Anharmonicity and Ultra-Low Thermal Conductivity in Lead-Free Halide Double Perovskites

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The lead-free halide double perovskite class of materials offers a promising venue for resolving issues related to toxicity of Pb and long-term stability of the lead-containing halide perovskites. We present a first-principles study of the lattice vibrations in C82AgBiBr6, the prototypical compound in this class, and show that the lattice dynamics of C82AgBiBr6 is highly anharmonic, largely in regards to tilting of AgBr6 and BiBr6 octahedra. Using an energy and temperature dependent phonon spectral function, we then show how the experimentally observed cubic-to-tetragonal phase transformation is caused by the collapse of a soft phonon branch. We finally reveal that the softness and anharmonicity of C82AgBiBr6 yield an ultra-low thermal conductivity, unexpected of high symmetry cubic structures.

Lead halide perovskites, which have emerged as one of the most promising and intensively studied class of semiconductors for optoelectronic applications[1–3], are extremely anharmonic materials[4–8]. The atomic dynamics in these APbX3 systems, where A is either Cs or an organic cation such as methylammonium (MA) or formamidinium (FA) and X = F, Cl, Br or I, is highly complex, with large observed differences between local and average structures [6, 9–11]. These systems typically have low frequency, often unstable, octahedral tilting modes and complex anharmonic movements of the A site ion, in particular related to the rotational dynamics of the organic molecule [6]. This complex atomic motion has a large impact on electronic properties through a strong electron-phonon interaction [12–14] and thus becomes highly influential on the optoelectronic performance of these materials.

The so-called lead free halide double perovskites (HDP) [15, 16], where the divalent Pb2+ cations are replaced by pairs of mono- and trivalent cations such as Ag+, Bi3+, and In3+, are envisioned to solve crucial issues of the single lead halide perovskites relating to poor long-term stability and the presence of toxic Pb. Unfortunately, they typically have bandgaps that are larger-than-optimal for photovoltaic applications [17]. There is, however, a vast chemical space within this class of materials which can be explored in attempts to tune crucial properties. The electron-phonon coupling appears to be strong in these systems [18, 19], which makes a thorough characterization of the nature of the anharmonic lattice vibrations highly desirable also in these materials.

Generally, the tendency towards octahedral tilting instabilities of the aristotype cubic perovskite structure can be understood in terms of an undersized A site cation, as can be quantified by the Goldschmidt tolerance factor [20]. The phase transformations from lower symmetry structures, with tilted octahedra, to the cubic perovskite structure of the single lead halide perovskites has proved to be complex, with tilts of the octahedra away from their high symmetry setting locally present even above the apparent phase transformation temperatures [9–11].

In the lead-free HDPs, this tendency towards octahedral tilting instabilites remains largely unexplored. While a few HDPs have been shown to be dynamically unstable at 0 K and subsequently stabilized by anharmonic phonon-phonon interactions at room temperature [21], the underlying nature of the anharmonicity and its consequences remain unknown. Furthermore, it was very recently experimentally demonstrated that the prototypical lead free HDP C82AgBiBr6 has a cubic-to-tetragonal phase transformation at TC ≈ 122 K upon cooling [22], which lacks a theoretical description.

In this Letter, we thoroughly investigate the nature of the lattice vibrations in C82AgBiBr6 from first principles. We demonstrate that its lattice dynamics is highly anharmonic even at room temperature, and that the nature of this anharmonicity is qualitatively different from that in the single halide perovskites. The octahedral tilting potential energy surfaces (PESs) of C82AgBiBr6, in contrast to the single perovskite halide analogous, are very flat, which results in a qualitatively different nature of the dynamics of these octahedra. We fit an effective Hamiltonian from ab initio molecular dynamics (AIMD) and demonstrate that this high anharmonicity necessitates the use of terms up to the 4th order in atomic displacements for an accurate description. We next show how the collapse of a soft zone-center phonon reproduces the experimentally observed phase transformation. Finally, we demonstrate that the softness and anharmonicity of C82AgBiBr6 results in an ultra-low lattice thermal conductivity, with a non-conventional ∼T−0.5 temperature dependence.

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FIG. 1. (a) Illustration of the cubic double perovskite crystal structure of Cs$_2$AgBiBr$_6$. (b) View along the out-of-phase tilting axis of the low temperature tetragonal, a$^-$$b^+$$c^0$, phase. Light green and brown spheres represent Cs and Br ions, respectively, while the Bi and Ag ions are located at the centers of pink and gray octahedra, respectively. (c) Static harmonic phonon dispersion relation and (partial) density of states (DOS) of Cs$_2$AgBiBr$_6$. Negative numbers denote imaginary frequencies. (d) 1D potential energy surface (PES) of three different octahedral tilting modes (see text for details), the inset is a zoom in of the low-energy part of the PES. (e) and (f) 2D a$^-$$b^+$$c^0$ PES of Cs$_2$AgBiBr$_6$ and CsPbBr$_3$, respectively, as a function of the out-of-phase tilt a$^-$ and in-phase tilt b$^+$. The tilt amplitude is given as the offset of one Br ion in units of the lattice constant of the double perovskite (two times the lattice constants of the single perovskite in the CsPbBr$_3$ case).

The Density Functional Theory (DFT) calculations were performed in the projector-augmented wave (PAW) [23] framework as implemented in the Vienna Ab Initio Simulation Package (VASP) [24–26]. The PBEsol [27] form of the exchange and correlation functional was used. Static phonon calculations and AIMD simulations were performed using 320 atom supercells while 40 and 80 atom supercells were used for mapping out PESs. The AIMD simulations were done in the NVT ensemble using a Nose-Hoover thermostat with the default Nose mass as set by VASP and a 2 fs timestep. See Supplemental Material [28] for full details on computational methodology.

We start by investigating the vibrations of Cs$_2$AgBiBr$_6$ in its cubic structure (Fig. 1 (a)) under the static harmonic approximation. Fig. 1 shows the static harmonic phonon dispersion and density of states (DOS). The most eye-catching feature is the presence of several phonon branches with imaginary frequencies, indicating dynamical instability. In particular, there is an imaginary and essentially dispersionless phonon branch between the Γ and X points. The modes on this branch correspond to tilts of the AgBr$_6$ and BiBr$_6$ octahedra. At the X-point the mode is a pure in-phase tilt-pattern i.e., sequential octahedra along the tilt axes are tilted by the same magnitude and in the same direction, a$^+$$b^0$$c^0$ in Glazer notation [29]. The Γ-point mode is a a$^-$$b^+$$c^0$ tilting mode, but with very small b and c axes tilts.

The calculated PESs of in-phase and out-of-phase tilting modes in Cs$_2$AgBiBr$_6$ are shown in Fig. 1 (d). As expected, the PESs display minima offset from zero tilt amplitude for both the in-phase and out-of-phase tilting modes. Both minima are, however, very shallow with depths $\sim 0.3$ and 0.6 meV/atom for the in-phase and out-of-phase tilting modes, respectively. Thus, even at thermal energies low compared to room temperature, these minima will be easily escaped from and the effective PESs will be very flat.

At points between X and Γ the modes on the imaginary phonon branch correspond to more complicated tilt patterns. At $\mathbf{q} = (0, 0.25, 0.25)$, i.e., halfway between Γ and X, every second octahedron along the tilt axis stays untitled, while the remaining octahedra are tilted in an out-of-phase fashion (illustrations are given in Fig. S4 [28]). The PESs for this mode is shown in Fig. 1 (d),
where we again see a very flat energy landscape. The fact that the different octahedral tilting modes along the soft phonon branch yield very similar, flat, PESs indicates that the bonding between the tilting planes along the tilting axis is weak.

The high symmetry cubic phase then appears as a spatial and/or dynamical average over distinct low symmetry minima. In Cs$_2$AgBiBr$_6$, the octahedra instead tilt on flat energy landscapes such that, above the critical temperature, there will be large amplitude Br motion, but the high symmetry phase should be the center of atomic oscillations at any relevant timescale. This implies that the lattice dynamics and the phase transformation in Cs$_2$AgBiBr$_6$ as opposed to e.g. CsPbBr$_3$, should be describable in a renormalized phonon picture.

To this end we have performed AIMD simulations for a set of temperatures at equilibrium volumes [28] and used the temperature dependent effective potential (TDEP) [30–32] method to map out an effective fourth-order Hamiltonian,

\[
H = U_0 + \sum_i \frac{p_i^2}{2m_i} + \frac{1}{2} \sum_{ij\alpha\beta} \Phi^{\alpha\beta}_{ij} u_i^\alpha u_j^\beta + \frac{1}{3!} \sum_{ijk\alpha\beta\gamma} \Phi^{\alpha\beta\gamma}_{ijk} u_i^\alpha u_j^\beta u_k^\gamma + \frac{1}{4!} \sum_{ijkl\alpha\beta\gamma\delta} \Phi^{\alpha\beta\gamma\delta}_{ijkl} u_i^\alpha u_j^\beta u_k^\gamma u_l^\delta.
\]

Here, $U_0$ is a constant energy, $p_i$ and $m_i$ are the momentum and mass of atom $i$, respectively, $u_i^\alpha$ is the displacement of atom $i$, in the cartesian direction $\alpha$, from its position in the reference double perovskite structure and $\Phi^{\alpha\beta}_{ij}$, $\Phi^{\alpha\beta\gamma}_{ijk}$, and $\Phi^{\alpha\beta\gamma\delta}_{ijkl}$ are the elements of the second, third and fourth order inter-atomic force constants (IFCs), respectively.

We fit IFCs of increasing order in a sequential fashion, i.e., we first find the best possible fit of the AIMD forces using just the second order IFCs, then fit the third order IFCs to the residual atomic forces, and then similarly for the fourth order IFCs. This fitting scheme ensures that $H_0$ in Eq. 1 is the largest, while the effect of $H_3$ and $H_4$ can be treated as perturbations.

From $H_0$ we obtain a set of renormalized phonon normal-mode frequencies $\omega_q$, where $q$ is the wave vector and $s$ the branch index. To lowest order in perturbation theory $H_3$ and $H_4$ yield, respectively, contributions to the phonon self-energy [33] $\Sigma_q(\Omega) = \Sigma_q^{(3)}(\Omega) + i\Gamma_q^{(3)}(\Omega)$, where $\Sigma_q^{(3)}(\Omega) = \Delta_q^{(3)}(\Omega) + i\Gamma_q^{(3)}(\Omega)$ is complex and frequency (\Omega) dependent, while the contribution from $H_4$, $\Sigma_q^{(4)} = \Delta_q^{(4)}$, is purely real and static. The explicit form of this self-energy is well known [34] and is reproduced in our notation in the Supplemental Material [28]. Generally, in a "dressed" phonon picture, one might expect the contribution of the fourth order IFCs to be small as their contribution tend to be renormalized into the second order IFCs. Indeed, they are most often not treated or shown to be negligible [35, 36]. As we will show below, however, this contribution turns out to be crucial for Cs$_2$AgBiBr$_6$.

From these quantities we obtain a phonon spectral function $S(q, \Omega)$[28, 33], which is shown in Fig. 2 (a) for

![FIG. 2. (a) Phonon spectral function, $S(q, \Omega)$, of Cs$_2$AgBiBr$_6$ at 100 and 300 K. (b) Frequency squared of the soft mode at the $\Gamma$-point with varying corrections, see text for details. The red and blue lines are second order polynomial fits, while the yellow line is merely a straight line to guide the eye. The vertical black line indicates the experimental transition temperature [22].](image-url)
temperatures 100 and 300 K. Comparing to the static phonon dispersion in Fig. 1 it is clear that the unstable modes have been anharmonically stabilized. We can also see that at room temperature (300 K) certain phonon branches, in particular in the range $\sim 2.2 - 3$ THz and the highest two branches between $\sim 4.4 - 5$ THz, are severely anharmonically broadened. At the $\Gamma$-point these modes are dominated by displacements along the Bi-Br bonds, indicating a high degree of anharmonicity of these bonds.

Fig. 2 (b) shows the temperature dependence of the square of the frequency of the soft phonon mode at the $\Gamma$-point. The collapse of this mode should be responsible for the experimentally observed structural transition. Indeed, freezing-in this mode, followed by a full relaxation results in the experimentally observed low temperature [22] a temperature of $\sim 50$ K, which is in fair agreement with the experimentally observed phase transformation temperature of $\sim 122$ K. We note that the precise frequency of these kind of soft optical modes is known to be sensitive to, in particular, volume and exchange-correlation functional [36].

In Fig. 2 (b) we also show the temperature dependence of this frequency corrected to lowest order by $H_3$ (yellow squares) and by $H_3$ and $H_4$ (red diamonds) (taken as the positions of the corresponding peak of the spectral function evaluated with the self-energies $\Sigma^{(3)}(\Omega)$ and $\Sigma^{(3)}(\Omega) + \Sigma^{(4)}$, respectively). While the latter case yields a low temperature extrapolation very similar to the pure TDEP frequencies, the former is instead completely different, indicating the importance of the $H_4$ contribution to the effective Hamiltonian in describing $\text{Cs}_2\text{AgBiBr}_6$. Further confirmation of this fact can be found by inspecting the low frequency behavior of the acoustic phonon modes, in particular the two transverse acoustic modes in the $\Gamma$-$K$ direction, whose slopes correspond to the elastic constants (in Voigt notation) $C'' = (C_{11} - C_{12})/2$ and $C_{44'}$, respectively. As we may see from Fig. 2 these branches are predicted to be essentially degenerate for low frequencies at 300 K, implying elastic isotropy, as can be quantified by a close-to-unity Zener ratio, $C_{44'C'} \approx 1$. We have explicitly confirmed this prediction by calculating the elastic constants from AIMD using deformed supercells and a stress-strain relation [28]. Our calculated values are $C_{11} \approx 29.2$ GPa, $C_{12} \approx 15.5$ GPa and $C_{44} \approx 6.9$ GPa, giving $A_Z \approx 1.01$. In stark contrast, $S(\mathbf{q}, \Omega)$ evaluated using only $\Sigma^{(3)}(\Omega)$ predicts, incorrectly, substantial elastic anisotropy. Indeed, the later even incorrectly predicts a collapse of one of these transverse acoustic branches around 500 K (See Fig. S3 [28]).

Having established that $\text{Cs}_2\text{AgBiBr}_6$ is i) highly anharmonic and ii) very soft (as evidenced by the small elastic constants), we expect a rather low lattice thermal conductivity, $\kappa_l$. We estimate $\kappa_l$ of $\text{Cs}_2\text{AgBiBr}_6$ by solving the linearized phonon Boltzmann transport equation (BTE) including three-phonon and isotope scattering (details in the Supplemental Material [28]). The results are shown by blue circles in Fig. 3, where we, as expected, find very low thermal conductivities. Indeed, the 300 K value of 0.33 Wm$^{-1}$K$^{-1}$ firmly establishes $\text{Cs}_2\text{AgBiBr}_6$ as a solid with ultra-low lattice thermal conductivity. Our obtained $\kappa_l$ roughly follows a temperature dependence of $T^{-0.5}$, significantly different from the common $T^{-1}$ dependence usually obeyed by weakly anharmonic solids with thermal conductivities dominated by three-phonon scattering. Such non-standard temperature dependence of thermal conductivities have recently been found in several complex and/or highly anharmonic systems [35, 38–40] and indicates strong, temperature induced, renormalization of the interacting phonon system responsible for heat transfer. Indeed, we find that a $\sim T^{-1}$ behaviour is recovered if we evaluate the thermal conductivity using the 100 K IFCs at all temperatures (red diamonds in Fig. 3).

An additional feature, other than the softness and the anharmonicity, responsible for the low thermal conductivity of $\text{Cs}_2\text{AgBiBr}_6$ can be found by inspecting the spectrally resolved thermal conductivity, $\kappa(\omega)$, shown in the inset of Fig. 3. While we can see that, as expected, the majority of the heat is carried by low frequency modes, we also see a marked drop in $\kappa(\omega)$, centered around 1 THz. This drop can be seen to coincide with a sharply peaked Cs partial phonon DOS. In fact, since the Cs ions reside in oversized cubo-octahedral voids in the double
perovskite structure, they effectively act as intrinsic rattlers. Correspondingly, the phonon dispersion relation is very flat in a frequency region around 1 THz, as can be appreciated from Fig. 1 (c) or Fig. 2 (a), and we can see the distinctive “avoided crossing” behaviour, characteristic of solids with intrinsic rattlers [41–44], for instance of the highest acoustic mode in the T-L direction around 1 THz.

Ultra-low thermal conductivities have also been demonstrated in both hybrid halide perovskites [45] and fully inorganic single halide perovskites [46]. This has important implications in, for instance, charge carrier cooling. Our results thus firmly put Cs$_2$AgBiBr$_6$ into the set of halide perovskites with ultra-low lattice thermal conductivities. Differently from the single halide perovskites, however, Cs$_2$AgBiBr$_6$ has a high symmetry cubic structure. This combination of a high-symmetry structure (yielding high band-edge degeneracy) and low thermal conductivity is, in fact, quite rare and is believed to be a recipe for high-performance thermoelectric materials [47].

In summary, we have investigated the anharmonic lattice vibrations of the prototypical lead free halide double perovskite Cs$_2$AgBiBr$_6$, in particular in relation to octahedral tilting. We find a branch of unstable phonon modes corresponding to different types of octahedral tilting. Tracing out a set of these modes gives very flat potential energy surfaces. We perform a set of AIMD simulations and fit an effective Hamiltonian, from which we i) reproduce the phonon collapse responsible for the experimentally observed phase transformation, ii) show that Cs$_2$AgBiBr$_6$ is highly anharmonic at room temperature and iii) demonstrate the importance of the high order terms up to fourth order in this Hamiltonian. We finally show that the softness and anharmonic nature of the system result in an ultra-low thermal conductivity, our theoretical estimate is 0.33 Wm$^{-1}$K$^{-1}$ at room temperature.

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