

## Low-frequency Raman spectroscopy and elastic softness of hybrid lead halide perovskites

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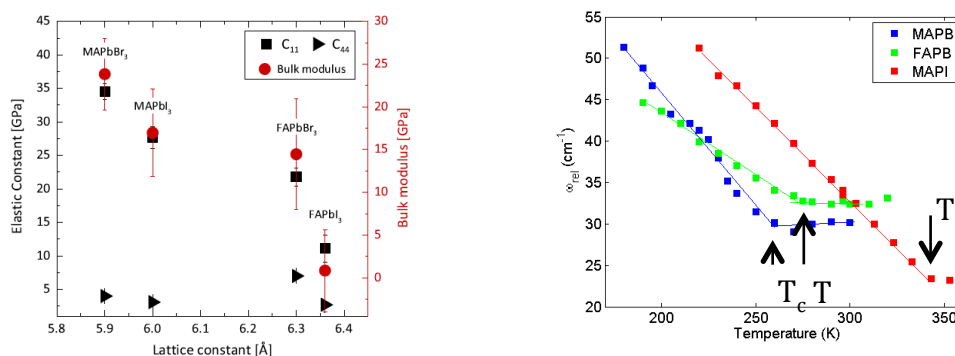
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Hybrid organic-inorganic perovskites are intensively studied as promising materials for various applications, taking advantage of their low cost and easy processing. Although much recent attention has been devoted towards unraveling their microscopic optoelectronic properties, the low frequency dynamics (e.g. their softness) is currently still lacking a comprehensive understanding as compared to that already reached for classic semiconductors.

Here we investigate the low frequency dynamics in four different hybrid perovskite single crystals: MAPbBr<sub>3</sub>, FAPbBr<sub>3</sub>, MAPbI<sub>3</sub> and  $\alpha$ -FAPbI<sub>3</sub>. Using coherent inelastic neutron scattering spectroscopy and Brillouin light scattering, we investigate the low frequency acoustic phonons [1,2]. A very small shear C<sub>44</sub> elastic constant is found for all the compounds as well as sizeable elastic anisotropy. The extremely low bulk modulus and negative C<sub>12</sub> in  $\alpha$ -FAPbI<sub>3</sub> substantiates its very unstable nature and in FAPbBr<sub>3</sub>, a tendency towards an incipient ferroelastic transition, is interpreted as further evidence of the influence of plasticity in hybrid perovskites. We observe a systematic lower sound group velocity in the technologically important iodide-based compounds compared to the bromide-based ones [2]. The findings suggest that low thermal conductivity and hot phonon bottleneck phenomena are expected to be enhanced by low elastic stiffness, particularly in the case of the ultrasoft  $\alpha$ -FAPbI<sub>3</sub> (Fig. 1a).

The low-frequency dynamics is further investigated by Raman spectroscopy. The scattering from the low-frequency optical phonons has been collected across the cubic to tetragonal transition. With the resolution and contrast available by our experiment ( $\sim 4\text{-}5\text{ cm}^{-1}$  at the bottom of the elastic line) we do not observe the divergence of a central peak. However, the lowest frequency vibration, almost temperature independent in the cubic phase, hardens on cooling in the tetragonal phase. These conclusions apply in three of the four samples (analysis in  $\alpha$ -FAPbI<sub>3</sub> still in progress) suggesting a common framework for the analysis of the low-frequency vibrational dynamics of this family compounds (Fig. 1b). In CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> the Raman spectroscopy across the full set of phase transitions down to 20 K will also be discussed.



**Fig. 1 (a)** Elastic constants C<sub>11</sub> and C<sub>44</sub> and bulk modulus in the cubic phase as a function of the changing of lattice constant between compounds (neutrons). **(b)** Temperature dependence of the relaxational frequency  $\omega_{rel} = \omega_0^2/\Gamma$  of the lowest frequency phonon (Raman).

[1] A. Létoublon et al., Journal of Physical Chemistry Letters 7, 3776 (2016).

[2] A.C. Ferreira et al, preprint arXiv:1801.08701 <<https://arxiv.org/abs/1801.08701>>

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