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Anharmonicity and Disorder in the Black Phases of CsPbI₃ used for Stable Inorganic Perovskite Solar Cells

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Abstract — Hybrid perovskite materials have emerged over the past five years as absorber layers for new high-efficiency yet low-cost solar cells (PSCs) that combine the advantages of organic and inorganic semiconductors. Here, employing the linear response (DFPT) approach of Density Functional Theory (DFT) and frozen phonon calculations, we reveal strong anharmonic effects in the inorganic CsPbI₃ perovskite. We also show through high resolution in-situ synchrotron XRD measurements that CsPbI₃ can be undercooled below its transition temperature and temporarily maintained in its perovskite structure down to room temperature, stabilizing a metastable perovskite polytype (black γ -phase) crucial for photovoltaic applications. Among the four phases of CsPbI₃, we found that this phase is the only one to behave harmonically around equilibrium. Last, we explain the Rashba effect in these materials as a consequence of the symmetry breaking induced by the double-well instabilities.

I. INTRODUCTION

A new generation of solar cells combining the advantages of organic and inorganic semiconductors, hybrid Perovskite Solar Cells (PSCs) saw the light of day a few years ago when they were for the first time used as absorbing materials in dye-sensitized solar cells (DSCs) [1]. After only 6 years of research, PSCs have jumped from that first 4% efficient cell in 2009 to devices with certified efficiencies over 20% [2] in 2015, becoming the first truly low cost and highly efficient generation of solar cells.

The recent report of a 13.4% efficient cesium lead iodide perovskite quantum dot solar cell [3] has demonstrated that purely inorganic perovskite solar cells have definitively become a stable and efficient alternative to their hybrid cousins. In particular, the vibrational properties of the inorganic and lead-free perovskite CsSnI₃ have recently been studied in detail using ab-initio calculations. Walsh *et al.* employed [4] the quasiharmonic approximation to study the temperature-dependent lattice dynamics of the four different phases of CsSnI₃. Thygesen *et al.* reported [5] strong anharmonic effects in CsSnI₃ (including soft phonon modes) using self-consistent phonon theory and frozen phonons, and showed that these soft modes were stabilized at experimental

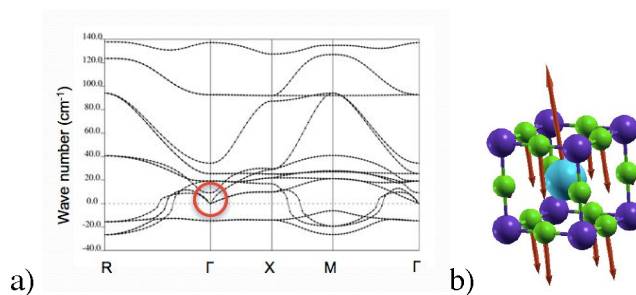
conditions through anharmonic phonon-phonon interactions between the Cs ions and their iodine cages. These works demonstrate the important role of temperature in accurately describing anharmonic perovskite materials such as CsSnI₃. In this paper, we study the vibrational properties and the energy landscape [6] of all four phases of CsPbI₃, including a tetragonal phase that has never been reported before [7].

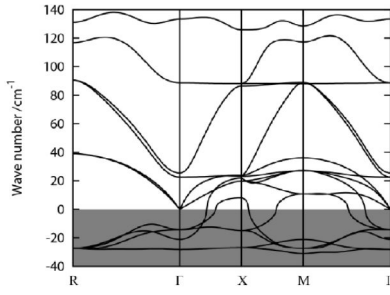
II. RESULTS

A. Case study: cubic CsPbI₃

The phonon spectrum of inorganic perovskite CsPbI₃'s cubic phase is reported Fig. 1a. The linear response (DFPT) approach of Density Functional Theory (DFT) is used with NR-NC pseudopotentials and the LDA approximation. The presence of soft modes at different high-symmetry points in the Brillouin zone can be explained by the fact that the cubic phase is stable only at high temperature, where both energetic and entropic contributions determine the free energy F . In theory, anharmonic stabilization of these unstable modes occurs with taking into account temperature (entropy) effects.

What is more surprising is the presence of imaginary modes at the Γ k-point, where one expects to find analytic acoustic modes as the lowest frequency modes. The dynamical matrix's eigenvector corresponding to this soft mode is anti-symmetrical (see Fig. 1b), consistent with the irreducible representations of the Pm3m symmetry group [8].





c) Fig. 1. Phonons modes of cubic CsPbI₃. a) Results of this work (using very tight convergence thresholds). b) Displacement eigenvector corresponding to phonon soft mode found at Γ . The blue, purple and green atoms respectively denote Cs, Pb and I. c) Results from Kawai *et al.* [9].

These instabilities and in particular this anomaly at Γ for the cubic phase of CsPbI₃ have already been reported by Kawai *et al.* [9] (see Fig. 1c), but they provided no explanation or further analysis. These results are however coherent with neutron scattering measurements [8] clearly indicating that the energy of the whole acoustic phonon density of states is remarkably low at 80 °C.

We think that these instabilities indicate strong anharmonic effects (also confirmed by the unusually large Debye-Waller factors measured previously [8]) and a very flat energy profile around equilibrium in CsPbI₃. This very flat profile could affect the reported low-to-negative frequency values in two ways: (i) by affecting the numerical evaluation of the frequency values itself, and (ii) by making it harder for the program to relax to the proper energy minimizing structure. In order to assess these two hypothesis, we first (i) used smaller and smaller DFPT convergence thresholds and second (ii) performed frozen phonon calculations to investigate anharmonicity up to the forth order. The use of smaller convergence thresholds (phonon scf threshold of 10^{-14} instead of 10^{-12}) allowed us to eliminate many negative modes at Γ compared to Kawai *et al.*'s work [9] (Fig. 1c).

Frozen phonon-perturbed bands were computed for the soft mode at Γ . A displacement of the form:

$$\mathbf{u}_\kappa(\mathbf{R}, \eta) = \eta \cdot e^{i\mathbf{q}_\Gamma \cdot \mathbf{R}} \mathbf{r}_{\kappa\nu\Gamma}(\mathbf{q}_\Gamma) \quad (1)$$

was imposed on each ion κ , starting from the relaxed positions, and for various values of the unitless parameter η , where \mathbf{q}_Γ is the reciprocal point and \mathbf{R} the corresponding eigenvector obtained from DFPT phonon calculations.

Within the adiabatic approximation the electronic system instantaneously changes after new ionic positions are reached, and the anharmonic energy is given by:

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

The results, shown on Fig. 2, fit well with this forth-order model, confirming anharmonic effects in cubic CsPbI₃ and the hypothesis (ii) that we were not at the equilibrium structure.

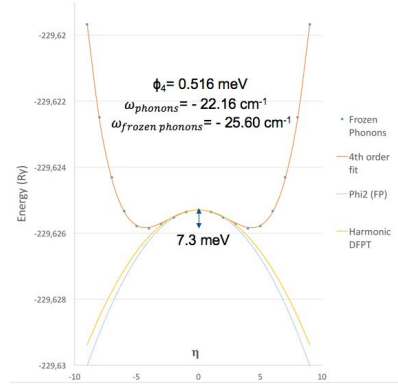


Fig. 2. Frozen phonon energy calculation of cubic CsPbI₃ for the soft eigen mode at Γ versus the displacement parameter η . The maximum displacement ($\eta = 10$) corresponds to around 0.8 Å. ω_{phonons} and ϕ_κ are obtained by fitting the energy with equation 2.

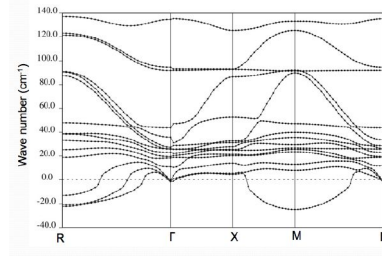


Fig. 3. Phonons modes of cubic CsPbI₃ at the new equilibrium position determined in Fig. 2. Using both a tight convergence threshold and the results of our frozen phonon calculations allowed us to remove the soft modes at Γ .

Given the very small height of the barrier (7.3 meV), we can assume that the perovskite structure actually oscillates between both equilibrium positions under temperature effects. Performing new phonon calculations at the new equilibrium positions definitely removed the remaining soft mode (see Fig. 3). As a conclusion, both (i) using smaller DFPT convergence thresholds and (ii) finding the right minimum thanks to frozen phonon calculations allowed us to investigate and abolish the soft modes at Γ for the cubic phase of CsPbI₃.

As for the orthorhombic δ -phase of CsPbI₃, similar methods were applied since we also found soft modes at Γ . We found a higher potential barrier (140 meV) and once more a good agreement between frozen calculations and DFPT on the second-order coefficients. Similar to the cubic case, the soft modes at Γ were successfully eliminated [see Ref. 6].

B. Black-phases of CsPbI₃

Our SXRD data shows that CsPbI₃ can be undercooled below its transition temperature and temporarily retain its

perovskite structure down to room temperature as shown by high resolution synchrotron X-ray diffraction (figure 4), using an in-situ experimental setup. The structural analysis confirms the change of the yellow phase (α -phase) to its black polytype (α -phase) on heating but upon cooling the perovskite does not return to its original yellow phase immediately. Instead, CsPbI₃ adopts the metastable perovskite polytype on cooling back to room temperature, revealing a phase transition pathway reminiscent of CsSnBr₃ and CsSnI₃, where the high symmetry cubic phase (α -phase) distorts initially to a tetragonal phase (β -phase) followed by a further change to the orthorhombic (γ -phase) which persists down to room temperature.

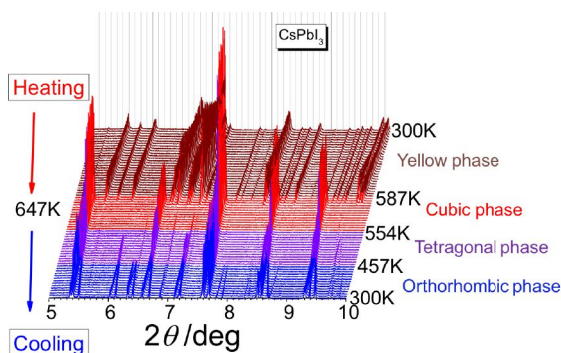


Fig. 4. SXR D spectra for CsPbI₃. The original yellow phase, converts to the black phase upon heating, but does not return to the original structure upon cooling [7].

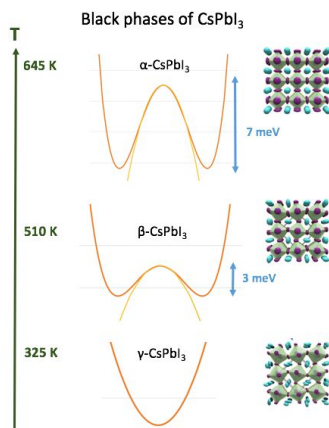


Fig. 5. Potential energy surface obtained from frozen-phonon calculations for the 3 (experimentally determined by SXR D) black-phases of CsPbI₃ [7].

Using this new experimental data, we lead the same frozen-phonon analysis on the β - and γ -phases. The results are

summarized on figure 5: out of the 4 phases of CsPbI₃, the γ -phase is the only one to behave harmonically. A symmetry-based tight-binding model, validated by self-consistent GW calculations including spin-orbit coupling, affords further insight into their electronic properties, with evidence of Rashba effect for both cubic and tetragonal phases when using the symmetry breaking structures obtained through frozen phonon calculations [see Ref.7].

IV. CONCLUSION

We have found a way to obtain a phonon spectrum free of abnormal soft modes of CsPbI₃, using tight convergence thresholds and frozen-phonon calculations. Our results highlight the anharmonic behavior of CsPbI₃, showing that this perovskite structure can oscillate between two equilibrium states at room temperature for 3 of its 4 phases, including a tetragonal phase that we experimentally evidence for the first time. Avoiding the anharmonic order-disorder entropy term of the non-perovskite yellow δ -phase is key in order to keep CsPbI₃ in its black phase at room temperature.

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