

Reviewers' comments:

Reviewer #1 (Remarks to the Author):

The manuscript by Bourges and co-workers describes a study by single-crystal inelastic neutron scattering and Raman spectroscopy of the low-frequency vibrational modes in the well-studied series of organic lead halide perovskites. The key observations are that these modes show little dispersion but dampen abruptly as the temperature increases, indicating localised, anharmonic vibrations. These observations have important implications for both these materials' optoelectronic properties and for modelling them computationally (which has previously been done mostly in the harmonic or quasiharmonic approximations). This appears to be competent experimental work, although the surrounding discussion is in places unclear; it will be of interest to, and provide a comparison point for, future experimental and computational studies of these important materials.

I am not sure it is entirely accurate to describe the order-disorder phase transitions in these materials as reconstructive (p.1), since the perovskite topology is maintained throughout (in contrast, for instance, with CsPbI<sub>3</sub>). Nor is it clear what it might mean for one phase transition to be "less reconstructive" than another (p.2).

The sequence of phase transitions on cooling is described only in general. Although the phase transitions themselves are not the focus of this manuscript, the authors should at least specify the space group of all four compounds at the temperature at which measurements were made, and discuss any relevant differences.

I found the discussion of why the lowest-frequency modes might show little dispersion (pp.3-4) rather hard to follow, and suggest that the authors might wish to clarify it.

In contrast to the authors' claim that "mode attribution to the respective structural vibrations has been carefully discussed" (p.2), I found this section of the discussion (pp.6-7) also rather vague. Although various mode frequencies and motion types from previous studies are discussed, no explicit identification of any mode from this study with any specific vibrational mode is given. This would be a helpful addition, for instance, to Table I. This is important not just for clarity but also, for instance, to confirm the assertion that the difference between Raman and INS spectra is due to the different scattering factors of these techniques (p.4) - this is a quantitative claim that should be, but is not at present, backed up by calculation.

There is some sensible discussion of the incoherent scattering that is expected from protium nuclei, but it is not entirely clear why the experiments were not simply performed with deuterated samples instead.

The experimental section is generally given in good detail to allow the experiments to be repeated; one small missing detail is the size of the crystals used.

The manuscript is generally well expressed but would benefit from English language proofreading and spell-checking before publication.

Reviewer #2 (Remarks to the Author):

Please refer to the attached pdf.

Review of COMMSPHYS-19-0561-T

The manuscript presents the results of inelastic neutron scattering (INS) and Raman scattering from optical phonons in four different hybrid (organic-inorganic) lead halide perovskites (in the manuscript - HOP). The measurements were done at room temperature and 5 K. The crucial role of phonons in the extraordinary optoelectronic properties of HOP is well known as pointed out in the manuscript introduction. The acoustic phonons in HOP have already been studied by INS in the manuscript Refs. 18 and 19. One of the goals in the present work was to measure the optical phonons by the same methodology as that of the acoustic phonons and thus to reveal the interrelation between charge carrier-phonon and phonon-phonon relaxations.

The authors used one of the most powerful techniques for studying phonons throughout the Brillouin zone – INS although only for a limited number of high-symmetry points and a single intermediate point in the high-symmetry directions. The major new results are:

- (1) The experimental proof of the strong anharmonicity in HOP for temperatures higher than ~80K.
- (2) The observation of dispersionless optical phonons throughout the Brillouin zone at 5K.
- (3) At RT the optical phonons were found overdamped and no optical modes were observed in INS.

The result (1) has already been demonstrated in Ref. 50 for the gamma-point Raman active phonons and also suggested by a number of first-principles lattice dynamics calculations. The experimental demonstration of anharmonicity of the non-zero wave vector phonons is an important result that completes the phonon anharmonicity picture in HOP.

A clearly discernible optical phonon dispersion is seen in the lattice dynamics simulations, which opposes the result (2). Although the first-principles lattice dynamics of HOP is complicated and may not be completely reliable, the reason for this discrepancy might be also in the inherent limitation of INS. Here is one possible scenario. The phonon dispersion is the energy change of a given phonon symmetry mode with phonon wavevector. The phonon mode resolution of INS is much lower compared to that of the Raman scattering as demonstrated in Fig. 3 at the gamma-point. In addition, more phonon branches as the IR ones both LO and TO are packed closely around the Raman modes. The lattice dynamics typically yields a maximum dispersion of 2-3 meV from gamma to R or X points of some of the optical phonons with energies in the range 2-10 meV. The INS shows a single, relatively broad, peak at ~5 meV that apparently represents scattering from a bundle of modes. Given these energy constraints it is possible that INS is incapable to detect a mode specific phonon dispersion in such closely packed optical modes. A comment of this possibility will be beneficial for the presentation of this work.

The result (3) is clearly presented in the manuscript supplementary note (SN). This result, however, challenges the findings in Ref. 44 where the optical phonon dispersion at RT was measured in MAPI and MAPB by means of X-ray scattering. The authors try to give energy resolution arguments for why the results in Ref. 44 may not be reliable but the same is also valid to certain degree for INS. In this connection it is important to note that the core group of authors of the

current manuscript reports the observation of optical phonons in MAPB at 280 K (close to RT) in their earlier paper, Ref. 18, Fig. 4. Which result is then correct the one in this manuscript or that in Ref. 18?

I also want to note that the authors make a broadly overstated claim that "...The dispersionless nature of these optical modes implicates a glassy-like thermal conductivity, important to the hot phonon bottleneck effect in HOPs..." To my opinion this statement is not justified. It is rather a way to emphasize the importance of the observation of dispersionless optical modes. The thermal conductivity in semiconductors and insulators as HOP is carried out mostly by acoustic phonons. In some materials and semiconductor nanostructures contribution from optical phonons might be more sizable but this is a rather specific property. In HOP, the claimed dispersionless optical phonons should not participate in the thermal conductivity merely because their group velocity is zero. It has been showed in Ref. 19 that anharmonicity softens the acoustic phonon dispersion (group velocity), which results in low thermal conductivity. The acoustic phonons and their dispersion are well measured at RT (Refs. 18 and 19). To have a glass-like thermal conductivity the authors have to show that at least the scattering of acoustic phonons by not well-defined optical phonons at RT is dominating acoustic-acoustic phonon scattering. However, if this is correct then why are the acoustic modes not overdamped? In addition, this work shows that optical phonons are overdamped due to anharmonicity, that is, their lifetime is very short at RT. How can that be reconciled with the hot phonon bottleneck effect? Our common understanding of this effect is that optically excited hot charge carriers (not yet thermalized) relax via the Fröhlich interaction with emissions of LO polar phonons as for instance the IR modes because HOPs are centrosymmetric. In order to build up the hot phonon bottleneck one needs to suppress the LO phonon relaxation (phonon-phonon decay or scattering), which is just the opposite of what is shown in this work. A clarification or reformulation of the claim is needed.

In summary, this work has enough merit to be further considered for potential publication in the Communication Physics, Nature, after revision. Also, I hate to point it out but some English proofreading is needed for the revised version.

Dear Editor,

See Below our detailed replies to the reviewer #1 and #2 comments point by point. (the page and references numbers correspond to the resubmitted manuscript).

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Reviewer #1 (Remarks to the Author):

The manuscript by Bourges and co-workers describes a study by single-crystal inelastic neutron scattering and Raman spectroscopy of the low-frequency vibrational modes in the well-studied series of organic lead halide perovskites. The key observations are that these modes show little dispersion but dampen abruptly as the temperature increases, indicating localised, anharmonic vibrations. These observations have important implications for both these materials' optoelectronic properties and for modelling them computationally (which has previously been done mostly in the harmonic or quasiharmonic approximations). This appears to be competent experimental work, although the surrounding discussion is in places unclear; it will be of interest to, and provide a comparison point for, future experimental and computational studies of these important materials.

We thank the referee for the appreciation of our work and of its importance for future experimental and theoretical studies.

I am not sure it is entirely accurate to describe the order-disorder phase transitions in these materials as reconstructive (p.1), since the perovskite topology is maintained throughout (in contrast, for instance, with CsPbI<sub>3</sub>). Nor is it clear what it might mean for one phase transition to be "less reconstructive" than another (p.2).

Two phase transitions systematically occur in lead halide perovskites. The low temperature one is reconstructive in MA-based iodide and bromide perovskites and therefore clearly first-order according to Landau's theory, because there is no group-subgroup relationship between the tetragonal and orthorhombic space groups. In CsPbI<sub>3</sub> as quoted by the reviewer, such relationship exists and the phase transition is therefore expected to be second-order or weakly first-order according to Landau's theory. In FA-based perovskites, the low temperature space groups are a matter of debate in the literature and the reconstructive character of the low temperature phase transition is therefore not completely elucidated. Most experimental techniques show nevertheless abrupt changes of the perovskite physical properties than in MA based compounds, which might be in favor of a non-reconstructive character. We clarify that point (page 1) to avoid further misunderstanding.

The sequence of phase transitions on cooling is described only in general. Although the phase transitions themselves are not the focus of this manuscript, the authors should at least specify the space group of all four compounds at the temperature at which measurements were made, and discuss any relevant differences.

We thank the referee to underline that point. We specify the low temperature space group of each compound (page 1). Discussion of the impact of the relative distortion of each HOP (comparison of FA-based and MA-based compounds) can be as well found in the discussion section.

I found the discussion of why the lowest-frequency modes might show little dispersion (pp.3-4) rather hard to follow, and suggest that the authors might wish to clarify it.

We have rephrased and reorganized that discussion on page 3-4 to clarify the point in question. The experimental limit is associated with medium and high energy bundles not the lowest-frequency modes.

In contrast to the authors' claim that "mode attribution to the respective structural vibrations has been carefully discussed" (p.2), I found this section of the discussion (pp.6-7) also rather vague. Although various mode frequencies and motion types from previous studies are discussed, no explicit identification of any mode from this study with any specific vibrational mode is given. This would be a helpful addition, for instance, to Table I. This is important not just for clarity but also, for instance, to confirm the assertion that the difference between Raman and INS spectra is due to the different scattering factors of these techniques (p.4) - this is a quantitative claim that should be, but is not at present, backed up by calculation.

We thank the referee to underline that difficult point. Due to the large number of phonon modes of the  $ABX_3$  structure, it is indeed rather difficult to make quantitative statements without a lattice dynamics calculation, which is turning to be not enough reliable (as quoted by the second referee) due to the large anharmonicity in these materials. As the referee pointed out, our measurements will serve for future and more accurate phonon dynamics computations, not the other way around. The difference on page 4 between the INS and Raman results is related to the accuracy of the technique not only due to the different scattering structure factors. As suggested by the referee, we add in the table I the typical phonon character as discussed in the text.

There is some sensible discussion of the incoherent scattering that is expected from protium nuclei, but it is not entirely clear why the experiments were not simply performed with deuterated samples instead.

Very large single crystals are required for inelastic neutron scattering, putting a very strong experimental constraint by comparison to other experimental techniques (such as Raman Scattering or X-ray diffraction). The crystal synthesis of very large single crystalline deuterated samples is usually very costly and was not available for all of the four compounds. This manuscript is a first comparative report on the most prominent phonons and their possible dispersion. We could address most of these features with protonated samples and make a proper comparison using similar conditions. We nevertheless agree with the referee that measurements with deuterated samples will be useful for future dedicated studies.

The experimental section is generally given in good detail to allow the experiments to be repeated; one small missing detail is the size of the crystals used.

We thank the referee to mention that omission. We now quote the samples volume in the methods section.

The manuscript is generally well expressed but would benefit from English language proofreading and spell-checking before publication.

The re-submitted manuscript has been carefully proofread.

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Reviewer #2 (Remarks to the Author): Review of COMMSPHYS-19-0561-T

The manuscript presents the results of inelastic neutron scattering (INS) and Raman scattering from optical phonons in four different hybrid (organic-inorganic) lead halide perovskites (in the manuscript - HOP). The measurements were done at room temperature and 5 K. The crucial role of phonons in the extraordinary optoelectronic properties of HOP is well known as pointed out in the manuscript introduction. The acoustic phonons in HOP have already been studied by INS in the manuscript Refs. 18 and 19. One of the goals in the present work was to measure the optical phonons by the same methodology as that of the acoustic phonons and thus to reveal the interrelation between charge carrier-phonon and phonon-phonon relaxations.

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The result (1) has already been demonstrated in Ref. 50 for the gamma-point Raman active phonons and also suggested by a number of first-principles lattice dynamics calculations. The experimental demonstration of anharmonicity of the non-zero wave vector phonons is an important result that completes the phonon anharmonicity picture in HOP.

We thank the referee for the appreciation of our work and the acknowledgement of the inelastic neutron scattering technique to determine the phonon spectrum.

A clearly discernible optical phonon dispersion is seen in the lattice dynamics simulations, which opposes the result (2). Although the first-principles lattice dynamics of HOP is complicated and may not be completely reliable, the reason for this discrepancy might be also in the inherent limitation of INS. Here is one possible scenario. The phonon dispersion is the

energy change of a given phonon symmetry mode with phonon wavevector. The phonon mode resolution of INS is much lower compared to that of the Raman scattering as demonstrated in Fig. 3 at the  $\Gamma$  point. In addition, more phonon branches as the IR ones both LO and TO are packed closely around the Raman modes. The lattice dynamics typically yields a maximum dispersion of 2-3 meV from  $\Gamma$  to R or X points of some of the optical phonons with energies in the range 2-10 meV. The INS shows a single, relatively broad, peak at  $\sim 5$  meV that apparently represents scattering from a bundle of modes. Given these energy constraints it is possible that INS is incapable to detect a mode specific phonon dispersion in such closely packed optical modes. A comment of this possibility will be beneficial for the presentation of this work.

We thank the referee for his comment. It is indeed difficult to make definitive quantitative statements due to the numerous closely packed phonon branches. However, the neutron energy resolution is better for cold neutron than thermal neutron. Therefore, the ability to separate different phonon modes varies considerably within the full energy range. A dispersion of 2-3 meV for MA-based compounds would have been seen for the cold neutron range (typically below 15 meV) but this is indeed more problematic above 15 meV in the thermal neutron range. Finally, the phonon modes in FA-based materials are clearly broader than the instrumental resolution for the cold neutrons. The resolution is thus not the limiting factor and the interplay between branch crossing and dispersion has to be discussed more in details. We have added a few sentences on page 3 to clarify that point as suggested by the reviewer.

The result (3) is clearly presented in the manuscript supplementary note (SN). This result, however, challenges the findings in Ref. 44 where the optical phonon dispersion at RT was measured in MAPI and MAPB by means of X-ray scattering. The authors try to give energy resolution arguments for why the results in Ref. 44 may not be reliable but the same is also valid to certain degree for INS. In this connection it is important to note that the core group of authors of the current manuscript reports the observation of optical phonons in MAPB at 280 K (close to RT) in their earlier paper, Ref. 18, Fig. 4. Which result is then correct the one in this manuscript or that in Ref. 18?

We thank the referee for the careful reading of the manuscript. One major difficulty of X-ray scattering, beyond the energy resolution width, is the Lorentzian shape of the instrumental shape whereas it is Gaussian for neutron scattering. This is an important difference in order to be able to separate closely packed modes. Indeed, in ref 18, a broader phonon group was reported at  $T=280$ K around 12 meV, corresponding to what is left of the (b) bundle at higher temperature. Both datasets are consistent to each other, but the various phonon contributions were deduced in ref18 only from a numerical fitting by a superposition of damped oscillators, while phonon resonances are directly observed at 5K. We have rephrased our sentence related to ref 18, to better stress the difference between RT and 5K observations for MAPB.

I also want to note that the authors make a broadly overstated claim that "...The dispersionless nature of these optical modes implicates a glassy-like thermal conductivity, important to the hot phonon bottleneck effect in HOPs..." To my opinion this statement is not justified. It is

rather a way to emphasize the importance of the observation of dispersionless optical modes. The thermal conductivity in semiconductors and insulators as HOP is carried out mostly by acoustic phonons. In some materials and semiconductor nanostructures contribution from optical phonons might be more sizable but this is a rather specific property. In HOP, the claimed dispersionless optical phonons should not participate in the thermal conductivity merely because their group velocity is zero. It has been showed in Ref. 19 that anharmonicity softens the acoustic phonon dispersion (group velocity), which results in low thermal conductivity. The acoustic phonons and their dispersion are well measured at RT (Refs. 18 and 19). To have a glass-like thermal conductivity the authors have to show that at least the scattering of acoustic phonons by not well-defined optical phonons at RT is dominating acoustic-acoustic phonon scattering. However, if this is correct then why are the acoustic modes not overdamped ? In addition, this work shows that optical phonons are overdamped due to anharmonicity, that is, their lifetime is very short at RT. How can that be reconciled with the hot phonon bottleneck effect? Our common understanding of this effect is that optically excited hot charge carriers (not yet thermalized) relax via the Fröhlich interaction with emissions of LO polar phonons as for instance the IR modes because HOPs are centrosymmetric. In order to build up the hot phonon bottleneck one needs to suppress the LO phonon relaxation (phonon-phonon decay or scattering), which is just the opposite of what is shown in this work. A clarification or reformulation of the claim is needed.

We thank the referee to mention that point. We have rephrased the paragraph to avoid mixing speculative discussions which are found in the literature and the description of the specific features observed in this work for the optical phonons.

In summary, this work has enough merit to be further considered for potential publication in the Communication Physics, Nature, after revision. Also, I hate to point it out but some English proofreading is needed for the revised version.

We thank the referee that our work merits publication in Communications. The re-submitted manuscript has been carefully proofread.



REVIEWERS' COMMENTS:

Reviewer #1 (Remarks to the Author):

Thanks to the authors for their careful revisions; I confirm that they have addressed all of my concerns satisfactorily.

Reviewer #2 (Remarks to the Author):

Please refer to the pdf attached.

In the revised manuscript the questions and comments raised by the referee are addressed in a satisfactory way. Every scientific paper has its own inherent ambiguity due to the limitation of experimental or theoretical methods used. Notably, the experimental results in this work are presented after accounting fairly for NIS limitations.

This work is focused on the phonons in HOPs. Phonons and electron-phonon interactions are known to play a key role in the optoelectronic properties of these materials. The most significant result is the experimental demonstration of weakly dispersive optical phonons at low temperature that become overdamped above 80 K due to strong anharmonicity. Remarkably, the optical phonons do not behave as quasiparticles at room temperature in the NIS measurements, whereas acoustic phonons show well defined dispersion (their previous papers). These results will be very beneficial for the future modeling of HOP, for understanding the electron-phonon interactions, and how to improve the performance of HOP based optoelectronic devices.

In conclusion, I recommend the current manuscript for publication in the Communications Physics, Nature.