

Supporting Information:

Structural Instabilities related to Highly Anharmonic Phonons in Halide Perovskite

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Introduction

This supporting information file is devoted to presenting some checks we made in order to show that 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.

Spin Orbit Coupling

Energy landscape

Spin-Orbit Coupling (SOC) is known to significantly affect the electronic band structure of lead halide perovskites. However our calculations suggest that its influence on the complex energy landscape of CsPbI₃, which is the subject of this paper, is not crucial. We have performed calculations with SOC using the PWSCF code of the QE package, with fully relativistic pseudopotentials obtained with the earlier 0.2.2 version of the pseudopotential library.¹ The relativistic pseudopotentials used have the same number of valence electrons as the scalar relativistic ones used for calculations without SOC (i.e., 9 for Cs, 7 for I, and 14 valence electrons for Pb).

First, as we have shown in the main paper, the energy landscape between the two proposed structures of the orthorhombic δ -phase, as shown in figure 5 of the article, is hardly affected by SOC. Furthermore, we present here below the comparison of the energy profiles of figures 3 and 7 with and without SOC.

The profiles shown in figures 3 and 7 of the main text, as well as in figure 1 here, are obtained from the equilibrium lattice parameter of the symmetric structure, for which the soft phonon eigenmode was calculated. As such, the non-symmetric structures have non-zero pressure. In order to check the pressure when taking into account SOC, we show in figure 2 the comparison of calculated pressures along the phonon profile for the orthorhombic struc-

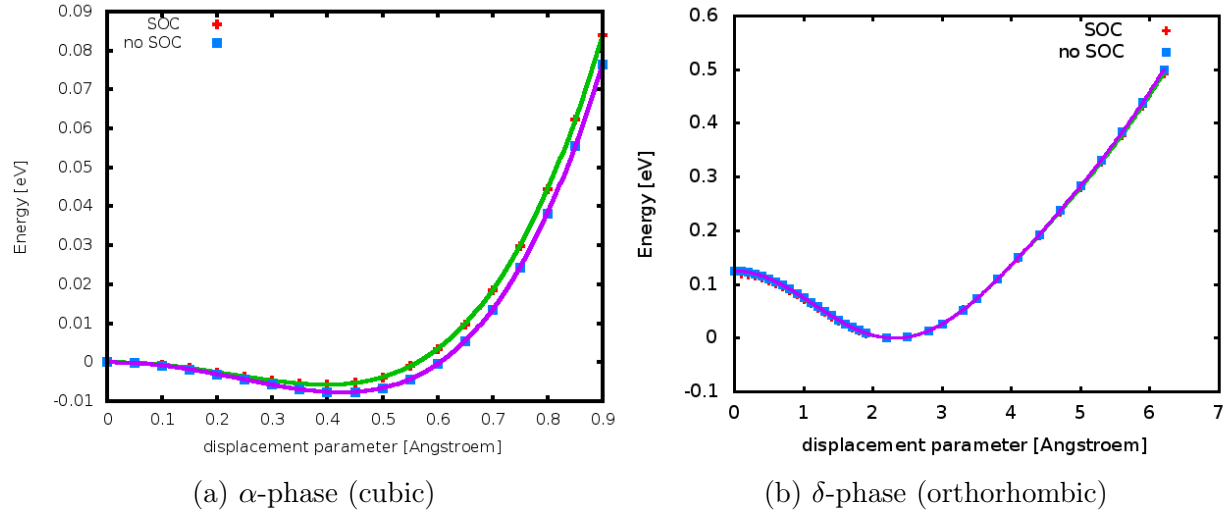


Figure 1: Energy profiles along soft phonon modes described in the main text as obtained with and without SOC. The abscissa is the distance in $3N$ dimensions (N =number of atoms). Lines are splines interpolations.

ture. We noticed that the pressure is much lower in the cubic phase than in the orthorhombic one, which could be ferroelastic.

Rashba splitting

As predicted for $MAPbI_3$, SOC induces Rashba splitting, making the band gap indirect.²⁻⁵ This is a consequence of the pseudocubic symmetry, associated to the presence of the organic molecule, as well as the strong spin-orbit coupling due to the Pb $6p$ states. The α -phase of $CsPbI_3$ is supposed to be cubic, with space group $Pm\bar{3}m$, and as such no Rashba splitting is expected. However, as a consequence of the instability that we have unveiled by following a soft mode eigenvector, the actual minimum indeed breaks the symmetry and allows for a dynamical Rashba splitting. We show in figure 3 that a significant Rashba splitting occurs at the true minimum of the now pseudocubic structure (corresponding to the minima of figure 3 from the main article), not only in the conduction band (as predicted for $MAPbI_3$) but also in the valence band.

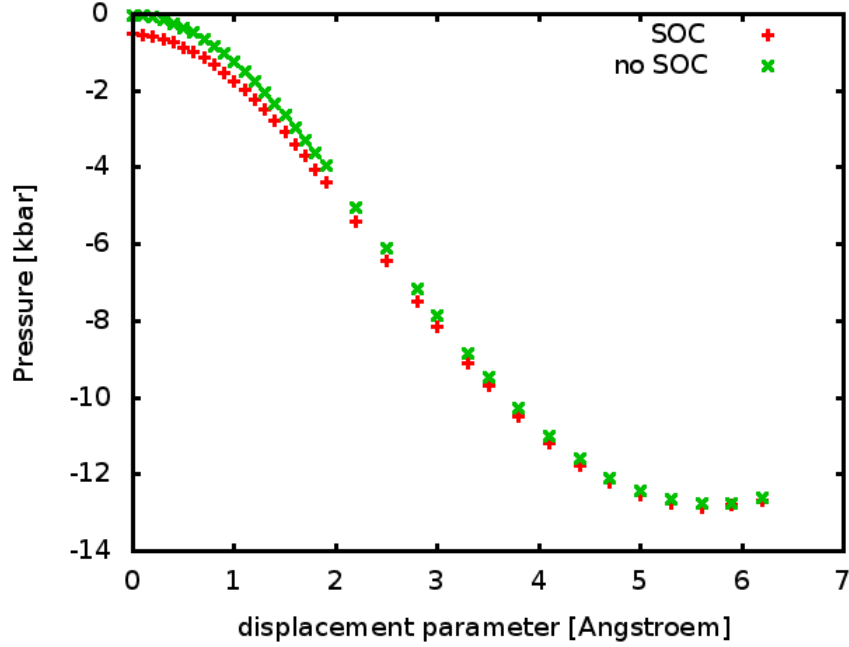


Figure 2: Pressure of calculated structures along the soft phonon eigenmode of the orthorhombic δ -phase with and without SOC.

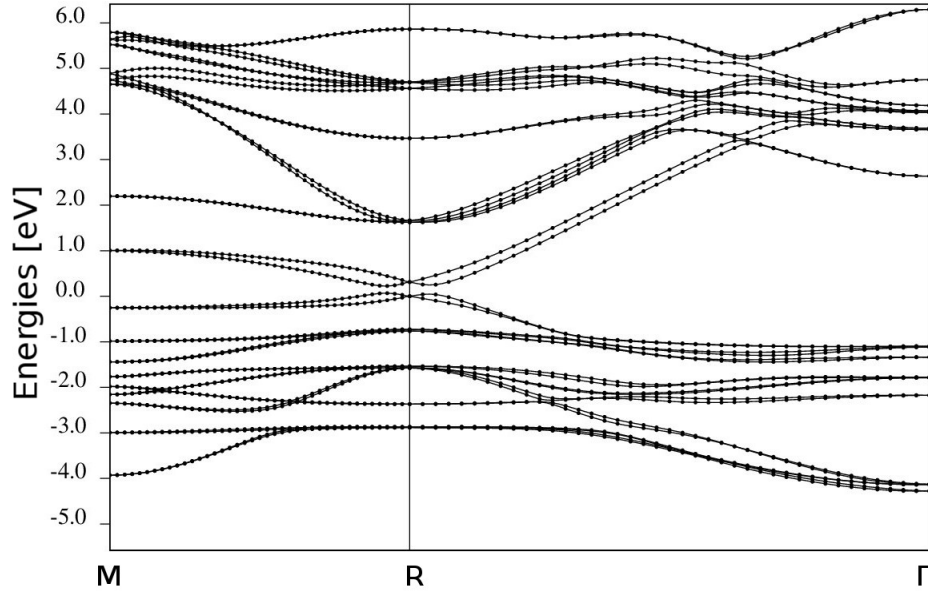


Figure 3: Band structure of distorted α -CsPbI₃ (the minimum of the energy profile in figure 3 of the main paper) along the M-R- Γ path in the BZ with SOC. Rashba splitting at the R-point occurs both in the valence and conduction bands.

Phonon frequencies

In this section we present some results for phonon modes calculated with spin orbit coupling. In figure 4 the dispersion relations for the cubic α -phase in the fully relaxed structure obtained from the minimum of figure 1a are presented. The branches are quite close to those obtained without SOC, with the exception that we still have a slightly negative eigenvalue at the Γ -point. We think that this might be an artifact coming from the electronic structure.

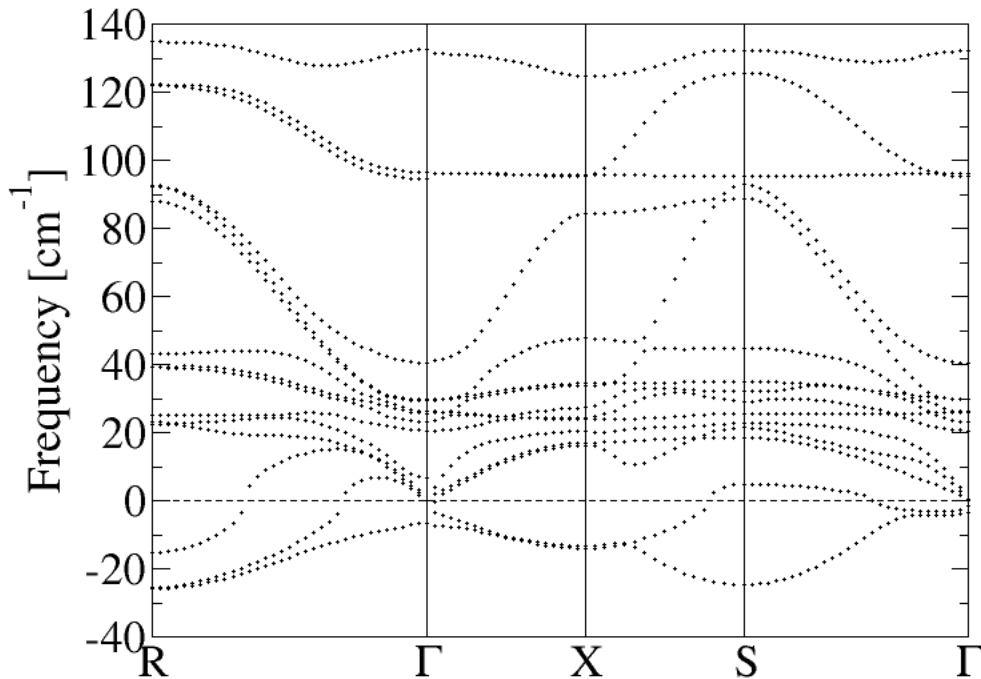


Figure 4: Phonon dispersions of the cubic α -phase of CsPbI_3 obtained with calculations including SOC.

The reader might have remarked, in the previous section, that taking into account SOC almost closes the electronic band gap for the α -phase. This known fact^{2,6} is probably affecting the phonons at Γ , where the enforcement of the acoustic sum rule is crucially dependent on the dielectric tensor and the Born effective charges. Close to the metallic transition, the calculation of these second derivatives of the energy might well be affected by numerical instabilities.

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.

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