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Structural Instabilities related to Highly Anharmonic Phonons in Halide Perovskites

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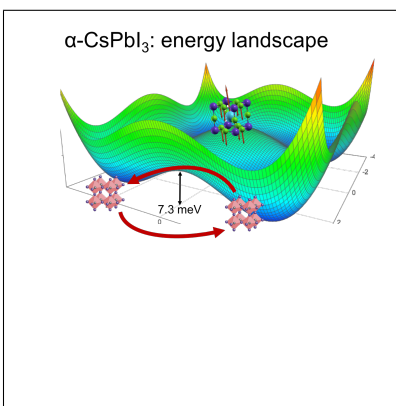
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Abstract

Hybrid organic-inorganic perovskites have emerged over the past five years as absorber layers for novel high-efficiency low-cost solar cells that combine the advantages of organic and inorganic semiconductors. Unfortunately, the physics behind the electronic transport in these materials is still poorly understood. Here, employing the linear response approach of Density Functional Theory, we reveal strong anharmonic effects in inorganic $CsPbI_3$ and a double-well phonon instability at the center of the Brillouin zone for both cubic and orthorhombic phases. Factoring these low-energy phonons into electron-phonon interactions and band gap calculations could help better understand the electrical transport properties in perovskites. Furthermore, previously reported soft phonon modes are here stabilized at the actual lower-symmetry equilibrium structure, which occur in a very flat energy landscape, highlighting the strong competition between the different phases of $CsPbI_3$. The perovskite oscillations through the corresponding energy barrier could explain the underlying ferroelectricity and the dynamical Rashba effect predicted in halide perovskites for photovoltaics.

Graphical TOC Entry



Hybrid Perovskite Solar Cells (PSCs), a new generation of solar cells which combines the advantages of organic and inorganic semiconductors, were born only a few years ago after perovskites were used as absorbing materials in dye-sensitized solar cells (DSCs).¹ After a mere 6 years of research, the efficiency of PSCs has jumped from 4% in 2009 to certified efficiencies over 20%² in 2015 and a record efficiency of 22.1%³ in 2016, becoming the first truly low-cost and highly efficient generation of solar cells.

Researchers started phonon calculations of hybrid $MAPbI_3$ perovskites as early as 2013, when Quarti *et al.*⁴ measured its Raman spectrum, assisted by Density Functional Theory (DFT) calculations which showed the importance of the torsional mode of the methylammonium cations as a marker of the orientational disorder of the material. As shown by various groups since then,⁵⁻⁷ this picture is further complicated by the reorientational dynamics of the organic component similar to what is usually observed in plastic crystals, since quasielastic neutron scattering measurements showed that dipolar $CH_3NH_3^+$ ions reorientate between the faces quite rapidly. Very recently, Whalley *et al.*⁸ and Beecher *et al.*⁹ found double-well instabilities present at the Brillouin Zone (BZ) boundary of $MAPbI_3$, much like what we report here in the $CsPbI_3$ case, as well as short phonon quasiparticle lifetimes and mean free paths. However, contrary to our findings for $CsPbI_3$, they did not find any instabilities at the center of the BZ for $MAPbI_3$. These structural effects in organohalide perovskites were studied in detail by Amat *et al.*¹⁰ who showed that the interplay of spin-orbit coupling (SOC) and octahedra tilting can have a strong impact on their electronic and optical properties, including the band gap.

It is only in the past two years that inorganic (mostly cesium-based) perovskites for photovoltaics have attracted more and more attention from the PSC community after being incorporated into complex but more stable mixed-halide mixed-cation perovskite structures (such as $[HC(NH_2)_2]_{0.83}Cs_{0.17}Pb(I_{0.6}Br_{0.4})_3$) demonstrating the feasibility of achieving above 25% efficiency four-terminal tandem cells¹¹ at the beginning of 2016.

In particular, the vibrational properties of inorganic and lead-free perovskite $CsSnI_3$

have been studied in detail using ab-initio calculations. Lora da Silva *et al.* employed¹² the quasiharmonic approximation to study the temperature-dependent lattice dynamics of the four different phases of cesium tin iodide. Patrick *et al.* reported¹³ strong anharmonic effects in $CsSnI_3$ (including soft phonon modes) using self-consistent phonon theory and frozen phonons, and showed that these soft modes were stabilized at experimental conditions through anharmonic phonon-phonon interactions between the Cs ions and their iodine cages. They further calculated the renormalization of the band gap due to vibrations. These two works demonstrate the important role of temperature in accurately analysing anharmonic perovskite materials like $CsSnI_3$.

The role of phonons in the phase transitions of perovskites containing lead and cesium was recognized long ago (e.g. $CsPbCl_3$ ¹⁴). This suggests that vibrational properties could control the structural transitions also for $CsPbI_3$, which is crucially important for most recent PSCs.

The vibrational properties of inorganic $CsPbI_3$ perovskites have not been extensively studied so far. Stoumpos *et al.* studied the dependence of $CsPbI_3$'s band gap on temperature and the reversibility of its phase changes from non-perovskite structures to perovskite structures at high temperature. They showed¹⁵ that the room temperature stable δ -phase (yellow) converts to the black perovskite α -phase upon heating above 360 °C. On cooling, the perovskite structure converts to the black perovskite β - and γ -phases at 260 and 175 °C, respectively. After a few days, a full recovery of the initial δ -phase is observed. A prediction of possible structural instabilities in $CsPbI_3$ and $RbPbI_3$ perovskite was made, on the basis of relatively high values of the Born effective charges, by Brgoch and co-workers¹⁶ ; but to the best of our knowledge it has remained a speculation until we present our results here.

In this paper, we study the vibrational properties of both the high-temperature cubic α -phase and the orthorhombic δ -phase of $CsPbI_3$, and compare them to the phonons of $MAPbI_3$'s cubic phase. For both phases, phonon spectra, derived using the linear approach of Density Functional Theory (Density Functional Perturbation Theory or DFPT), showed

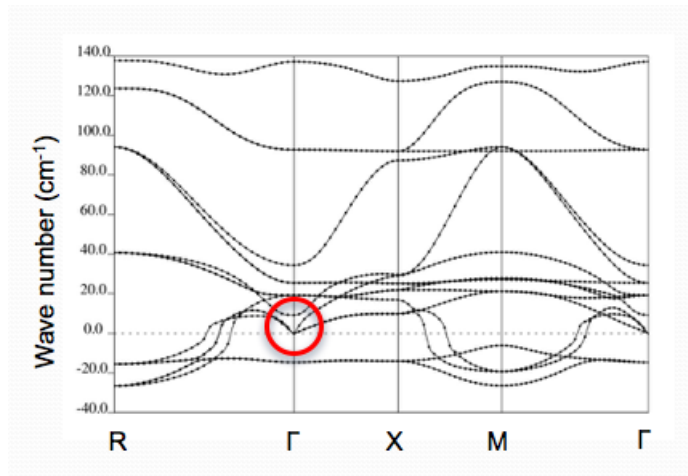
the existence of instabilities which we investigated in detail using total energy calculations along the corresponding phonon eigenvectors (frozen phonons framework). More information about the DFT and DFPT calculations can be found in the Computational Methods section at the end of the paper. Additional calculations on the influence of spin-orbit coupling on these results are also detailed in the Supporting Information file.

The phonon dispersion relations of inorganic perovskite $CsPbI_3$ in the cubic high temperature α -phase, with commonly accepted space group $Pm\bar{3}m$,¹⁷ are reported in figure 1a. The presence of soft modes at different high-symmetry points in the Brillouin zone can be explained by the fact that the α -phase is stable only at high temperature, where both energetic and entropic contributions determine the free energy F , and not at the (zero) temperature of DFT calculations. In principle, these modes are stabilized by taking into account temperature, i.e., the vibrational entropy and its contribution to the free energy.

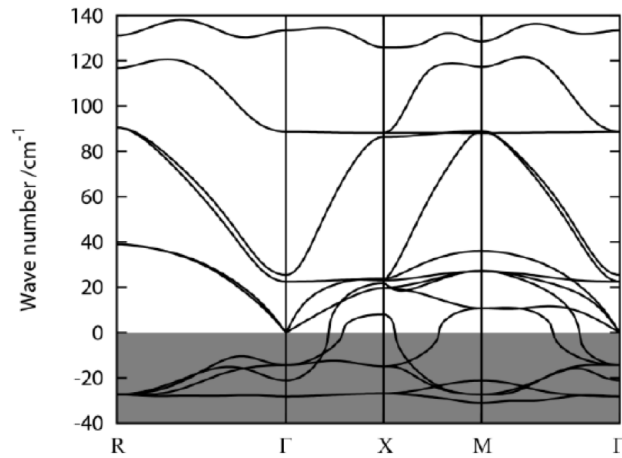
What is more surprising is the presence of imaginary modes at the Γ -point (one triply degenerated mode at -15 cm^{-1}), where one expects to find acoustic modes, linearly going to zero at Γ , as the lowest frequency modes. These instabilities and in particular this anomaly at Γ for the cubic phase of $CsPbI_3$ have already been reported by Kawai *et al.*¹⁸ (see figure 1b), but they offered no explanation or further analysis.

As circled in red on figure 1a, the Acoustic Sum Rule (ASR) was imposed in our calculations through post-processing of the dynamical matrix to ensure translational invariance. The ASR did bring back to zero the three-fold degenerated acoustic branches at the Γ -point but did not affect the soft mode, confirming its nature as an optical mode. We analyzed the dynamical matrix's eigenvector corresponding to this soft mode, and its anti-symmetrical characteristics (see figure 2) are consistent with the irreducible representations of the $Pm\bar{3}m$ symmetry group as reported by Even *et al.*⁷

The soft modes obtained here are coherent with previous neutron scattering measurements clearly indicating that the energy of the whole acoustic phonon density of states is remarkably low at 80°C .⁷ In particular, it was shown for $CsPbCl_3$ that the transverse acous-



(a) This work (very tight convergence threshold)



(b) Results from Kawai *et al.*, reprinted with permission from¹⁸ (copyright 2015 American Chemical Society)

Figure 1: Phonon modes of cubic $CsPbI_3$.

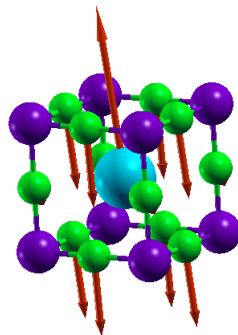


Figure 2: Displacement eigenvector corresponding to the soft phonon mode found at Γ for cubic $CsPbI_3$. Its irreducible representation is the infrared-active Γ_4^- representation. The blue, purple and green atoms respectively denote Cs, Pb and I.

tic (TA) branches always stay under 2 meV (16 cm^{-1})¹⁴ and that the optical phonons close to the R and M points also lie in the same energy range ($< 2 \text{ meV}$). Here, our calculations show instabilities of the same order of magnitude (around 20 cm^{-1}) coming from optical modes close to the M point (see figure 1a). Similar conclusions were drawn more recently for $CH_3NH_3PbI_3$ ⁹ and $CH_3NH_3PbBr_3$.¹⁹

We think that these instabilities indicate strong anharmonic effects (also confirmed by the unusually large Debye-Waller factors measured previously for $MAPbX_3$ compounds^{7,20}) and a very flat energy profile around equilibrium in $CsPbI_3$. This very flat profile could affect the reported low-to-negative frequency values in two ways: (i) by affecting the evaluation of the frequency values itself (due to numerical noise), and (ii) by preventing the structural relaxation algorithm to find the ground state structure. In order to assess these two hypotheses, we first (i) used smaller and smaller DFPT convergence thresholds and second (ii) performed frozen phonon calculations to investigate anharmonicity up to the fourth order.

The use of very tight thresholds for total energy convergence, forces during relaxations, and self-consistency of the linear response calculations (see Computational Methods section) reduced the number of imaginary phonons at Γ , but one triply degenerated soft mode remained (see figure 1a), compared to 5 as published by Kawai *et al.*¹⁸ (figure 1b).

Unfortunately the most widely-used approach to go further than the harmonic approximation and to calculate the free energy F by adding a volume (thus temperature) dependent vibrational free energy, the quasi-harmonic approximation,²¹ cannot be straightforwardly applied¹² due to the presence of these unstable phonon modes. Another technique is to guess the unstable directions using phonon eigenvectors obtained with the linear response approach of DFT. Here, we computed frozen phonon-perturbed total energies for the soft optical mode at Γ . A displacement of the form:

$$\mathbf{u}_\kappa(\eta) = \eta \cdot \mathbf{x}_{\kappa\Gamma}(\mathbf{q}_\Gamma) \quad (1)$$

was imposed on each ion κ , starting from the relaxed positions, and for various values of

the unitless displacement parameter η , where \mathbf{x} is the chosen soft mode eigenvector obtained from harmonic DFPT phonon calculations.

Using Landau theory²² and the adiabatic approximation, which assumes the electronic system instantaneously changes after new ionic positions are reached, the anharmonic energy^{14,23} as a function of displacement is given by:

$$U(\eta) = U_0 + \frac{\eta^2}{4} \hbar \omega_{\nu\Gamma}(\mathbf{q}_\Gamma) + \frac{\eta^4}{24} \Phi_{4,\nu\Gamma} + O(\eta^6) \quad (2)$$

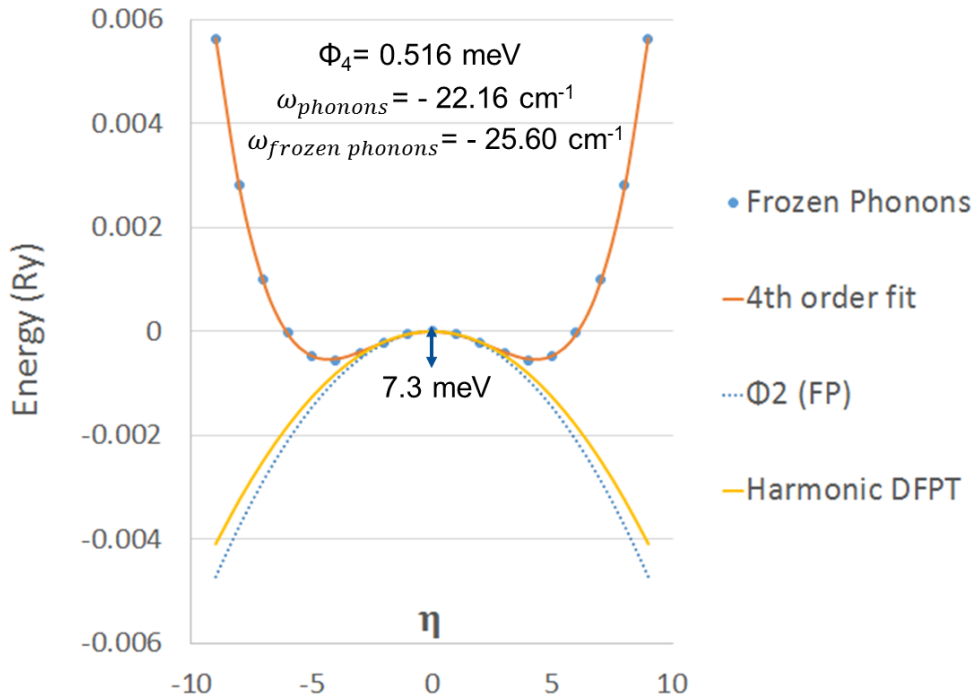


Figure 3: Potential-energy surface from frozen phonon calculations of cubic $CsPbI_3$ along the eigenvector of the unstable optical phonon at Γ as a function of displacement parameter η . The 3N dimensional displacement needed to reach the new minimum corresponds to around 0.43\AA . $\omega_{frozen\text{phonons}}$ and Φ_4 are obtained by fitting equation 2. As expected, the results show good agreement between frozen phonon and DFPT estimations of the second order coefficient (ω).

The results, shown in figure 3, fit well with this fourth-order model, confirming anharmonic effects in cubic $CsPbI_3$ and the hypothesis (ii) that we were not at the equilibrium structure. Given the very small height of the barrier (7.3 meV), we can assume that the

perovskite structure actually oscillates between both equilibrium positions. To get an idea of the order of magnitude of these oscillations, one can write:

$$\tau = \tau_0 e^{\frac{E}{k_B T}} \quad (3)$$

where k_B is the Boltzmann constant and E the energy barrier. Even if we consider, for τ_0 , the period of the lowest frequency optical phonon ($\omega \approx 17 \text{ cm}^{-1}$), this gives an oscillation timescale at room temperature of around $0.7 \cdot 10^{-12}$ s. These frozen phonon calculations are performed following the soft phonon mode and thus the new minimum here is not relaxed in volume. After volume relaxation, the energy barrier reads 8.4 meV.

The soft mode (infrared-active Γ_4^- representation, figure 2) that corresponds to the high-symmetry high-energy structure is a polar soft mode induced by the displacement of positively charged cesium ions in one direction, and the displacement of negatively charged iodine ions in the opposite direction. The oscillations of the perovskite along this polar soft mode and between the two low-symmetry equilibrium structures could explain why ferroelectricity has not been observed at a macroscopic scale in these perovskites, considering that a ferroelectric behavior is more likely induced at the scale of these fast fluctuations. Similarly, it was shown recently that for hybrid methylammonium-based perovskites, the coupled inorganic–organic degrees of freedom give rise to a spatially local and dynamical Rashba effect which fluctuates on the subpicosecond time scale typical of the methylammonium cation dynamics.²⁴ We think that the oscillations predicted here in the cubic and orthorhombic phases of $CsPbI_3$ could also be at the origin of a similar dynamical Rashba effect. Additional calculations on the dynamical Rashba effect induced by this symmetry breaking can be found in the Supporting Information file.

Performing new phonon calculations at the new (volume relaxed) equilibrium positions definitively removed the remaining soft mode (see figure 4). In conclusion, both (i) using smaller convergence thresholds and (ii) finding the actual minimum using frozen phonon calculations allowed us to investigate and abolish the soft modes at Γ for the cubic phase of

$CsPbI_3$. Similar phonon dispersions are obtained when taking into account SOC, as shown in the Supporting Information file, although caution must be observed due to the reduced band gap.

This means that this strongly anharmonic mode at Γ will not condensate at lower temperatures; it does not correspond to the transition to the yellow phase. On the contrary, the remaining phonon instabilities at the M and R points at the edge of the Brillouin zone are related to soft modes which condensate at lower temperatures to yield the β tetragonal and γ orthorhombic black phases of $CsPbI_3$.^{7,15}

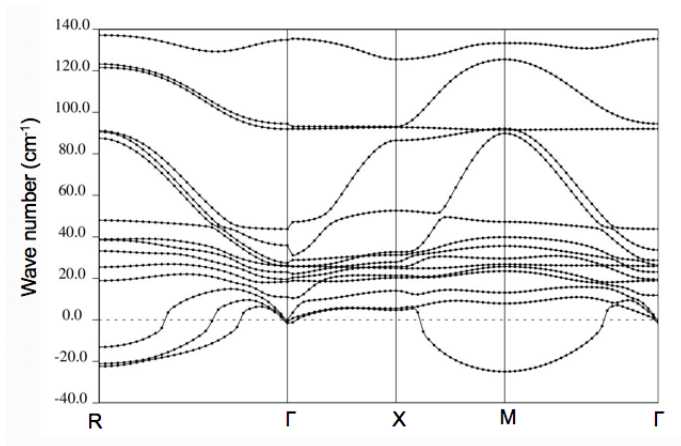


Figure 4: Phonon modes of cubic $CsPbI_3$ at the new equilibrium position determined in figure 3 after volume relaxation. Using both tight convergence thresholds and the results of our frozen phonon calculations allowed us to remove the soft modes at Γ .

The orthorhombic, yellow, low temperature, δ -phase of $CsPbI_3$ was studied experimentally quite a long time ago by Moeller²⁵ in 1959, who proposed a structure with the $Pnma$ space group. A similar $Pnma$ orthorhombic structure was obtained recently by Trots *et al.*¹⁷ in 2008 by powder diffraction studies. This structure is referred to as the yellow δ -phase and does not correspond to a simple distortion of the reference cubic perovskite lattice.²⁶ We relaxed the two structures and found a slightly lower energy for the second structure. As the difference in energy was very small, we interpolated a few configurations between them to check for a barrier, and, to our surprise, we found an even lower minimum (see figure 5), with a relatively flat energy landscape. The conclusions are the same when taking into

account spin-orbit coupling and lead semicore electrons.

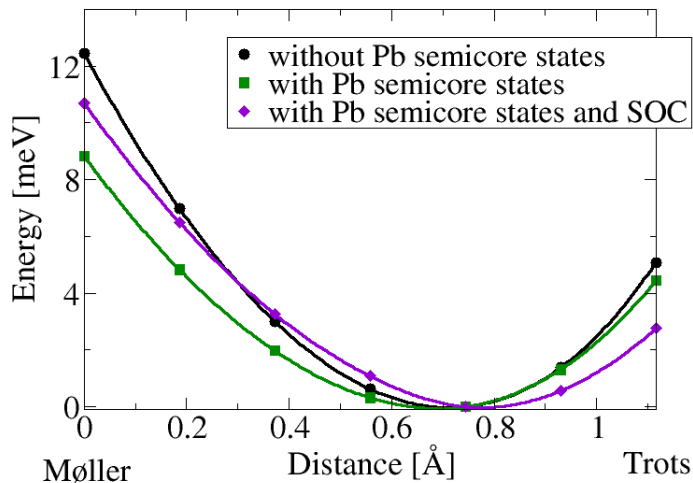


Figure 5: Equilibrium energy of $CsPbI_3$'s orthorhombic δ -phase ($T < 530K$). The 5 intermediate position sets are linearly interpolated between sets 1 ("Moeller")²⁵ and 7 ("Trots")¹⁷ which are equilibrium positions relaxed from experimental initial structures. The distance is given in 3N dimensions.

This is another signature of a possible anharmonic behavior in $CsPbI_3$. A further confirmation of this fact is that, even for the lowest energy structure of figure 5, we again found a few soft modes at the Γ -point, as shown in figure 6.

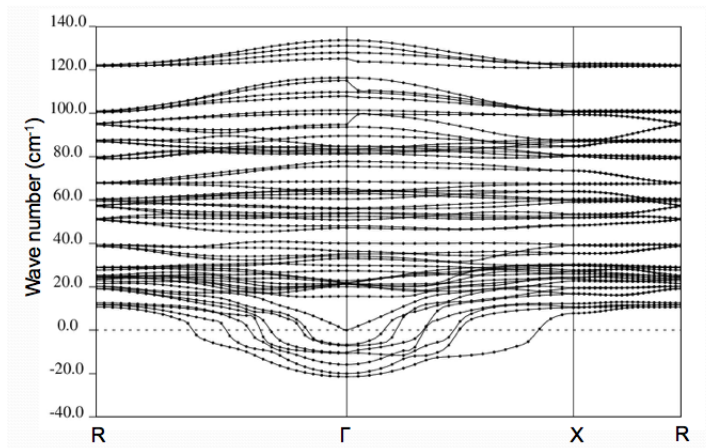


Figure 6: Phonon modes of orthorhombic δ - $CsPbI_3$ in the lowest energy structure of figure 5.

This phase being the stable phase at low temperature, we did not find any soft modes

at other high symmetry points. Similar to our work with the cubic phase, we followed the eigenvectors of the soft modes in order to explore the energy landscape. As with the cubic phase, frozen phonon calculations around the lowest energy structure of figure 5 were fitted up to the 4th order and showed (see figure 7) a similar double-well instability with a higher potential barrier (124 meV, meaning an oscillation time of around $0.6 \cdot 10^{-10}$ s at room temperature) and once more a good agreement between frozen calculations and DFPT on the second order coefficient. We recall that these frozen phonon calculations are performed following a soft phonon mode and thus that the new minimum here is not relaxed in volume. After volume relaxation, the energy barrier reads the much higher value of 2.39 eV. We think that this very significant difference could be the sign of a strong ferroelasticity in the δ -phase of $CsPbI_3$.

As in the cubic case, phonons were re-calculated at the (volume-relaxed) new equilibrium positions and all the soft modes at Γ were eliminated (see figure 8). This stable structure has a lower symmetry than the $Pnma$ space group and, as such, does not match with the black γ -phase described by Stoumpos,¹⁵ nor with the structure of the γ -phase of $CsSnI_3$.²⁷

We then compared the vibrational properties of the inorganic $CsPbI_3$ to those of $MAPbI_3$. The phonon spectrum of the pseudocubic phase of the hybrid perovskite $MAPbI_3$, obtained similarly using DFPT calculations, did not show any soft modes at Γ (figure 9). This spectrum also differs significantly as it contains high-frequency optical modes around 3000 cm^{-1} which are the signature of the MA^+ organic molecule vibrations.

This could suggest that $MAPbI_3$ behaves noticeably more harmonically than $CsPbI_3$. However, as shown very recently,^{8,9} this is due to the fact that symmetry breaking is facilitated by the presence of the organic molecule, but a similar behavior, with a double well potential around the most symmetric structure, is also present in $MAPbI_3$. This double well instability was found at the edge of the BZ (M and R points) and not at the Γ point. The barrier was reported to be somewhat higher, between 0.02 and 0.04 eV. Furthermore, we think that our simulation here is not able to capture the dynamical translation-rotation

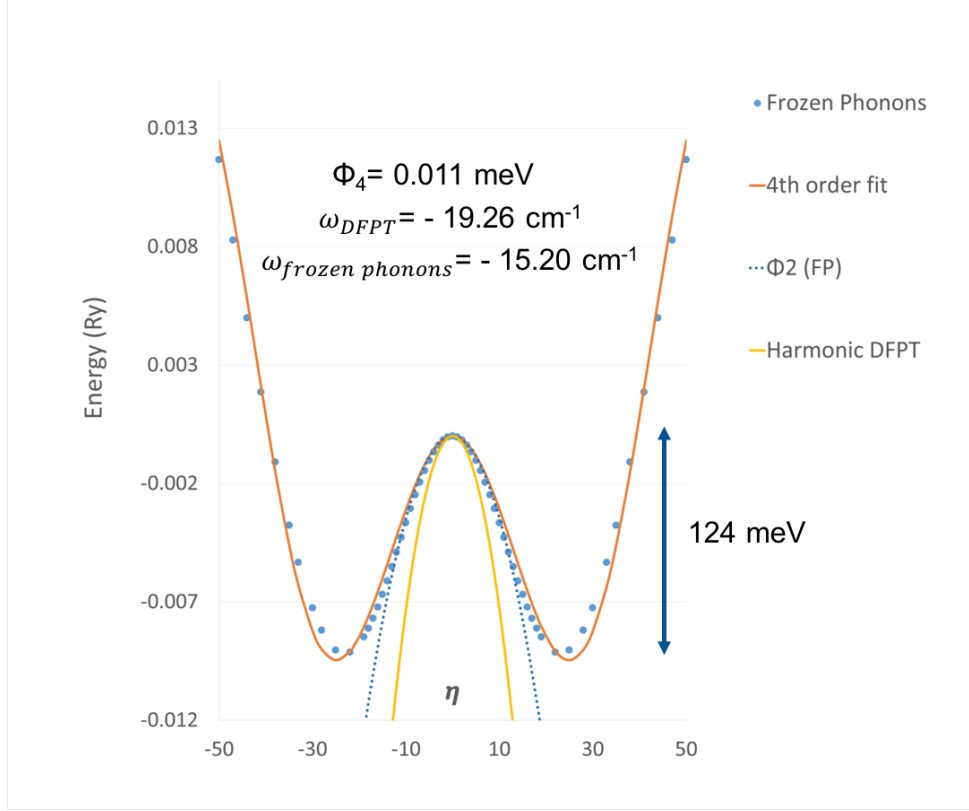


Figure 7: Potential energy surface from frozen phonon energy calculations of orthorhombic δ - $CsPbI_3$ along the eigenvector of the lowest soft phonon at Γ as a function of displacement parameter η . The 3N dimensional displacement needed to reach the new minimum corresponds to around 2.2\AA . $\omega_{frozen\text{phonons}}$ and Φ_4 are obtained by fitting equation 2. The results show good agreement between frozen calculations and DFPT on the second order coefficient (ω).

coupling (recently experimentally observed¹⁹) which may yield further contribution to the anharmonicity of the phonon modes in $MAPbI_3$.

To summarize, through energy landscape and phonon calculations for the inorganic perovskite $CsPbI_3$ we reveal that the assumed equilibrium structure of the high-temperature α -phase, of space group $Pm\bar{3}m$, results from a dynamical average between lower symmetry configurations in a very flat energy landscape.

For the orthorhombic low-temperature phase, similarly, we find a rather flat energy landscape between the two experimentally proposed variants of the yellow δ -phase, a lower symmetry equilibrium configuration and double well potentials with energy barriers on the order

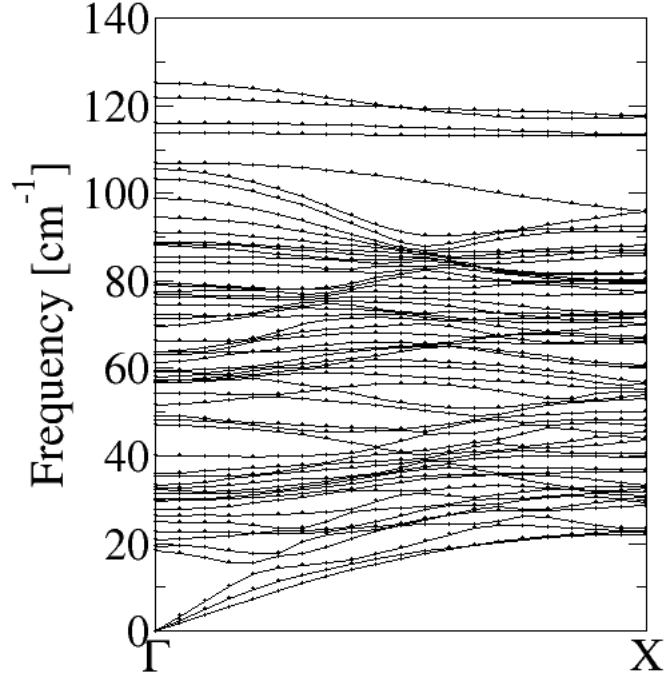


Figure 8: Phonon modes of orthorhombic $\delta\text{-CsPbI}_3$ at the new equilibrium position determined in figure 7 after volume relaxation. Using both tight convergence thresholds and the results of our frozen phonon calculations allowed us to remove the soft modes at Γ .

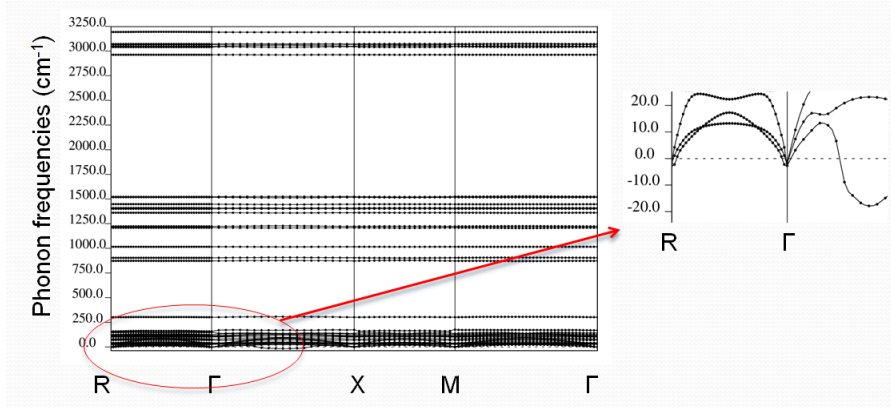


Figure 9: Phonon frequencies of pseudocubic MAPbI_3 .

of a tenth of an eV around it.

As for the hybrid MAPbI_3 perovskite, translation-rotation coupling of the organic molecule needs to be considered in order to fully investigate its anharmonicity.

These findings highlight the strong competition between the yellow δ -phase and the black $\alpha/\beta/\gamma$ -phases, and suggest that the cation network suffers from dynamical disorder even at

relatively low temperature. The unrealized ferroelectricity in these perovskites could be replaced by the polar structural fluctuations we report here, also leading to a dynamical Rashba effect as previously proposed for similar perovskite structures.^{24,28,29} Since SOC almost closes the electronic band gap for the α -phase, the calculation of phonon frequencies close to the metallic transition might well be affected by numerical instabilities (see Supporting Information). The effect of spin orbit coupling on the vibrational properties of halide perovskites, both organic and inorganic, will certainly be of high interest in future studies.

Further work is needed to take into account these low-energy highly occupied phonon states in order to give new theoretical estimates of electronic and optical properties (e.g. the band gap or the exciton binding energy³⁰) and to improve electron-phonon coupling calculations. Indeed, electron-phonon coupling was shown to deeply impact the charge-carrier mobilities^{31,32} in these perovskites. Mixing Cs with other cations, like the organic ones used in most recent versions of hybrid PSCs, affects the coupling in the double-well network, which could help explain the mechanisms through which mixed-cation PSCs have shown interesting improvements in efficiency and stability with respect to *MAPbI₃*-based perovskite solar cells.

Computational Methods

Electronic-structure calculations were performed within the Density-Functional Theory (DFT)^{33,34} framework, as implemented in the Quantum Espresso code.³⁵

All total energy and force calculations in this work were performed with the Local Density Approximation (LDA), expanding the wave functions in a plane-wave basis set. Unless otherwise specified, non-relativistic (scalar-relativistic for Pb) and norm-conserving pseudopotentials were used, with the Cs $[5s^25p^66s^1]$, I $[5s^25p^5]$ and Pb $[5d^{10}6s^26p^2]$ electrons treated as valence states. We also performed additional calculations with fully relativistic US pseudopotentials (for Pb) and PAW (Cs and I) datasets (with the same number of va-

lence electrons as in the scalar case) in order to check the influence of spin-orbit coupling (see results in the Supporting Information file). These relativistic pseudopotentials were generated using the PS Library 0.2.2.³⁶

Plane-wave cutoffs of 70 Ry (*CsPbI₃*) and 80 Ry (*MAPbI₃*) were used. The Brillouin zone (BZ) was sampled with Γ -centered Monkhorst-Pack meshes³⁷ with subdivisions of α -*CsPbI₃*: 8x8x8; δ -*CsPbI₃*: 10x5x3 and *MAPbI₃*: 8x8x8.

Phonon calculations were performed using the linear response approach of DFT, as known as DFPT (Density-Functional Perturbation Theory),²¹ as implemented in the Quantum Espresso code.³⁵ High-frequency dielectric tensors and Born effective charges were calculated with the linear response and used to calculate long range contributions to the dynamical matrices at Γ . All phonon dispersions were performed using at least 5 q-points/ \AA^{-1} in each direction.

In order to eliminate some of the soft phonon modes, very tight convergence thresholds of 10^{-4} Ry/bohr for the force calculations and 10^{-14} for the phonon self-consistent algorithm were used.

Author Information

Notes

The authors declare no competing financial interest.

Biographies

Arthur Marronnier is a Ph.D. candidate at Paris-Saclay University within Ecole Polytechnique Graduate School. After completing his undergraduate studies and a Master of Science in Solid State Physics from École Polytechnique in Paris (France), he pursued another Master of Science at Stanford University in California in order to specialize in hybrid photovoltaics (within Pr. McGehee's group), followed by an advanced graduate degree in Public Policy

for Renewable Energies. Arthur earned a PhD grant from the French Department of Energy (IPEF, state engineer) and started his PhD in the LPICM lab of Ecole Polytechnique in 2015. His current research is focused on anharmonicity, instabilities and oxygen defects in halide perovskites for photovoltaics.

Heejae Lee is a Ph.D. candidate at Paris-Saclay University within Ecole Polytechnique Graduate School. He joined LPICM and Prof. Bonnassieux's group after completing a dual master course between Kyung-Hee University (KHU), Korea and Ecole Polytechnique, France. Prof. Jin Jang and Prof. Bonnassieux were the supervisors of his master course. His current research is focused on the electrical transport and aging characteristics of hybrid perovskite thin films.

Bernard Geffroy is currently a research engineer at CEA Saclay (Paris-Saclay University, France) in the Laboratory of Innovation in Surface Chemistry and Nanosciences (LICSEN). He graduated from CNAM (Engineer in physical chemistry), Paris 1987. His current research interests are OLEDs, OPVs (design, fabrication and characterization) and organic/inorganic hybrid photovoltaics (SiNWs, ZnO nanostructures, hybrid perovskite). He is the author or co-author of 120 publications in international scientific journals, 1 chapter book and 5 patents. He is an Editor of The European Physical Journal Applied Physics (EPJAP).

Yvan Bonnassieux is currently a Professor at Ecole polytechnique (Paris-Saclay University, France) and deputy manager of the LPICM laboratory (laboratory of the interface and thin Layers physics). Former student of the ENS of Cachan, he received his PhD in 1998 and HDR in 2011. His current research themes include compact modelling, design and characterization of components and circuits of organic and large area electronics. He was also an invited professor at Columbia University in 2015. He is the author or joint author of more than 80 publications in scientific magazines, 120 communications in international conferences and 4 patents.

Jacky Even has been full Professor at INSA Rennes engineering school since 1999. He

received a PhD in Physics from the University of Paris VI in 1992. He was assistant professor at the Physics Department of Rennes University (1992–1999), where he gained broad experience in phase transitions and solid-state chemical reactions in molecular materials, using theoretical and experimental approaches: neutron and X-ray scattering, Raman/FTIR spectroscopy, calorimetry, among others. In 1999, he created FOTON laboratory’s simulation team, to address fundamental questions on semiconductors at the atomistic level as well as to perform optoelectronic device simulations. Besides hybrid perovskite materials and colloidal nanoplatelets, his theoretical activity is now dedicated to semiconductor nanostructures, photovoltaic and light-emitting (LED, laser, ...) devices for silicon photonics, and optical telecommunication.

Guido Roma is a research-engineer at Service de Recherches de Métallurgie Physique (SRMP), CEA-Saclay (Paris-Saclay University, France). After graduating from the University of Modena and receiving a PhD at the University of Rome Tor Vergata (Italy), he spent four years at CECAM (Centre Européen de Calcul Atomique et Moléculaire, Lyon, France) before joining SRMP in 2000. He holds a habilitation from the University of Paris VI (2012). His main experience is on point defects thermodynamics and kinetics, starting from a first principles description of electronic and vibrational properties, with a focus on insulators and semiconductors. His interests range from irradiation effects on materials for nuclear applications to functional materials for energy, in particular photovoltaics, a field in which he got involved during a stay at the University of Mainz (Germany) between 2011 and 2014.

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Supporting Information Available

The following files are available free of charge.

- SI.pdf: This Supporting Information file is devoted to presenting some checks that we made in order to show that some of the approximations used in this paper do not affect its conclusions. In particular, most of the results presented in the paper have been obtained by neglecting spin-orbit coupling.

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