Experimental report

26/01/2024

Proposal: 7-01-591 **Council:** 4/2023

Title: Acoustic phonons and temperature dependence of low energy Phonons in 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
IN12	7	4	31/10/2023	04/11/2023
ORIENTEXPRESS	1	1	31/10/2023	01/11/2023

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 measure in CsPbBr3 various features: i) to determine the elastic constants in the cubic phase, ii) to follow the temperature dependence of low energy optical phonons and iii) to measure a possible soft phonons and central peak near the tetragonal-cubic phase transitions.

Acoustic and optical phonons in inorganic halide perovskites $CsPbBr_3$

Experimenters : Philippe Bourges, Simon Thébaud, Antoine Létoublon, Jacky Even, Stéphane Raymond

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. On IN12, we have studied a sample of the inorganic compound $CsPbBr_3$. This material is stable under ambiant conditions in an orthorhombic phase, but undergoes phase transitions to tetragonal and then cubic structures above room temperature. 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 $CsPbBr_3$ sample used in this combined experiment, ILL-7-01-591(4 days) and CRG-3020 (2 days), 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 horizontal scattering plane on IN12 included the (1,-2,1) and (1,0,-1) reciprocal lattice vectors in orthorhombic notations. The neutron energy used was 5 meV with a beryllium filter installed on the diffracted beam. After a series of energy scans performed at room-temperature to identify the acoustic branches and optical phonons, the sample was cooled down step by step to 25 K to study the temperature dependence of scans at high symmetry points in reciprocal spaces (M, Z, Γ). However, being quite brittle, the sample cracked into pieces during the temperature change back to ambiant conditions, about ~40% of the sample was lost during the heating.

In this experiment on IN12, we follow low energy phonon branches in the orthorhombic phase. We first observe acoustic phonon branches. For instance, the left figure shows the phonon spectra of the transverse mode and the right part represents the deduced dispersion of the transverse acoustic mode (which in principle is measuring the C_{44} elastic constant assuming a weak orthorhombic distortion). A sound

velocity of 6.6 meV.Å≡ 1005 m/s is found, very similar to the one reported in organic perovskites [Fer18], suggesting as well a soft lattice. Other acoustic branches were also measured, allowing to determine C_{11}, still assuming a weak orthorhombic distortion.

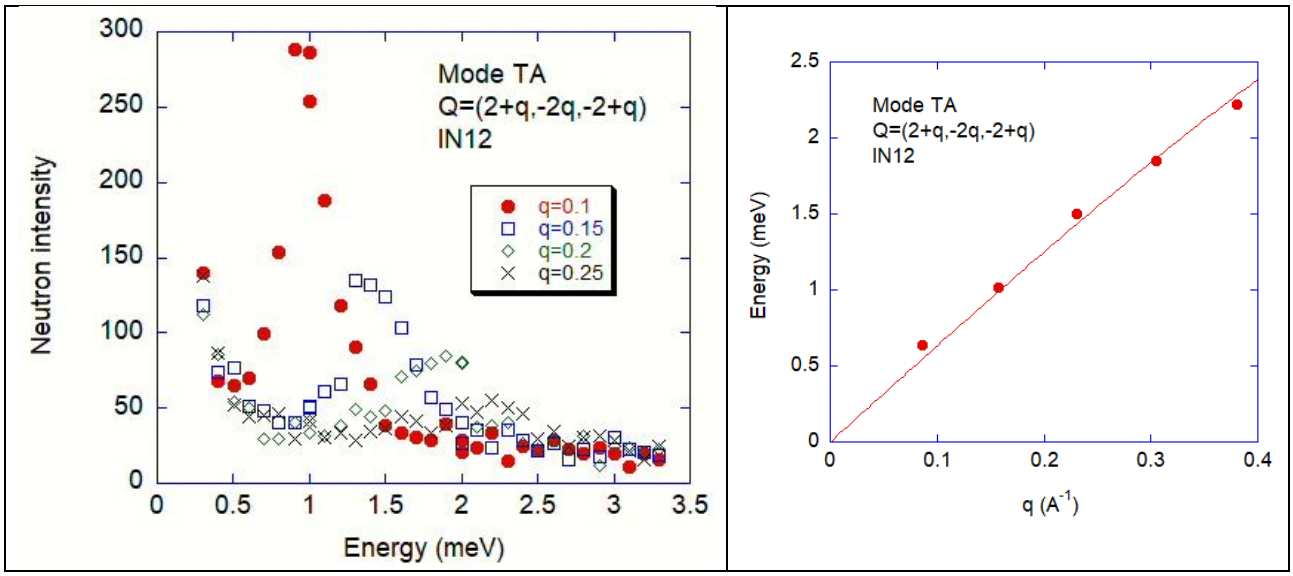

Figure: Phonons in CsPbBr3 (a) Transverse acoustic phonons spectra measrured at Kf=1.55 $Å^{-1}$ **(b)** Transverse acoustic branch measured on IN12 in CsPbBr3

Further, inelastic scans were performed at different Q-points in the reciprocal space to measured optical phonons. At the high-symmetry point (5/2,-1,-3/2) that corresponds to a M point in the cubic phase, an optical phonon can be clearly seen near 4 meV. Systematically, quasi-elastic excitations are observed in agreement with the previous neutron measurements [Lan21]. However, in contrast with [Lan21], nothing remarkable was noticed upon cooling down with no clear sharpening neither of the quasielastic response nor of the optical phonon branches.

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[Ama23] M.-R. Amara, et al, Nano Lett. 23, 3607-3613 (2023).