into the local structure and underlying motions of the organic cation in this important material. To this end, we propose to conduct INS experiments on LAGRANGE as a function of pressure across the phase transition associated with the onset of cation disorder. We believe that this work would pave the way for a detailed mapping of important regions of the phase diagram of MAPI that remain entirely unexplored, and where the interplay between cation disorder and function can be explored under controlled conditions, including the emergence of global disorder via amorphisation.

Experimental Report: Cation Order & Disorder in Photovoltaic Hybrid Perovskites – The Need for Neutron Spectroscopy under Pressure

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***Synopsis*:** LAGRANGE has been used to explore the pressure- and temperature-dependence of the librational dynamics (6–45 meV) of methylammonium cations in $MAPbI_3$, across the low-temperature regime (primarily 40–140 K), and at moderate-pressures (5, 10, and 18 kbars). Despite of limited beam-time allocated (72 hours) and considerable intrinsic technical challenges of a high-pressure INS experiment, the research goal has been fully addressed. The obtained experimental data in combination with extensive *ab initio* simulations (in progress) will facilitate understanding of the evolution of the local structure in this quintessential hybrid organic-inorganic perovskite material under pressure, and will expand the previously inaccessible phase boundaries of $MAPbI_3$.

I. PHASE DIAGRAM OF $MAPBI_3$

Pressure offers a means of accessing the rich phase behaviour of Hybrid Organic-inorganic Perovskites (HOIPs), as illustrated with the specific example of $MAPbI_3$ (see **Figure 1**). To date, the high-pressure studies beyond ambient temperature have been, however, sparse.

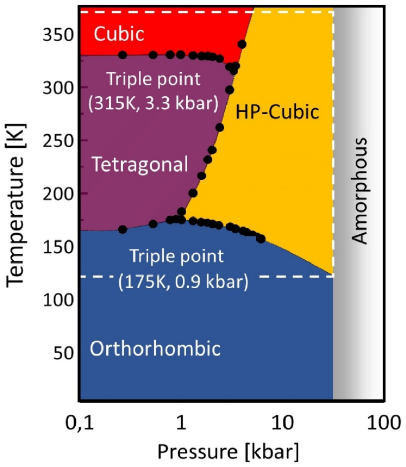

FIG. 1: Phase diagram of $MAPbI_3$ from the dielectric data of Ref. [1] (black dots), extrapolated to lower-temperatures and higher pressures (yellow and blue areas). Dashed white area shows the pressure-temperature regime explored by our research team with synchrotron diffraction experiments. Amorphization occurs around 25-30 kbars at ambient temperature.

In principle, it is commonly accepted that $MAPbI_3$ shows three different crystal structures at ambient pressure depending on the temperature, i.e. the low-temperature orthorhombic phase for $T < 160$ K; the tetragonal phase for 160 K $< T <$ 330 K; and the high-temperature cubic phase for $T > 330$ K, with two triple-points detected and two more phases (HP-Cubic and Amorphous) existing at extreme conditions. We have recently expanded the previously studied phase boundaries of $MAPbI_3$ with synchrotron diffraction experiments in diamond anvil cells (dashed white area in **Figure 1**), and found potentially extended regimes of stability of the high-pressure cubic phase (HP-Cubic), yet with the low-temperature part of the phase-diagram left unexplored.

With a high-flux, good resolution and broadband capabilities, LAGRANGE emerges as excellent instrument to address the emerging questions on the phase boundaries and evolution of the local structure of of $MAPbI_3$ at extreme conditions. This capitalises recent high-pressure developments by Ivanov *et al.*, [2], making it possible to collect INS data on LAGRANGE up to 2–3 GPa.

II. EXPERIMENTAL PLAN

We have originally requested 6-days on LAGRANGE, to measure at $P = 2$, 5, 10, and 20 kbars in variable-temperature conditions (between 300 K and 10 K) in order to cross the transition between the cation-ordered and disordered phases. We planned to use two high-pressure cells in tandem. 6-days were essential to complete these crucial measurements along with other necessary experimental checks. Due to reduced beam-time, this experimental plan had to be revised.

Only one high-pressure cell was eventually available, allowing to measure up to 18 kbars. Although only 3-days of the beam-time were granted, we took a challenge

to measure at $P = 5$, 10, and 18 kbars at selected temperatures between 180 K and 10 K. Performing these measurements from scratch in such a tight beam-time schedule would be impossible without using reference data. To this end, we relied on a high-resolution INS spectrum of $MAPbI_3$ measured at 10 K (ambient pressure) with TOSCA (see **Figure 2**). [3]

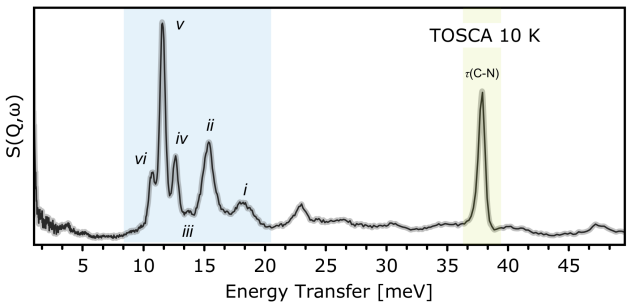

FIG. 2: Reference ambient-pressure INS spectrum of $MAPbI_3$ measured at 10 K on TOSCA. [4] See Ref. [4] for a detailed intepretation of the highlighted regimes.

The INS spectrum has been exhaustively interpreted in our previous works based on the state-of-the-art *ab initio* modelling. [3, 4] $MAPbI_3$ shows two distinct spectral regimes with fundamental transitions at low energy transfers, i.e. the range (*i*) at c.a. 10–20 meV, and (*ii*) at c.a. 35–40 meV. The former one expresses the external librational modes of MA^+ cations, whereas the latter is due to internal disrotatory mode of the cation, which is superb sensitive to local environment and the hydrogen-bonding framework. [3] Owing to scanning options of LAGRANGE, we have restrict the measurements to these particularly informative spectral parts. The range (*i*) required using both Si(111) and Si(311) monochromators, which was particularly time-consuming.

One of the greatest challenges of this experiment was to separate the signals from the sample and the high-pressure cell, the latter strongly contributing to both regimes under interest. As a matter of compromise, we have selected a double cadmium shielding to reduce the contaminating signal.

TABLE I: Summarized output from high-pressure LAGRANGE experiment on $MAPbI_3$. Successfully collected data with Si(111) + Si(311) monochromators (ca. 10–20 meV) are marked as (*i*), and the ones measured with Cu(220) are denoted as (*ii*). S/N denotes too-weak signal from the sample to be detected.

P /T	10 K	40 K	90 K	140 K	180 K
5 kbar	(*i*) + (*ii*)	(*i*) + (*ii*)	(*i*) + (*ii*)	–	S/N
10 kbar	(*i*) + (*ii*)	(*i*) + (*ii*)	(*i*) + (*ii*)	S/N	S/N
18 kbar	S/N + (*ii*)	S/N + (*ii*)	S/N + (*ii*)	S/N	S/N

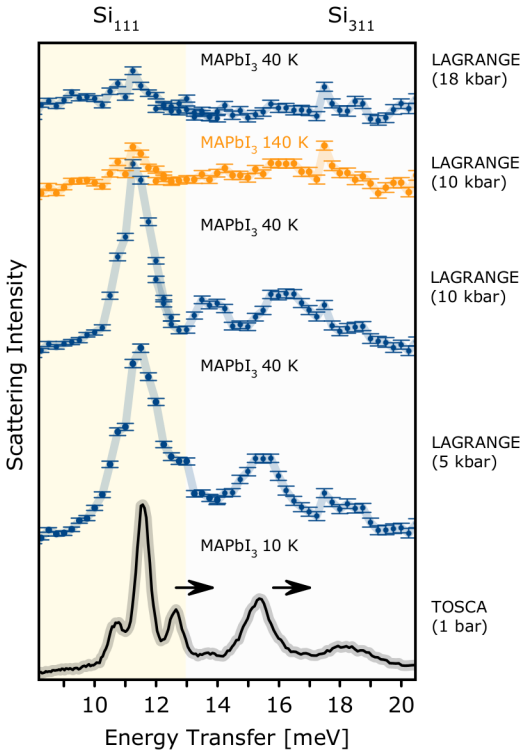

FIG. 3: INS spectra of $MAPbI_3$ in the lower energy transfer regime (*i*), recorded at base temperature and ambient pressure with TOSCA, [4, 5] as compared to selected outputs from high-pressure experiments on LAGRANGE.

III. RESULTS AND DISCUSSION

Table 1 summarizes the experimental output. Selected INS spectra in the low energy transfer regime (*i*) are depicted in **Figure 3**.

In none of the cases the INS signal could be detected above 90 K (140 K and 180 K), making it impossible to study the temperature boundaries of the orthorhombic phase (contrary to initial assumption that the temperature-dependent cation mobility can be constrained by external pressure). At moderate pressures, the low-temperature phase could be studied up to 90 K in both energy-transfer regimes (*i*) and (*ii*). At 18 kbars, the sample could only be detected in regime (*ii*), due to a considerable loss of scattering intensity. This is illustrated in **Figure 3**, with comparison between the 10 kbar and 18 kbar spectra. Hampering of the spectral intensity in regime (*i*) is most likely due to an orientational disorder of the MA^+ cations, resulting in an inhomogenous broadening and strong damping of the spectral intensity, in line with our previous findings on the low-temperature INS response of MA^+ in tetragonal environments. [4, 5] According to **Figure 3**, and the comparison between the ambient-pressure TOSCA spectrum and the INS spectra measured on LAGRANGE, there is a strong influence

of the external pressure on the well-defined features at c.a. 13 and 16 meV, ascribed to librational transitions affected by hydrogen bonding, whereas the most intense peak at 11 meV remains pressure-independent.

The interpretation of the experimental requires the use of *ab initio* predictions, which are in progress, involving both lattice dynamics calculations in quasi-harmonic approximation as well as anharmonic *ab initio* MD (AIMD) simulations. We anticipate that both experimental and computational data will provide detailed insights into the pressure-evolution of the low-temperature orthorhombic phase as well as deliver quantitative description of the vibrational dynamics of MA^+ at both temperature- and pressure-variable conditions.

ACKNOWLEDGMENTS

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AUTHORS CONTRIBUTIONS

K. Drużbicki - Co-proposer; B. Braunewell - Participant; M. Jiménez-Ruiz - Local Contact; A. Ivanov - Local Contact; R. Sadykov - Constructor of the High-pressure Cell; F. Fernandez-Alonso - Project Leader.

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