Experimental report

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Proposal: 7-01-589 **Council:** 4/2023

Title: Phonon survey of inorganic halide perovskites CsPbBr3

Research area: Physics

This proposal is a new proposal

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Samples: CsPbBr3

Instrument	Requested days	Allocated days	From	To
IN5	5	4	20/11/2023	24/11/2023
ORIENTEXPRESS	1	1	07/11/2023	08/11/2023

Abstract:

In the last 10 years, 3D halide perovskites have opened a new route towards low-cost manufacture of solar cells while offering currently certified conversion efficiencies of about 25%. These halide perovskite materials are hybrid or fully inorganic semiconductors forming a perovskite lattice. We have previously performed detailed inelastic neutron scattering investigations of the lattice dynamics of organic hybrid formamidinium and methylammmonium based, iodide and bromide Pb-based perovskites. These information are still lacking for the 3D inorganic perovskites CsPbX3 (x=I,Br) although more precise phonon calculations have been performed. We here propose to survey the full phonon spectrum of CsPbBr3 using the time-of-flight instrument IN5. We wish to measure ~ 180 deg rotation by 1 deg step at low temperature (5 K) where the phonon damping will be reduced and another measuremen at high temperature (say 430 K in the cubic phase of CsPbBr3).

Optical phonons in inorganic halide perovskites $CsPbBr_3$

Experimenters : Philippe Bourges, Simon Thébaud, Antoine Létoublon, Olivier Durand, Jacques Ollivier

Halide perovskite materials, of composition ABX_3 (A either a small organic molecule such as methylammonium or a Cs atom, B a metal such as Pb or Sn, X a halide) are extremely promising materials for various optoelectronic applications, from photovoltaic energy conversion to quantum technologies. However, their vibrational dynamics and electron-lattice couplings are still ill-understood, despite their crucial impact on carrier dynamics and optoelectronic properties.

In this experiment on IN5, we have studied a sample of the inorganic compound $CsPbBr_3$, which is used in colloïdal quantum dots for low-temperature single and entangled photon emission. This material is stable under ambiant conditions in an orthorhombic phase, but undergoes phase transitions to tetragonal and then cubic structures above room temperature. In addition to the direct relevance of this compound for low-temperature quantum dot devices, it is an important reference compared to methylammonium or formamidinium-based perovskites that are ubiquitous in room-temperature applications like photovoltaics. The lattice dynamics of these compounds, which has been the focus of previous studies [Let16,Fer18,Fer20,Heh22], is complicated by the presence of an organic molecule in the unit cell. Therefore, studying the vibrational spectrum of $CsPbBr_3$ will lead to a general understanding of the lattice dynamics of halide perovskites. Previous neutron scattering studies on inorganic perovskites have focused on low-frequency modes involved in the orthorhombic-tetragonal and tetragonal-cubic phase transitions [Fuj74, Lan21]. Additional information on vibration modes coupled to optoelectronic degrees of freedom come from photoluminescence sidebands pointing to optic zone-center phonons at 3 meV, 6 meV, 9 meV and 19 meV [Ama23].

The sample used in the experiment was a single crystal grown at KAUST, Saudi Arabia. Since Br-based perovskite have been seen in past experiments to react strongly with aluminium, we have used a vanadium sample holder and glue (GE varnish) to hold it. We had previously characterized its orthorhombic phase and crystalline orientation using X-ray diffraction (at the FOTON Institute in Rennes) and neutron diffraction (at ILL on OrientExpress) measurements. The main diffraction plane on IN5 included the (1,-2,1) and (1,0,-1) reciprocal lattice vectors in orthorhombic notations. The neutron wavelength used was 3.3 angström, with a single scan performed at 2.8 Angström to get more energy range in a specific part of the reciprocal space. Multiple scans were performed at room-temperature to accumulate signal, then the sample was brought down to 100 K for the last scans. Being quite brittle, it cracked into pieces during the temperature change back to ambiant conditions.

The scan at room temperature features bragg peaks at the expected points in reciprocal space (with the exception of one unexpected peak suggesting the presence of a misoriented grain in the sample). Around some of the Bragg peaks, both transverse and longitudinal phonon dispersions can be clearly seen (see fig. 1a), giving access to the elastic constants of the material. No optical phonon signature is visible at the Gamma point probably due to lack of signal, but optical phonons can clearly be seen at 4 meV at the high-symmetry point (5/2,-1,-3/2) that corresponds to a M point in the cubic phase (see fig 1b). These modes are steeply dispersed, reaching 10 meV at the neighboring (2,-1,-1) point for instance. They disappear in the 100 K scan, either due to a signal loss related to Bose factors or due to a stiffening of the modes with decreasing temperature. The second interpretation leaves open the possibility of a soft mode behavior at the the orthorhombic to tetragonal phase transition. Phonon and INS spectra of $CsPbBr_3$ are currently being simulated to help in the interpretation of the data.

In addition, a quasielastic signal is present throughout the reciprocal space, which may be indicative of rattling dynamics of the cations as was seen in previous experimental studies on organic-inorganic perovskites. A quick scan with only the sample holder and glue was performed so that the contribution to the quasielastic peak from the glue can be substracted.

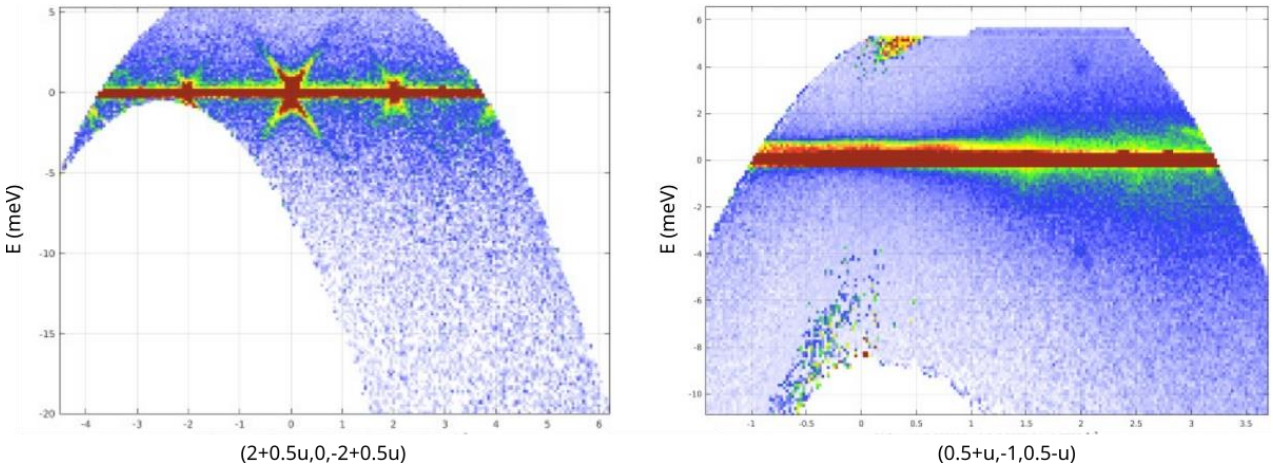

Fig. 1 : a) Cut of the neutron intensity map a) along a G-M direction, showing acoustic phonon dispersions. b) a long a R-M direction featuring steeply dispersed optical phonons.

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