

Theoretical Investigations of Anharmonic Effects and Phonon Transport in the Cubic Phase of Crystalline Perovskite CsPbCl_3

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ABSTRACT: The role of anharmonic effects on lattice dynamics and thermal transport has been investigated in the cubic phase of CsPbCl_3 perovskite. Limitations of the harmonic approximation which lead to phonon instabilities in the Brillouin zone were addressed based on self-consistent phonon theory in combination with first-principles calculations and by incorporation of frequency renormalization effects from bubble and loop diagrams. This theoretical approach demonstrates significant improvements compared to results obtained using self-consistent phonon dynamic matrix. Both the cubic-to-tetragonal phase transition temperature as well as the predicted lattice thermal conductivity values show good agreement with selected sets of available experimental data. The accuracy of the predicted thermal conductivity data is also tested against systems significantly larger than those allowed by

quantum calculations, by using molecular dynamic simulations with machine-learning force fields.

KEYWORDS: density functional theory, lattice dynamics, phonons, lattice thermal conductivity

1. INTRODUCTION

For the past few decades, a large scientific interest has been devoted to the study of perovskite materials. This has been motivated by existence of unique sets of properties such as high thermal stability, low thermal conductivity, tunability of the electronic and optical properties, coupled with increasingly more efficient low-cost processing techniques.¹⁻² All these attributes helped in making perovskite materials of interest in a wide range of applications extending from thermal barriers for gas turbines³⁻⁴ or solid oxide fuel cells for energy conversion,⁵ to gas sensors⁶ and optoelectronic devices.⁷ Within the class of perovskites, the metal halide materials with general formula ABX_3 , where A is a monovalent cation, B is bivalent cation and X is a halide anion are emerging as a novel class of materials referenced in a recent publication⁸ as the gold standard for development of next technologies in energy storage, as piezoelectric energy generators, X-ray detectors, gas sensors and various photovoltaic applications. In this study we focus on the case of all inorganic cesium lead halide, $CsPbCl_3$ perovskite. This material has been characterized to have a synergistic combination of properties with a band gap of about 3.0 eV useful for photoelectric response near-ultraviolet region and posing also a

high thermal stability.⁹⁻¹⁰ In CsPbCl₃ crystal the Pb atoms are located at the corners of a pseudocubic lattice coordinated to corner-sharing PbCl₆ octahedra while Cs atoms rattle around the cube center. Regarding the crystallographic properties previous studies have shown that CsPbCl₃ undergoes multiple solid-solid phase transitions in a relative narrow range of temperatures.¹¹⁻¹³ Based on neutron scattering technique Fujii *et al.*¹³ have determined that above 320 K the crystal adopts a cubic symmetry with $Pm\bar{3}m$ space group and the crystal remains stable in this phase up to the melting temperature at 884 K. Below 320 K, transition to a tetragonal phase takes place followed by an orthorhombic phase at 316 K and a monoclinic phase at 310 K.¹³ These phase transitions were interpreted to correspond to freezing or condensation of rotational modes of PbCl₆ octahedra around the principal axes of the crystal.¹³ As indicated above, an important advantage of CsPbCl₃ relative to other similar inorganic halides is its increased thermal stability. Based on calorimetric studies the formation enthalpies of CsPbX₃, X=I, Br, Cl perovskites have been determined by Wang and Navrotsky.¹⁴ Within this compound family, it was determined¹⁴ that CsPbCl₃ has the highest thermodynamic stability (formation enthalpy of -22.59 ± 1.59 kJ/mol) while CsPbI₃ has the lowest (formation enthalpy of -2.83 ± 0.90 kJ/mol) consistent with variation of Goldschmidt tolerance factor,¹⁵ which changes from $t=0.879$ for CsPbCl₃ to $t=0.851$ for CsPbI₃. Furthermore, among various possible crystallographic phases, the cubic CsPbCl₃ perovskite was characterized¹⁴ as a high temperature entropy-stabilized phase relative to its low temperature polymorphs.

Complementing the experimental efforts, several computational studies performed primarily using density functional theory (DFT) calculations have investigated the fundamental properties of CsPbCl₃ crystal. Among these, a handful of studies were dedicated to calculation of the structural, elastic, optical and electronic properties of CsPbCl₃¹⁶⁻¹⁸ or of the related metal halide CsPbX₃, (X=Cl, Br, I) family.¹⁸ Modulation of the electronic and optical properties was shown to be highly effective upon doping as demonstrated for example by Ko *et al.*¹⁹ based on first-principles calculations within the virtual crystal approximation for the CsPb(Br_{1-x}Cl_x)₃ set of solid solutions or by Bhat *et al.*²⁰ for the case of Co²⁺ doping in CsPbCl₃. In this latest case, a substantial band gap decrease taking place upon Co doping was found to be directly correlated to an increase in photocatalytic activity under visible light illumination.²⁰ Theoretical investigations have been also dedicated to description of specific thermodynamic properties. Ghebouli *et al.*¹⁶ determined the heat capacity C_v of CsPbCl₃ at high temperatures and pressure conditions using a quasi-harmonic Debye model. Ikyas and Elias¹⁷ have determined the phonon dispersion of CsPbCl₃ and confirmed the dynamical instability of the perovskite structure in the harmonic approximation as evidenced by several imaginary modes present throughout Brillouin zone.

A highly relevant set of properties of halide perovskites are thermal transport characteristics. The renewed interest in thermal transport stems from the discovery of unique properties of the halide perovskites including ultralow thermal conductivity, favorable carrier mobility and superior Seebeck coefficients which make them attractive for diverse applications

as thermoelectric materials with a high figure of merit²¹ or as electrically conductive thermal barrier coatings.²² In particular, using a low-temperature solution process Lee *et al.*²² have reported the synthesis of single-crystal all-inorganic halide perovskites nanowires and discovered that these systems have ultralow lattice thermal conductivity with values ~ 0.4 W/mK. The specific halide perovskites analyzed²² were CsPbI₃ (0.45 ± 0.05 W/mK), CsPbBr₃ (0.42 ± 0.05 W/mK) and CsSnI₃ (0.38 ± 0.04 W/mK), and their ultralow thermal conductivity values were attributed to strong phonon-phonon scattering via a cluster rattling mechanism.²² Beside experiments, theoretical approaches have been also considered to identify perovskite compounds with low lattice thermal conductivities. Among these, it has been found that replacing divalent Pb⁺² by pairs of monovalent and trivalent cations with formation of lead-free halide double perovskites²³⁻²⁴ or using high throughput virtual screening of large libraries of compounds²⁵ represent promising strategies for identification of new candidate perovskites with tailored ultralow thermal conductivities.

Available experimental measurements for the lattice thermal conductivity of CsPbCl₃ perovskite provide a somewhat less consistent picture. Kubičár *et al.*²⁶ have determined the thermophysical properties of single crystal CsPbCl₃ in the temperature range 283–338 K using a pulse transient method and a thermal conductivity value of 0.55 ± 0.32 W/mK was reported at 323 K, above the measured tetragonal to cubic phase transition value at 320 K. In a subsequent study,²⁷ the same group has reported two related values for lattice thermal conductivity of CsPbCl₃ of 0.530 W/mK at 295 K and 0.535 W/mK at 323 K, below and above

the tetragonal/cubic transition temperature, respectively. He *et al.*²⁸ have also determined the thermal conductivity of large size CsPbCl₃ single crystals in the temperature range 300-800 K using the measured values for thermal diffusivity, specific heat capacity and density. For crystals with more than several cubic centimeters in volume the corresponding thermal conductivity was found to remain below 0.60 W/mK over the entire temperature range investigated which is comparable to those reported for CsPbB₃ (0.42 W/mK) or for MAPb₃ (0.34 W/mK). The unexpected aspect in the results reported by He *et al.*²⁸ is the trend with temperature of the lattice thermal conductivity that increases from about 0.49 W/mK at 325 K to about 0.53 W/mK at 525 K, and then 0.60 W/mK at 775 K. This trend is opposite to findings obtained by Lee *et al.*²² for CsPbI₃, CsPbBr₃, and CsSnI₃ where a decrease in lattice thermal conductivity with temperature has been reported for all these systems. Different from results of either Kubičár *et al.*²⁶ or He *et al.*²⁸ are the data obtained by Hager *et al.*²⁹ for the case of CsPbCl₃ thin films. At ambient temperature, an ultra-low value of lattice thermal conductivity of 0.49 ± 0.04 W/mK has been found for the tetragonal phase, similar to results reported previously.²⁷⁻²⁸ However, upon transition to the cubic phase a large increase in lattice thermal conductivity to 1.60 ± 0.08 W/mK at > 319 K has been reported.²⁹ A clear motivation for this increase relative to results reported in the other experimental studies of the cubic phase of CsPbCl₃ or for other similar CsPbX₃ (X=I, Br) systems²² in the cubic phase was not provided.

A key feature in the thermal stability or the ultralow thermal conductivity of perovskites is played by the presence of a strong lattice anharmonicity. Based on a neutron

diffraction study, Sakata *et al.*³⁰ have shown that large anharmonic potentials are characteristics for both Cs and Cl atoms while a harmonic potential is adequate for Pb atom. Additional refinements of anharmonic effects have been reported by Hutton *et al.*³¹ based on elastic neutron diffraction experiments who found a particularly large anharmonicity for Cl atom near the cubic to tetragonal phase transition temperature. Yang *et al.*³² have analyzed the issue of spontaneous octahedral tilting for cesium-lead CsPbX_3 and cesium-tin CsSnX_3 , (X=F,Cl,Br,I) halide perovskites and found based on lattice-dynamics calculations that all these systems display vibrational instabilities due to octahedral tilting, corresponding to an anharmonic double-well potential. Wang *et al.*³³ have identified a complex synergy in the case of the double perovskite $\text{Cs}_2\text{NaInCl}_6$ involving tilting of the NaCl_6 and InCl_6 octahedral units, and rattling of Cs^+ atoms as the source of the strong anharmonicity present in these systems. Zheng *et al.*³⁴ have demonstrated that in the case of crystalline perovskite BaZrO_3 anharmonic phonon renormalization and coherent thermal transport are essential factors for accurate determination of lattice thermal conductivity. In a subsequent paper, Zheng *et al.*³⁵ have identified a novel transition in the mechanism of lattice thermal conductivity in $\text{Cs}_2\text{AgBiBr}_6$ from particle-like propagation to wave-like tunnelling at about 310 K, which was associated with a breakdown of the conventional Peierls-Boltzmann transport formalism. It should be noted that materials with strong anharmonicity and ultralow lattice thermal conductivity can be also present in non-perovskite materials. Examples of such cases are Tl_3VSe_4 ³⁶ and cubic $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ tetrahedrites.³⁷ For the first system particle-like propagation of phonon excitations were found to provide good agreement of the calculated lattice thermal conductivity with

experimental data while in the second case the off-diagonal terms of the heat-flux operator corresponding to the incoherent contributions characteristic to disordered systems were identified as the primary source of strong anharmonicity.

Description of the anharmonic lattice dynamics and its effect upon thermal transport is a challenging topic and to date several methods such as temperature-dependent effective potential (TDEP),³⁸ self-consistent phonon (SCPH) theory,³⁹ self-consistent ab initio lattice dynamics (SCAILD),⁴⁰ or stochastic self-consistent harmonic approximation (SSCHA)⁴¹ have been proposed.

In this paper, we have considered the momentum-space self-consistent phonon (SCP) methodology developed by Tadano and Tsuneyuki,⁴²⁻⁴³ which includes both nuclear quantum and anharmonic effects in a consistent fashion and presents a demonstrated computational efficiency, able to generate SCP data on a grid of temperatures. This method as implemented into ALAMODE code⁴⁴⁻⁴⁵ has been shown to be highly successful in determining the lattice dynamics properties of several perovskite systems.^{42, 46-49} Extension of this methodology to include the effects from the bubble diagram⁴⁶ along with contributions from three-phonon interactions allowed us to determine the lattice thermal conductivity of CsPbCl₃ in the cubic phase with inclusion of both Peierls and coherent terms.⁵⁰ We further compare the SCP-based results with an alternative approach to evaluate lattice thermal conductivity based on molecular dynamics simulations performed with supercells with a significantly larger number of atoms than those used in first-principles calculations. This is made possible by the use of third-generation

neuroevolution potentials (NEPs)⁵¹ in combination with homogeneous non-equilibrium molecular dynamics simulations⁵² as implemented into GPUMD package.⁵¹ For CsPbCl₃, two groups have reported recently the development of machine-learned potentials with particular emphasis on analysis of the mechanical behavior and of the temperature induced transitions among various phases of this crystal.⁵³⁻⁵⁴ Both studies have generated these potentials by fitting DFT datasets for energy, force and virial tensors of different training configurations generated as function of temperature and at different compression levels. The study reported by Shi *et al.*⁵³ have used PBE exchange-correlation functional to extract the corresponding DFT data. Fransson *et al.*⁵⁴ have analyzed the effect of different exchange-correlation functionals to predict different CsPbX₃ (X=Cl, Br, I) phases and concluded that results obtained using vdW-DF-cx and SCAN+rVV10 provide the closest agreement with experiment. In this study, we utilize the NEP potentials developed by Shi *et al.*⁵³ at PBE level and by Fransson *et al.*⁵⁴ at vdW-DF-cx level to calculate the lattice thermal conductivity of CsPbCl₃ using MD simulations and compare the corresponding results to those obtained using ALAMODE.

The organization of the paper is as follows: Section II describes the computational methods used. The results of the theoretical analyses are reported in Section III. Section IV summarizes our main conclusions.

2. COMPUTATIONAL METHOD

2.1 DFT calculations. Density functional theory calculations were carried out using Vienna *ab initio* simulation package (VASP)⁵⁵⁻⁵⁶ with the PBEsol⁵⁷ exchange-correlation functional. The recommended projector augmented wave (PAW)⁵⁸⁻⁵⁹ pseudopotentials (potpaw_PBE.64 version provided in VASP code) were used to describe electron-ion interactions together with a plane-wave basis set with a cutoff energy of 660 eV. Optimization of the CsPbCl₃ primitive cell was done using a 8×8×8 Monkhorst-Pack k-point grid⁶⁰ and tight energy 10⁻⁸ eV convergence criteria. For calculations of the dynamical matrix non-analytic corrections were included and for this purpose the macroscopic dielectric tensor and Born effective charges were determined using density functional perturbation theory⁶¹ with a denser k-point grid of 24×24×24.

2.2 Force constant calculations. The harmonic interatomic force constants have been obtained from 4×4×4 supercells by finite displacement method using displacements of 0.02 Å and a reduced k-point grid of 2×2×2. All possible harmonic terms were included in analysis. The anharmonic force constants have been determined for the case of 2×2×2 supercells for which ab initio molecular dynamics simulations in *NVT* ensemble were performed at 50 K. From the corresponding trajectories snapshot configurations were extracted every 50 steps and an additional random displacement of 0.1 Å was applied to reduce the cross correlation between snapshot structures. Atomic forces for these configurations were determined using DFT calculations with a 4×4×4 *k*-point grid and tight convergence criteria of 10⁻⁸ eV. In calculation of the anharmonic force constants, interactions up to the eighth order were

considered. For third and fourth-order terms, interactions contained on-site, two-body and three-body terms while for higher order terms only the on-site and two-body terms were included. No interaction cutoff was imposed on third and fourth order terms while for all the other higher interaction terms a real-space cutoff radius of 15.0 Å was applied. When generating the interatomic force constants (IFCs), we considered the constraints necessary to satisfy the permutation symmetry and the acoustic sum rule with the consideration of periodic images as recommended by Masuki *et al.*⁶²

2.3 Anharmonic phonon renormalization. The anharmonic phonon renormalization has been performed by considering the first-order correction from the quartic anharmonicity as implemented in ALAMODE code,^{42, 46} *i.e.* the loop diagram, hereafter denoted as SC1, using an iteratively solving equation

$$(\omega_q^S)^2 = (C_q^\dagger \Lambda_q^{(\text{HA})} C_q)_{\nu\nu} + \frac{1}{2N_{q'}} \sum_{q'} \Phi_4(q; -q; q'; -q') \times \frac{\hbar}{2\omega_q^S} [1 + 2n(\omega_q^S)] \quad (1)$$

where $\Lambda_q^{(\text{HA})} = \text{diag}(\omega_{q1}^2, \dots, \omega_{qn}^2)$, ω_{qv} is the harmonic phonon frequency with the crystal momentum q and branch index ν , $n(\omega) = [\exp(\beta\hbar\omega) - 1]^{-1}$ is the Bose-Einstein distribution function, $\Phi_4(q; -q; q'; -q')$ is the fourth-order IFCs in the normal coordinate basis of the SCP and $\hbar$ is the reduced Planck constant. The off-diagonal terms of the loop self-energy were also included when solving the self-consistent phonon equation. In this work, the temperature dependent equation (1) was solved using a q mesh set of $2 \times 2 \times 2$ which is commensurate with the supercell size used in calculations while convergence of the anharmonic frequencies was

obtained using a finer q' mesh of $12 \times 12 \times 12$. As shown in Figure S1, this grid selection ensures minimal deviations relative to larger grid sizes of $14 \times 14 \times 14$ and $16 \times 16 \times 16$ of the calculated vibrational frequencies for either SC1 and QPNL results and for different high-symmetry points.

For the renormalized phonon energies determined in first order self-consistent phonon method contributions due to cubic anharmonicity have been included by solving the following self-consistent equation within quasi-particle (QP) approximation⁴⁶

$$\Omega_{qv}^2 = (\omega_{qv}^S)^2 - 2\omega_{qv}^S \text{Re} \Sigma_{qv}^B[G^S, \Phi_3](\omega = \Omega_{qv}) \quad (2)$$

where ω_{qv}^S is the SC1 frequency, $\Sigma_{qv}^B[G^S, \Phi_3](\omega = \Omega_{qv})$ is the phonon bubble self-energy evaluated at Ω_{qv} frequency, Φ_3 is the third-order force constant included in the self-energy calculation. For the nonlinear QP equation (2), hereafter denoted as QPNL, additional simplified treatments are possible,⁴⁶ namely QP[0] method in which a static approximation ($\omega = 0$) is taken or QP[S] in which $\omega = \omega_{qv}^S$. In this work, the results of all three QP[0], QP[S] and QPNL methods to generate the renormalized phonon energies with inclusion of both cubic and quartic anharmonicities were considered. Once the anharmonic phonon frequencies were determined the corresponding vibrational free energies were evaluated⁴⁵ with a dense $20 \times 20 \times 20$ q -point mesh.

An alternative way to analyze theoretical data is based on the phonon spectral function of the bubble diagram which was calculated^{43, 63} as

$$A_q(\omega) = \frac{1}{\pi} \frac{4(\omega_q^S)^2 \Gamma_q^B(\omega)}{[\omega^2 - (\omega_q^S)^2 - 2\omega_q^S \Delta_q^B(\omega)]^2 + [2\omega_q^S \Delta_q^B(\omega)]^2} \quad (3)$$

where $\Delta_q^B(\omega)$ and $\Gamma_q^B(\omega)$ are the real and imaginary parts of the bubble self-energy at frequency ω .

2.4. Lattice expansion. The thermal expansion effects were also included in our analysis. For this purpose, starting with the DFT optimized lattice constant this was changed in increments of 1% in the range -3% to 3% and the entire computational procedure as described above has been repeated. From the calculated Helmholtz free energies $F(V, T)$, the lattice constants at different temperatures have been determined by fitting a Birch-Murnaghan equation of state.⁶⁴ For each of the temperature dependent $V^{(s)}(T)$ volumes of interest, the corresponding dielectric tensors, Born effective charges, the renormalized second-order IFC and anharmonic IFCs were determined by linear interpolation based on the corresponding values at the closest two volumes.

2.5 Calculations of the lattice thermal conductivity. Based on the set of effective second-order force constants calculated using either SC1 or QP methods, the lattice thermal conductivity was determined. For this purpose we followed the unified theory of thermal transport in crystals and glasses as developed previously by Simoncelli *et al.*⁵⁰ According to this methodology the total lattice thermal conductivity is expressed as the sum of Peierls terms (κ_P) within relaxation-time approximation and the coherent contributions (κ_C), *i.e.* $\kappa_L = \kappa_P + \kappa_C$. Following notation introduced in Ref.⁴⁶, the total lattice conductivity can be expressed as

$$\kappa_L = \frac{1}{N_q V} \sum_{q\nu\nu'} \frac{c_{q\nu}\omega_{q\nu} + c_{q\nu'}\omega_{q\nu'}}{\omega_{q\nu} + \omega_{q\nu'}} \mathbf{v}_{q\nu\nu'} \otimes \mathbf{v}_{q\nu'\nu} \frac{\Gamma_{q\nu} + \Gamma_{q\nu'}}{(\omega_{q\nu} - \omega_{q\nu'})^2 + (\Gamma_{q\nu} + \Gamma_{q\nu'})^2} \quad (4)$$

where the lattice contains N_q unit cells, each of them having a volume V , $c_{q\nu}$ is the mode heat capacity and $\mathbf{v}$ is the group velocity matrix. The diagonal terms ($\nu = \nu'$) in Eq. (4) represent the Peierls κ^p contribution to the conductivity associated to particle-like propagation of phonon wavepackets while the off-diagonal terms represent the coherent contribution κ^c representing wave-like tunneling of the phonons.^{46, 50} In calculations of the lattice thermal conductivity of CsPbCl₃ a $40 \times 40 \times 40$ q mesh has been used. As seen from Figure S2, this selection of the q mesh grid ensures a very good convergence of the calculated lattice thermal conductivity at either SC1 or QPNL levels of theory, with deviations of -0.007 and -0.005 W/(mK) from values obtained with a substantial larger grid of $50 \times 50 \times 50$.

2.6 Non equilibrium molecular dynamics simulations with neuroevolution potentials. As an alternative approach, the lattice thermal conductivity of CsPbCl₃ was calculated using molecular dynamics simulations with two different machine learning potentials developed before.⁵³⁻⁵⁴ The advantage of this approach is that significantly larger size systems than those used in previously described quantum calculations are possible while higher order anharmonicities are also included via molecular dynamics simulations. For the cubic phase of CsPbCl₃ we have used models with $18 \times 18 \times 18$ supercells containing 29,160 atoms. The equation of motions were integrated using the neuroevolution (NEP) potentials developed from DFT trained data by Shi *et al.*⁵³ at PBE level, respectively by Fransson *et al.*⁵⁴ at vdW-DF-

cx level, in combination with homogeneous non-equilibrium molecular dynamics (HNEMD) simulations as implemented in the GPUMD package.^{51, 65} Details of the machine learning potentials used including the loss function versus training steps, the accuracy of energy and force predictions relative to DFT reference data and transferability of the model used for different crystallographic phases of CsPbCl₃ are provided in references 53 and 54, respectively. In the current work, lattice expansion for the cubic phase of CsPbCl₃ has been determined from NpT simulations performed at the target temperature for 20 ns using a timestep of 1 fs. These have been followed by NVT simulations for 20 ns using a Nosé-Hoover chain thermostat with a driving force parameter set $5 \times 10^{-5} \text{ \AA}^{-1}$. Averages over 10 independent runs were collected for each data point.

3. RESULTS AND DISCUSSION

3.1. Lattice dynamics and anharmonicity. Optimization of bulk lattice of CsPbCl₃ in its ideal cubic perovskite structure with $Pm\bar{3}m$ cubic symmetry leads to a lattice constant of 5.609 Å based on DFT calculations with PBEsol exchange correlation functional. This value agrees very well to neutron diffraction experimental measurements of 5.6039 Å of Ahtee *et al.*⁶⁶ at 331 K or the value of 5.605 Å obtained using elastic neutron diffraction at 325 K by Hutton and Nemes.⁶⁷

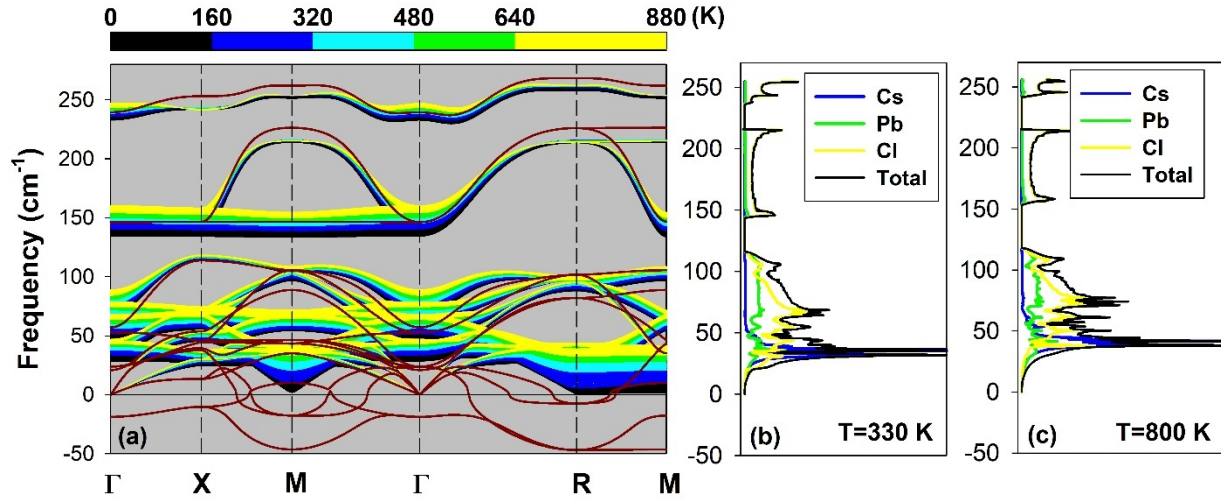


Figure 1. (a) The calculated anharmonically renormalized phonon dispersion of CsPbCl_3 in the cubic phase as function of temperature together with the corresponding atom-projected partial and total phonon density of states at (b) 330 K and (c) 800 K. For comparison, in the left panel the phonon dispersion results obtained in the harmonic approximation (dark maroon lines) are also included.

Under the harmonic approximation, the calculated phonon dispersion along the high-symmetry lines of the Brillouin zone is characterized by the presence of modes with negative frequencies as shown in Figure 1a by dark maroon lines. Such modes are present in the whole Brillouin zone with the largest most negative values observed at M (0.5, 0.5, 0.0) and R (0.5, 0.5, 0.5) points of the Brillouin zone. These results indicate the dynamically unstable nature of the lattice particularly at low temperatures when described under the harmonic approximation. Upon inclusion of the anharmonic effects via the phonon renormalization approach described above, all modes become positive, corresponding to a dynamically stable lattice. There is also a visible hardening of the soft modes with temperature increase as indicated by both the band

structure evolution with temperature or by the atom-projected phonon density of states (PDOS) at 330 and 800 K of Figure 1. It can be seen that the primary contributions to the soft modes of CsPbCl₃ is provided by Cs and Cl atoms as shown from atomic participation ratio projected on the phonon bands (see Figure S3) and from the PDOS distributions in Figures 1b,c.

Additional insight into the nature of the soft modes at R and M points of the Brillouin zone was obtained from the analysis of the potential energy surface along the respective Q_1 and Q_2 normal mode coordinates. As shown in Figure 2, each soft mode is characterized by a double-well potential explaining the observed lattice anharmonicity. The corresponding eigenvectors of these modes correspond to out-of-phase and respectively to in-phase motions of the PbCl₆ octahedra. Notably when these potential energy dependencies are decomposed into harmonic and higher order anharmonic terms, the harmonic potential V2 (see Figure 2) has negative contributions with a maximum located at $Q_1=0$ or $Q_2=0$, respectively. This finding explains the presence of imaginary frequencies in the case of phonon calculations performed under the harmonic approximation.

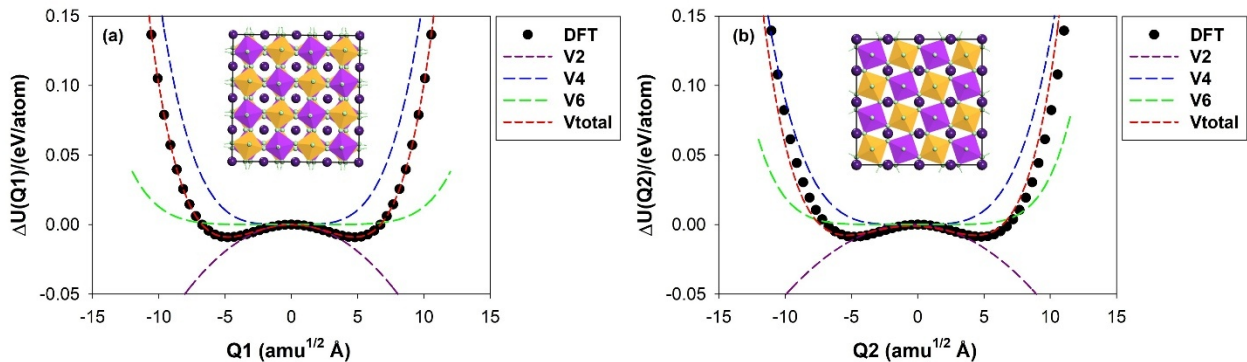


Figure 2. The calculated potential energy surface as function of normal mode coordinates Q1 and Q2 at the (a) R and (b) M points of the Brillouin zone. In each case decomposition of the total potential in contributions of the second (V2), fourth (V4) and sixth (V6) order terms are also indicated. The inset panels include pictorial views of the corresponding eigenvectors representing in-phase and respectively out-of-phase tilting of PbCl₆ octahedra.

The effect of temperature increase upon lattice dimension of CsPbCl₃ has been determined based on phonon calculations performed within the first-order self-consistent phonon theory (SC1), which includes the renormalization effect by the quartic anharmonicity. The corresponding dependence on temperature of the lattice constant is indicated with black rectangles in Figure 3a. Relative to the DFT optimized value at zero temperature, the lattice constant increases when phonon excitations at the SC1 level are included. For example, at 330 K a new equilibrium lattice constant of 5.642 Å has been obtained that compares reasonably well (within 0.68%) relative to experimental data obtained by Hutton and Nemes.⁶⁷ In Figure 3a, we have also included the experimental temperature dependencies of the lattice constant obtained by Sadanandam *et al.*⁶⁸ and He *et al.*,²⁸ respectively. As shown in Figure 3a, evolution with temperature of the calculated lattice constant within the SC1 theory follows closely the corresponding experimental data. From this data a linear expansion coefficient of $0.22 \times 10^{-4} \text{ K}^{-1}$ has been determined which compares reasonable well with various sets of experimental results ranging from $(0.22-0.30) \times 10^{-4} \text{ K}^{-1}$ for the cubic phase of CsPbCl₃ as reported in a review article by Haeger *et al.*⁶⁹

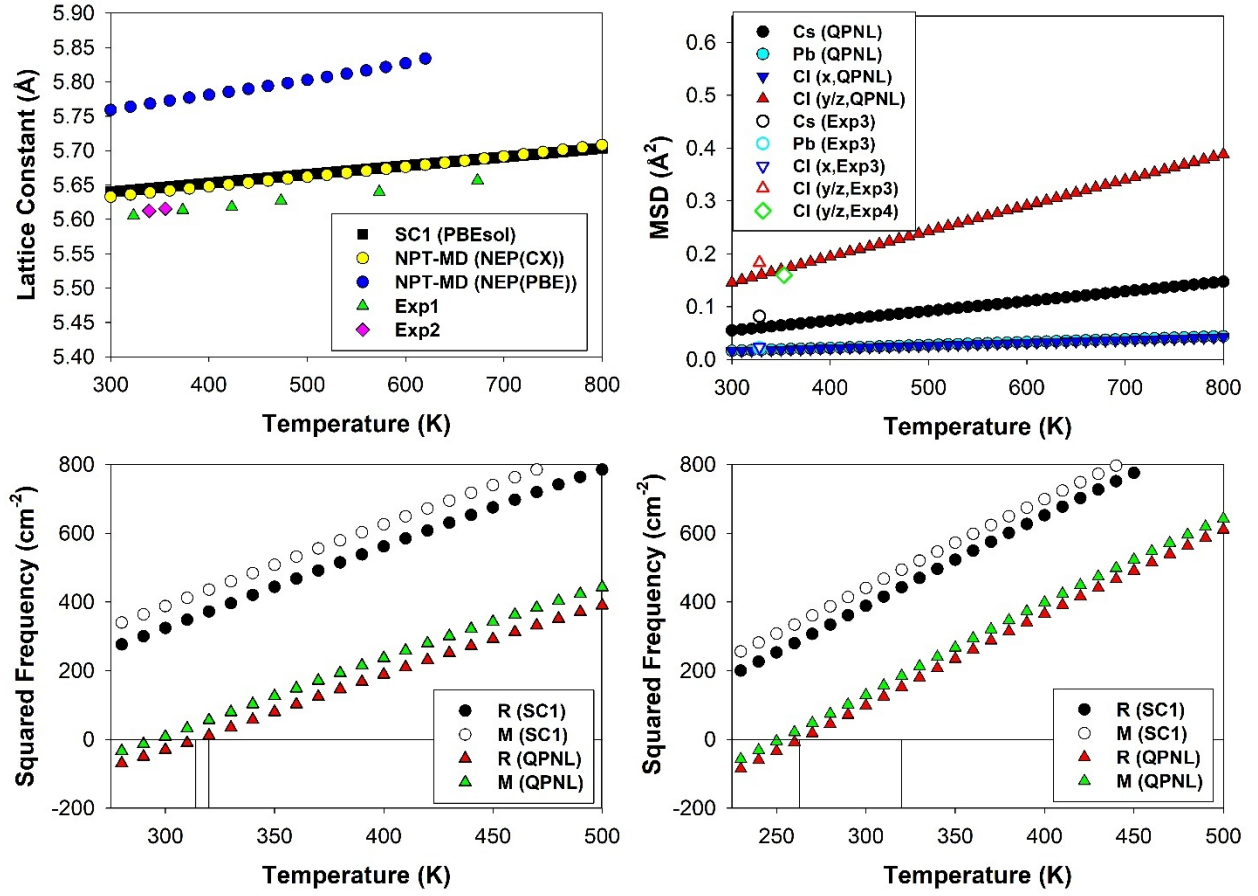


Figure 3. (a) Comparison of the calculated lattice expansion obtained using the SC1 method in ALAMODE and the results of NpT -MD simulations using GPUMD code with NEP(CX) and NEP(PBE) machine learned potentials together with experimental Exp1⁶⁸ and Exp2²⁸ results. (b) Comparison of the calculated mean-squared-displacements (MSD) for various atoms at QPNL level together with experimental Exp3⁷⁰ and Exp4¹³ data. Temperature dependence of the squared frequencies of R and M soft modes corresponding to (c) $V=V_0$ (DFT) and (d) $V=V(\text{SC1})$ calculated at the SC1 and QPNL levels. The indicated negative values were determined using the QP[0] method.

Previous experimental studies^{12, 71} have indicated that upon cooling, single crystal CsPbCl₃ undergoes a phase transition from cubic to tetragonal at $T=320$ K which was assigned to correspond to a first order phase transition. For example, in their nuclear magnetic resonance (NMR) measurements of phase transition in CsPbCl₃, Lim and Kim⁶⁶ have observed abrupt discontinuities in nuclear-spin-lattice relaxation time parameters of ¹³³Cs in the crystal close to transition temperature indicating a first order phase transition. For the present study, it is relevant to determine if the presence of such a phase transition can be predicted using current computational settings. For this purpose, we evaluated the temperature dependence of the squared of the frequencies for the soft modes and estimated the phase transition temperature from a linear fit with a Currie-Weiss temperature dependence law. In the QPNL method, solutions of the self-consistent equation (2) can be identified only for temperatures larger than T_c while for $T < T_c$, the QP[0] frequencies have been used. The results obtained using anharmonic phonon renormalization (SC1) method with the DFT optimized volume are shown in Figure 3c. In this case the predicted phase transition temperature is around 151 K, significantly smaller than the observed T_c at 320 K.^{12, 71} In contradistinction, in the case of phonon calculations performed at the QPNL level, the agreement with experimental data is significantly improved with predicted transition temperatures of 314 K and 295 K for the R and M soft modes, respectively. Similar results for the transition temperatures are obtained using the QP[0] method, but in the case of QP[S] the calculated T_c decreases to 300 K and 279 K for the two modes. These findings are similar to those obtained previously⁴⁶ for α -CsPbBr₃, where the best agreement to experimental values was observed in the case of calculations

performed using the QPNL method. In that work it has been pointed out that prediction of T_c value is dependent not only on the theoretical level used to include the loop and bubble contributions but also on the specific lattice constant. We have analyzed a similar aspect in this work and we present in Figure 3d the results obtained using the temperature dependent optimized lattice constants as determined at different levels of theory. As seen in the figure, the level of agreement with experimental data of predicted T_c values decreases. This behavior arises because the Grüneisen parameter, $\gamma_{qv} = -\frac{\partial \log \omega_{qv}}{\partial \log V}$, which quantifies the anharmonicity of phonons with volume change is negative for the soft modes R and M points. As a result, an increase in phonon frequency takes place for the observed lattice expansion $V(\text{SC1}) > V_0(\text{DFT})$. Considering lattice thermal expansion, the QPNL level of theory continues to provide the most accurate prediction of the phase transition temperature (T_c) compared to experimental data. However, there is a net decrease by about 44-52 cm^{-1} in the predicted T_c relative to values obtained using $V_0(\text{DFT})$, consistent with previous findings for $\alpha\text{-CsPbBr}_3$ case.⁴⁶

Additional insight into the effect of strong anharmonic effects in CsPbCl_3 can be learned from the work of Harada *et al.*⁷⁰ Based on neutron diffraction investigations of the cubic phase of CsPbCl_3 at 328 K, anomalously large thermal vibrations for Cs and Cl atoms have been identified. In particular, the potential energy surface around the Cl atom was found to be highly anisotropic and very shallow in the (001) plane, perpendicular on Cl-Pb direction. This shallow potential will facilitate large displacements of the Cl atoms, particularly low-frequency rotations of the PbCl_6 octahedra that are susceptible to anharmonic effects. The

existence of large anharmonicity in potential energy surface of CsPbCl₃ was also reported by Fujii *et al.*¹³ who have determined based on inelastic neutron-scattering experiments a large mean square displacement for the Cl atom of 0.16 Å² at $T=353$ K.³⁵ This value was characterized¹³ as being about one order of magnitude larger than those seen in usual ionic crystals.

We have analyzed the mean-square-displacements (MSD) of various atoms in the CsPbCl₃ cell at different theoretical levels and the corresponding results are summarized in panels a-c of Figure S4. Inspection of the data indicates that substantial differences exist in the MSD sets for different atoms with values increasing from Pb to Cs and Cl atoms. In particular, our results confirm the presence of a large anisotropy for the potential energy surface around the Cl atom with substantially larger MSD values for the y and z components than for the x component. Different theoretical levels used in calculations have also influenced the final results obtained with the MSD values calculated at the SC1 level being the smallest as can be seen from data in Figure S4. Among the QP[0], QP[S] and QPNL set of results, the largest values are obtained for the y/z components of Cl atom when predicted at the QP[0] and QPNL levels. A direct comparison of the calculated MSD data at the QPNL level with experimental results reported by Harada *et al.*⁷⁰ at 328 K and respectively by Fujii *et al.*¹³ at 353 K is provided in Figure 3b. As seen from this figure, the agreement with the QPNL data is quite good not only to describe the differences in the MSD values for different atoms but also the high anisotropy present for different Cartesian components in the Cl case. This high anisotropy and

the associated large displacements observed for Cl atom were emphasized⁷⁰ to play an important role in the observed phase transition of CsPbCl₃ crystal.

Additional insight into the accuracy of the phonon calculations can be obtained based on analysis of the spectral function. This has been done by calculating the frequency-dependent bubble self-energy which allows an accurate prediction of both the phonon frequency shift and of the phonon linewidth. Figure 4 provides a visual comparison of the results of spectral analysis with the anharmonic phonon dispersion curves as obtained using the SC1, QS[0] and QPNL methods both for temperatures below and respectively above the phase transition. In the case of the spectrum at 220 K, the largest difference from the calculated spectral function is observed in the case of SC1 data particularly in the region of the soft modes. For the QS[0] results, noticeable differences compared to spectral function are observed for phonon frequencies in the range 60-110 cm⁻¹ with some of the modes being underestimated by more than 10 cm⁻¹. Similar findings were reported for CsPbBr₃ crystal,⁴⁶ where it was concluded that, among various methods, QPNL provides the most accurate description of the phonon modes within the one-particle picture.

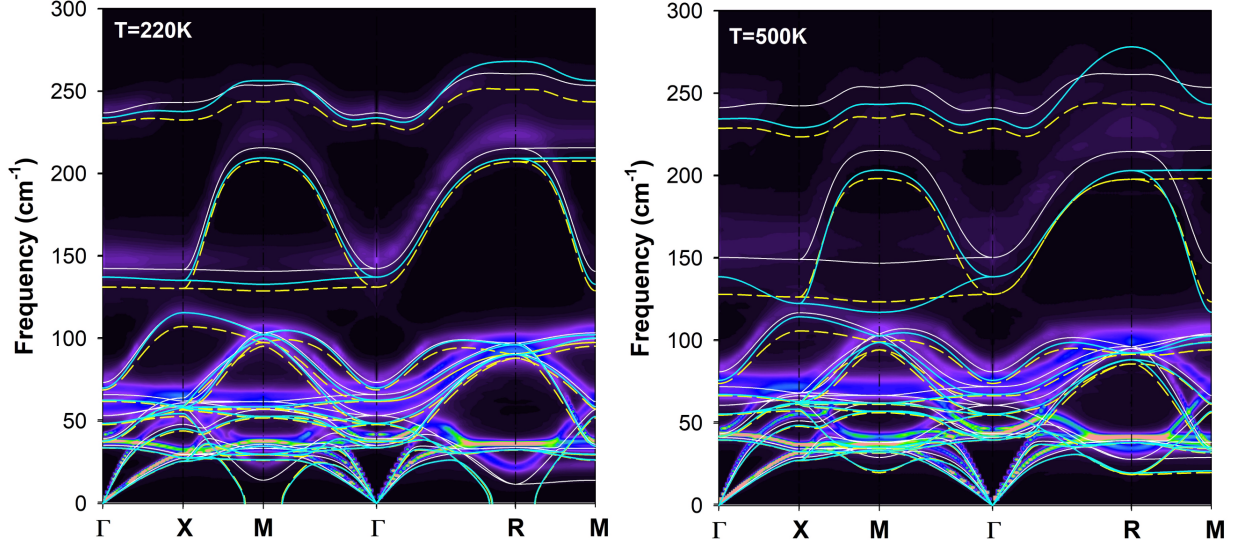


Figure 4. The calculated spectral function of CsPbCl₃ overimposed on the anharmonic phonon dispersion curves at 220 K and 500 K. The indicated white lines, yellow-dash lines and magenta lines correspond to the dispersion curves calculated at the SC1, QS[0] and QPNL levels.

The use of different QP theoretical levels to describe anharmonic effects in CsPbCl₃ has also direct influence on the corresponding Γ_{qv} phonon linewidths. These quantities have been determined based on the imaginary part of the phonon self-energy, $\Gamma_{qv}^B = \text{Im} \Sigma_{qv}^B[G, \Phi_3](\Omega_{qv})$ and the corresponding results are illustrated in Figure 5b. As can be seen, the phonon lifetimes calculated at the QPNL level have intermediate values between those determined at SC1 and QP[0] levels with the average phonon lifetimes below 70 cm⁻¹ at 500 K decreasing by a factor of 1.8 from 3.1 ps (SC1) to 1.7 ps (QP[0]). The overestimation of the phonon frequency seen for SC1 leads to an underestimation of the corresponding scattering

phase space, particularly for emission processes involving phonons with frequencies less than 70 cm^{-1} as shown in Figure S5.

Figure 5a analyzes the impact of different theoretical levels on lattice thermal conductivity of CsPbCl_3 , showing results at the SC1 and QP levels of theory for the Peierls terms κ_P and for the total $\kappa_L = \kappa_P + \kappa_C$ terms, which includes both the Peierls and coherent contributions as previously described in the methodological section. As seen in the figure, there are significant variations in lattice conductivity, with the largest values being seen for SC1 and the lowest for QP[0]. In particular, at 330 K the lattice conductivity κ_L decreases from 0.80 W/mK (SC1) to 0.48 W/mK (QP[0]) and 0.55 W/mK (QPNL), underlining the importance of different theoretical treatments of lattice anharmonicity. Coherent contributions (not shown) exhibit minimal variations across theoretical levels and temperature variations, with values, e.g. of 0.10, 0.12, 0.11 at 500 K for SC1, QP[0] and QPNL, respectively. As a result, the dependence on temperature of κ_L follows closely the corresponding κ_P term. Overall, the corrections done using the QP[0] and QPNL methods substantially decrease the lattice conductivity values relative to those determined at SC1 level. Furthermore, from the spectral dependence of the Peierls terms $\kappa_P(\omega)$ obtained using different theoretical levels and represented in Figure 5c, the largest contribution is seen to be determined by low-frequency phonons with a frequency less than 100 cm^{-1} where noticeable differences exist among the SC1, QP[0] and QPNL sets of results. In this frequency range, there are also important contributions to Peierls $\kappa_P(\omega)$ terms involving optical phonons with frequencies of 40 cm^{-1}

and higher. As the phonon group velocity does not show appreciable variations with various computational methods used (see Figure S6) it follows that the observed changes in κ_p values at different theoretical levels are primarily influenced by changes in the corresponding phonon lifetimes. At T=500K, variations of κ_p values from 0.62 W/mK at SC1 to 0.23 W/mK at QP[0] and 0.36 W/mK at QPNL follow closely the corresponding decrease in average phonon lifetimes by factors of 1.8 and 1.7, particularly for phonons below 70 cm⁻¹. Another important remark is that the small lattice thermal conductivity identified in CsPbCl₃ is related to the small phonon group velocity in this crystal, similar to previous findings for CsPbBr₃ case.⁴⁶ Furthermore, inspection of the atomic participation ratio projected on the phonon bands in Figure S3 indicates the presence of nearly localized bands for Cs atom. Flat phonon bands were associated to rattling mode of guest atoms inside clathrates and shown to increase the phonon-phonon scattering phase space, anharmonic hybridization between the acoustic and rattling modes, and thereby reduce the phonon lifetimes in a wide frequency range.⁷² Thus, the rattling-like mode of Cs can also contribute to realizing the relatively small phonon lifetimes of Cs perovskites, as pointed out in a recent study on double perovskite Cs₂AgBiB₆.³⁵

A key observation from the results in Figure 5a is that all QP datasets yield values below 0.6 W/mK. These low thermal conductivity values are consistent with experimental results obtained by He *et al.*,²⁸ who reported lattice thermal conductivity values lower than 0.6 W/mK in the temperature range 300-700 K. The lattice thermal conductivity was determined in this

study²⁸ based on the product $\kappa = DC_p\rho$ of the measured values for thermal diffusivity (D) and density (ρ), while the specific heat capacity (C_p) was calculated based on the Dulong-Petit law.

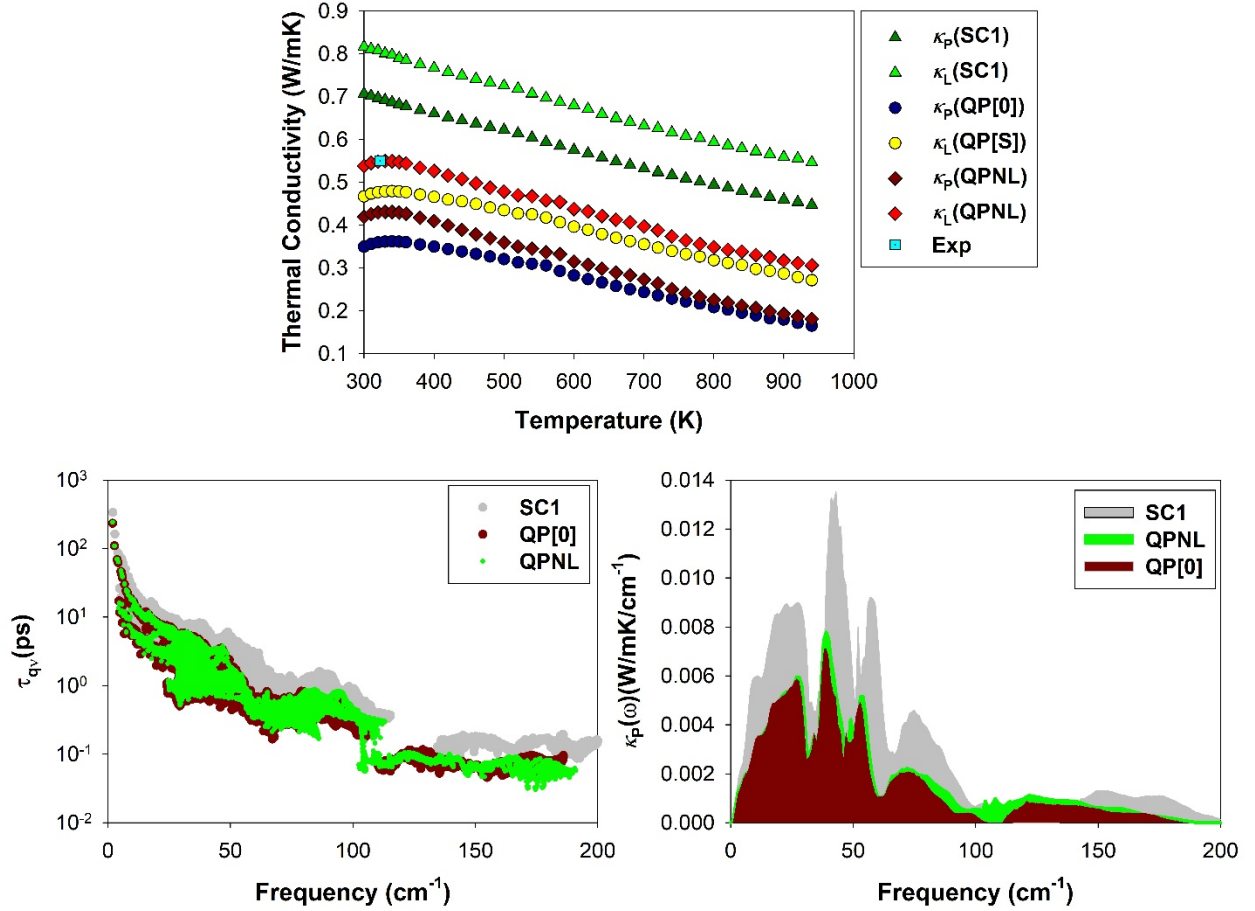


Figure 5. (a) The calculated total (κ_L) and Peierls terms (κ_P) lattice thermal conductivity for the cubic phase of CsPbCl₃ at different theoretical levels together with the experimental data (indicated with Exp acronym) of Kubičár *et al.*²⁶ at 323 K. (b) Phonon lifetimes at 500 K. (c) Spectral distribution of the Peierls terms at 500 K.

However, different from the increasing trend of the lattice thermal conductivity data with temperature reported by He *et al.*,²⁸ a continuous decrease is observed in our results, similar to

experimental results obtained by Lee *et al.*²² for CsPbI₃, CsPbBr₃, and CsSnI₃ systems. Our calculated lattice thermal conductivity results can be also compared with experimental data of Kubičár *et al.*²⁶ at 323 K that are shown in Figure 5a. As can be observed, the QPNL method provides a very good agreement with Kubičár *et al.*²⁶⁻²⁷ data, whereas the SC1 and QP[0] methods overestimate and underestimate their experimental values, respectively.

A final aspect analyzed in this work is related to prediction of the lattice thermal conductivity of CsPbCl₃ using machine learned potentials in combination with the HNEMD methods.⁵² As indicated earlier in this study two sets of NEP potentials have been used,⁵³⁻⁵⁴ able to describe the evolution with temperature of different phases of CsPbCl₃. Important for this study is the fact that above 300 K both potentials correctly predict the presence of the cubic phase for CsPbCl₃.

A first use of these NEP3 potentials for our systems was in predicting the crystalline lattice expansion at ambient pressure for the cubic phase of CsPbCl₃. This has been done for atomistic models containing large 18×18×18 supercells, initially taken to have the cubic symmetry of CsPbCl₃. Based on *NpT*-MD simulations we have determined the lattice expansion as function of temperature at ambient pressure and the corresponding results are reported in Figure 3a where they are compared with data obtained from the current SC1-based calculations as well as with various experimental data sets. The figure demonstrates a very good agreement for the lattice constant expansion as determined from SC1 analysis and NEP(CX) potential, with results of *NpT*-MD simulations almost superimposed on the

ALAMODE predicted values. The PBE results slightly overestimate the size of the lattice constant when compared to NEP(CX) or the experimental results, but overall, both NEP results follow closely the experimentally observed temperature dependence.

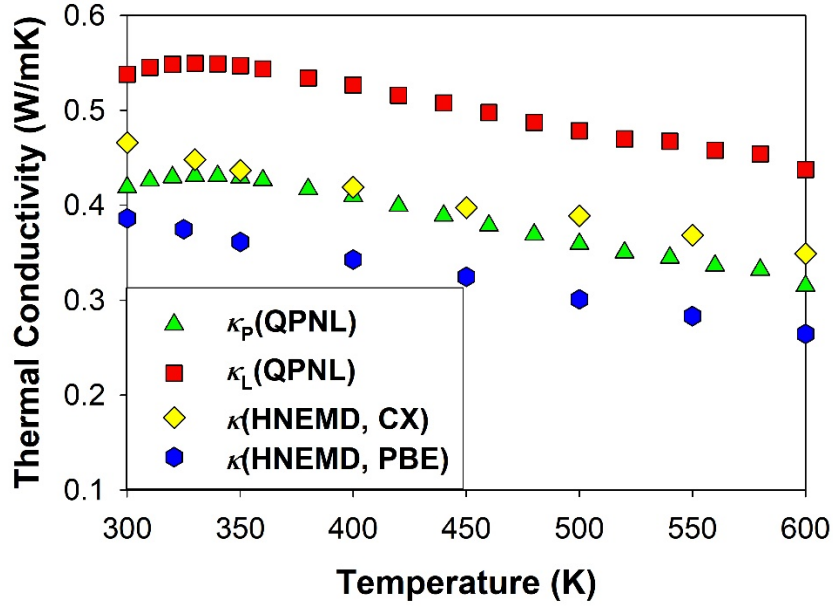


Figure 6. Comparison of the κ , κ_P lattice thermal conductivity terms obtained at the QPNL level using ALAMODE code with the HNEMD results determined using GPUMD code with NEP(CX) and NEP(PBE) machine learned neuroevolution potentials.

Using the NEP(CX) and NEP(PBE) sets of potentials the lattice thermal conductivity was determined next based on HNEM simulations. The corresponding results are shown in Figure 6 together with the set of κ_P and κ_L values obtained at the QPNL level. The NEP results represent the result of averaging 10 independent runs, each having a duration of 20 ns and

started with a different set of initial velocities. Figure 5 shows a very close agreement between the data obtained using NEP(CX) potentials and κ_l (QPNL) results while a slight underestimation is seen for NEP(PBE) data. Additionally, at 300 K, our result for lattice thermal conductivity using NEP(PBE) potential of 0.39 W/mK reproduces closely the value of 0.40 W/mK reported by the developers of this potential.⁵³ Overall, both sets of NEP predictions indicate a decreasing trend with temperature for the lattice thermal conductivity similar to our results obtained using the QPNL method. As previously emphasized, this contrasts with the increasing trend of lattice thermal conductivity with temperature reported by He *et al.*²⁸ It should be also noted that independent of the method and theoretical levels used, all three sets of results in Figure 6 indicate the existence of a low lattice thermal conductivity of CsPbCl₃ in the cubic phase, consistent to experimental values reported by Kubičár *et al.*²⁶ and He *et al.*²⁸ but distinct from the findings of Hager *et al.*²⁹ where a larger value of about 1.60 W/mK was reported for the cubic phase above 320 K. From the data in Figure 6 it is seen that the lattice thermal conductivity determined using NEP potentials are systematically smaller than κ_l (QPNL) values. A possible reason for this is that current ALAMODE calculations may overestimate thermal conductivity because they do not account for the four-phonon scattering process. However, as shown in Figure 5a with the current computational settings used in ALAMODE, a very good agreement has been obtained for κ_l (QPNL) with experimental data of Kubičár *et al.*²⁶ at 323 K. Conversely, the results of GPUMD(NEP) and potentially other machine-learned potentials inherently include force errors which, as shown in recent work,⁷³ can underestimate the calculated thermal conductivity.

In summary, among the theoretical methods considered in this study and implemented in ALAMODE code, the QPNL method consistently provides more accurate results compared to available experimental data. This accuracy is evident from prediction of lattice expansion coefficients, the phase transition temperature, the MSD values, and lattice thermal conductivity. A very good agreement was also obtained in the predicted lattice expansion between the SC1 analysis performed with ALAMODE and NpT -MD results generated using NEP(CX) potential. Furthermore, a similar decreasing trend with temperature has been found when comparing the QPNL lattice thermal conductivity data with the HNEM-MD results obtained using much larger size systems and for trajectories extending to 20 ns. The calculated κ_L (QPNL) values for CsPbCl_3 are found to be also close to those of other similar all-inorganic halide perovskites. For example, at 500 K the QPNL value for CsPbCl_3 calculated in this study of 0.48 W/mK compares favorably to the values of 0.50 W/mK reported for α - CsPbBr_3 ⁴⁶ or of 0.46 W/mK for α - CsSnBr_3 .⁷⁴

4. CONCLUSIONS

First-principles simulations have been conducted to predict the anharmonic lattice dynamics and lattice thermal conductivity of cubic CsPbCl_3 . The results obtained using self-consistent phonon approach were extended to include frequency renormalization effects by the bubble self-energy. The unstable soft modes present in the harmonic approximation have been found to correspond to in-phase and out-of-phase rotations of PbCl_6 octahedra. The analysis performed for diverse types of lattice properties including lattice expansion,

prediction of cubic to tetragonal phase transition, mean-square-displacements and lattice thermal conductivity show systematic improvement upon extending the self-consistent phonon approach to include bubble diagram treatments within quasiparticle approximation. Among different QP[0], QP[S] and QPNL levels of approximation, the QPNL treatment provided the most accurate results relative to experiments. In particular, the lattice thermal conductivity for CsPbCl₃ at 320 K is found to be practically identical to results reported by Kubičár *et al.*²⁶ while over the temperature range 300-800 K the calculated results are all below 0.6 W/mK, consistent with experimental findings reported by He *et al.*²⁸ Extension of the calculated results to systems much larger than those possible when using quantum calculations was obtained by performing equilibrium and non-equilibrium MD simulations using NEP3 neuroevolution potentials, developed previously for different phases of CsPbCl₃. The results obtained in this study for the lattice expansion and lattice thermal conductivity of the cubic phase, particularly when using NEP(CX) potentials⁴⁸ match ALAMODE results confirming not only the overall low thermal conductivity for CsPbCl₃ crystal but also the general decreasing trend with temperature, similar to results reported for other all-inorganic halide perovskites.

ASOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at
<https://>

The calculated convergence tests, atomic participation ratio of α -CsPbCl₃ projected on the phonon bands, the mean-square-displacements for different atoms in CsPbCl₃, mode-resolved scattering phase space and phonon group velocity (PDF).

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Notes

The authors declare no competing financial interest.

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TOC Graphic

