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1 Introduction

Halide perovskite materials emerged in the last decade as revolutionary materials for applications in solar cells,¹⁻⁴ lasers,⁵ light-emitting diodes,^{6,7} photodetectors,^{8,9} detectors of ionizing radiation,^{10,11} thermoelectric¹² and other devices.¹³ To understand the characteristics of these devices and to design improved materials and devices, it is essential to be able to predict the electronic structure of the material. Despite great interest in understanding the electronic structure of halide perovskites and numerous developments of the methods for electronic structure calculations and the software for performing such calculations, it is still rather challenging to accurately determine the electronic structure of halide perovskites.

It is currently well understood that in electronic structure calculations of halide perovskites one has to take into account the effects of spin–orbit interactions due to the presence of

Ab-initio calculations of temperature dependent electronic structures of inorganic halide perovskite materials[†]

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Despite wide interest in halide perovskite materials, it is still challenging to accurately calculate their electronic structure and its temperature dependence. In this work, we present ab-initio calculations of the temperature dependence of the electronic structure of CsPbX₃ materials (X = Cl, Br or I) in the cubic form and of the zero temperature electronic structure of the orthorhombic phase of these materials. Phononinduced temperature dependent band energy renormalization was calculated within the framework of Allen-Heine-Cardona theory, where we exploited the self-consistent procedure to determine both the energy level shifts and their broadenings. The phonon spectrum of the materials was obtained using the self-consistent phonon method since standard density functional perturbation theory calculations in harmonic approximation yield phonon modes with imaginary frequencies due to the fact that the cubic structure is not stable at zero temperature. Our results suggest that low energy phonon modes mostly contribute to phonon-induced band energy renormalization. The calculated values of the band gaps at lowest temperature where the material exhibits a cubic structure are in good agreement with experimental results from the literature. The same is the case for the slope of the temperature dependence of the band gap for the CsPbI₃ material where reliable experimental data are available in the literature. We also found that phonon-induced temperature dependence of the band gap is most pronounced for the conduction band minimum and valence band maximum, while other bands exhibit a weaker dependence.

heavy atoms such as lead.^{14–16} As in the case for many other semiconductors, standard local or semilocal approximations to density functional theory (DFT) underestimate the material band gap^{14–16} and more sophisticated approaches, such as the use of GW approximation^{17–19} or hybrid functionals,^{20,21} are necessary.

A group of challenges arises when it comes to predicting the electronic structures of halide perovskites at room or higher temperatures which are relevant for application in the mentioned devices. Temperature effects on the band gap and the overall electronic structure of perovskites are rather pronounced^{22–28} and one cannot simply consider the electronic structure calculated for fixed atoms in a crystal lattice as the electronic structure at higher temperatures.

The most successful theory for determining the temperature effects on the electronic structure of semiconductors is the Allen–Heine–Cardona theory.^{29–31} Within this theory, one expands the Hamiltonian up to second order terms in atomic displacements from the equilibrium position and perturbatively evaluates the change in band energies. In conjunction with the methods for the electronic structure calculation for fixed atomic positions, this theory was used to study the temperature dependence of the band gap and zero temperature band gap renormalization in a variety of semiconductors.^{31–36} However, this theory can be



Institute of Physics Belgrade, University of Belgrade, Pregrevica 118, 11080 Belgrade, Serbia. E-mail: milan.jocic@ipb.ac.rs, nenad.vukmirovic@ipb.ac.rs † Electronic supplementary information (ESI) available: Supplementary figures and cif files with initial and relaxed coordinates of the orthorhombic structure of CsPbX₃ materials. See DOI: https://doi.org/10.1039/d3cp02054a

straightforwardly applied to a particular material only if its crystal structure at a given temperature is the same as at zero temperature.

The last condition is not fulfilled in halide perovskite materials. Inorganic halide perovskite materials CsPbX₃ (X = Cl, Br or I) that are of main interest in this work exhibit a cubic structure at high temperatures only.^{37–42} As the temperature is lowered, they transform into a tetragonal structure and finally to an orthorhombic structure.^{37–40} Therefore, the cubic structure is not a stable structure at zero temperature. When one attempts to calculate the phonon dispersion in the material by assuming a cubic structure at zero temperature, phonon modes of imaginary frequencies are obtained^{40,43–45} and it is not clear how to treat such phonons within the Allen–Heine–Cardona theory.

Previous studies on the effects of temperature on halide perovskite semiconductors have not addressed other bands than the conduction band minimum (CBM) and the valence band maximum (VBM). While these two bands are most relevant for the determination of the band gap of the material, there is significant interest in knowing the energies of the other bands. These are important, for example, to understand the optical response of the material in the ultraviolet spectral range relevant for ultraviolet detectors.9 On the theoretical side, the knowledge of band energies at characteristic points in the Brillouin zone is necessary to construct multiband Hamiltonians46-49 that can further be used to predict the electronic states in halide perovskite nanostructures. While the renormalization of energies of the other bands can in principle be obtained in the same way as for CBM and VBM within Allen-Heine-Cardona theory, certain issues, related to the energy level broadening parameter δ , arise. On the one hand, band renormalization for other bands converges linearly with respect to δ when $\delta \rightarrow 0$ in contrast to Lorentzian convergence of CBM and VBM,³² which makes it more challenging to obtain the convergence of other bands. On the other hand, other bands typically exhibit larger broadening of energy levels compared with the CBM and VBM. Consequently, it is questionable if one should evaluate the $\delta \rightarrow 0$ limit for other bands at all. Preferably, the broadening of the energy levels should be evaluated simultaneously with the band energy renormalization.

In this work, we perform electronic structure calculations of the temperature dependence of the band gap and band energies for halide perovskite materials CsPbX₃ (X = Cl, Br or I) in a cubic crystal structure. Electronic structure calculations (without the effects of phonon-induced band renormalization) are performed using a hybrid functional that satisfies the Koopmans condition. The challenge of treating phonons within the Allen-Heine-Cardona theory is overcome by performing phonon band structure calculations at a finite temperature within the framework of self-consistent phonon (SCPH) theory, where all phonon modes remain stable. The challenge of the choice of energy level broadening is overcome by performing the calculation in which energy levels and their broadening are determined selfconsistently. We compare the obtained temperature dependence of the band gap for the cubic structure to experimental results from the literature. We also perform calculations of the orthorhombic structure at zero temperature and comment on the

overall temperature dependence of the band gap of $CsPbX_3$ materials from zero to high temperatures.

This paper is organized as follows. In Section 2, we present the main methods that were used in this work. Allen-Heine-Cardona theory is briefly reviewed in Section 2.1 along with the description of the two approaches that were used to calculate phonon-induced band energy renormalization within this theory. The SCPH method is reviewed in Section 2.2. In Section 3 we present the results obtained and the details of the calculations. We start with the results obtained using standard density functional theory (DFT) calculations with semilocal functionals that are presented in Section 3.1. In Section 3.2 we present the results obtained using a hybrid functional that gives improved values of the material band gap. Density functional perturbation theory (DFPT) based calculations of the phonon spectrum are reported in Section 3.3, while SCPH calculations of the phonon spectrum are presented in Section 3.4. In Sections 3.5 and 3.6 we present the main results of this work for the temperature dependence of renormalization of band energies, while we compare the results obtained with experiments in Section 3.7. We close the paper with a discussion and conclusions in Section 4.

2 Methods

2.1. Allen-Heine-Cardona theory

In this section, we briefly review the Allen–Heine–Cardona theory that describes phonon-induced band gap renormalization in semiconductor materials and present the procedure for self-consistent calculation of phonon-induced renormalization of band energies and their broadenings. The Hamiltonian of the system is given as

$$H = H_{\rm el} + H_{\rm ph} + H_{\rm el-ph}.$$
 (1)

The first term

$$H_{\rm el} = \sum_{kn} \varepsilon_{kn} \hat{c}^{\dagger}_{kn} \hat{c}_{kn}, \qquad (2)$$

describes the electrons, where \hat{c}_{kn}^{\dagger} and \hat{c}_{kn} are creation and annihilation operators, respectively, of an electron with wave vector \boldsymbol{k} and electronic band n whose energy is ε_{kn} . The second term

$$H_{\rm ph} = \sum_{q\nu} \hbar \omega_{q\nu} \left(\hat{a}^{\dagger}_{q\nu} \hat{a}_{q\nu} + \frac{1}{2} \right) \tag{3}$$

describes the phonons, where $\hat{a}_{q\nu}^{\dagger}$ and $\hat{a}_{q\nu}$ are phonon creation and annihilation operators, respectively, of a phonon with wave vector \boldsymbol{q} and phonon mode ν whose angular frequency is $\omega_{q\nu}$. The third term $H_{\text{el-ph}}$ is the Hamiltonian of the electron–phonon interaction. By including the terms up to second order with respect to atomic displacements, it takes the form

$$H_{\text{el-ph}} = \frac{1}{N_q^{1/2}} \sum_{\boldsymbol{k}nm} \sum_{\boldsymbol{q}\nu} g_{nm,\nu}^{\text{Fan}}(\boldsymbol{k},\boldsymbol{q}) \hat{c}_{\boldsymbol{k}+\boldsymbol{q}m}^{\dagger} \hat{c}_{\boldsymbol{k}n} (\hat{a}_{-\boldsymbol{q}\nu}^{\dagger} + \hat{a}_{\boldsymbol{q}\nu}) + \frac{1}{N_q} \sum_{\boldsymbol{k}nm} \sum_{\boldsymbol{q}\boldsymbol{q}'\nu\nu'} g_{nm,\nu\nu'}^{\text{DW}}(\boldsymbol{k},\boldsymbol{q},\boldsymbol{q}') \hat{c}_{\boldsymbol{k}+\boldsymbol{q}+\boldsymbol{q}'m}^{\dagger} \hat{c}_{\boldsymbol{k}n}$$
(4)
$$\times (\hat{a}_{-\boldsymbol{q}\nu}^{\dagger} + \hat{a}_{\boldsymbol{q}\nu}) (\hat{a}_{-\boldsymbol{q}'\nu'}^{\dagger} + \hat{a}_{\boldsymbol{q}'\nu'}),$$

where $g_{nm,\nu}^{Fan}(k,q)$ and $g_{nm,\nu\nu'}^{DW}(k,q,q')$ are first order Fan and second order Debye-Waller matrix elements of electron-phonon interactions and N_q is the number of points in reciprocal space. The first order Fan matrix element is given as:

$$g_{nm,\nu}^{\text{Fan}}(\boldsymbol{k},\boldsymbol{q}) = \sum_{\kappa\alpha} \left(\frac{\hbar}{2M_{\kappa}\omega_{\boldsymbol{q}\nu}}\right)^{1/2} \times \langle \boldsymbol{k} + \boldsymbol{q}n | \frac{\partial V_{\text{SCF}}}{\partial R_{\kappa\alpha}(\boldsymbol{q})} | \boldsymbol{k}m \rangle \xi_{\kappa\alpha,\nu}(\boldsymbol{q}) e^{i\boldsymbol{q}\cdot\boldsymbol{R}_{\kappa}}$$
(5)

where $\frac{\partial V_{\text{SCF}}}{\partial R_{\kappa\alpha}(q)}$ and $\xi_{\kappa\alpha,\nu}(q)$ are the perturbation of the Kohn–Sham

potential due to nuclear displacement and the phonon eigenvector, respectively, describing the displacement of atom κ with mass M_{κ} at position \mathbf{R}_{κ} in Cartesian direction α corresponding to phonon vector (mode) $\boldsymbol{q}(\nu)$. The self-energy stemming from the first term in eqn(4) reads

$$\Sigma_{kn}^{\mathrm{Fan}}(\omega,T) = \frac{1}{N_q} \sum_{m,q\nu} \left| g_{nm,\nu}^{\mathrm{Fan}}(\boldsymbol{k},\boldsymbol{q}) \right|^2 \\ \times \left(\frac{n_{q\nu}(T) + 1 - f_{\boldsymbol{k}+\boldsymbol{q}m}}{\omega - \varepsilon_{\boldsymbol{k}+\boldsymbol{q}m} - \omega_{q\nu} + i\delta} + \frac{n_{q\nu}(T) + f_{\boldsymbol{k}+\boldsymbol{q}m}}{\omega - \varepsilon_{\boldsymbol{k}+\boldsymbol{q}m} + \omega_{q\nu} + i\delta} \right)$$
(6)

where $n_{qv}(T)$ is the Bose-Einstein occupation factor at a temperature T, f_{k+qm} is the Fermi–Dirac occupation factor and δ is a positive infinitesimal. The self-energy from the second term in eqn (4) takes the form

$$\Sigma_{\boldsymbol{k}nm}^{\text{DW}}(T) = \frac{1}{N_q} \sum_{\boldsymbol{q}\nu} g_{nm,\nu\nu}^{\text{DW}}(\boldsymbol{k},\boldsymbol{q},-\boldsymbol{q})(2n_{\boldsymbol{q}\nu}(T)+1), \quad (7)$$

where the second order electron-phonon matrix elements $g_{nm,n/}^{DW}$ (k, q, -q) from eqn (7) can be expressed in terms of first order electron-phonon matrix elements by making use of translational invariance and rigid-ion approximation.^{29,50}

The renormalization of energy levels can be calculated from the self-energies. Within the so-called on-the-mass-shell (OTMS) approximation,⁵¹ the renormalized energy of band nat point k in the Brillouin zone is

$$E_{kn}(T) = \varepsilon_{kn} + \operatorname{Re}\Sigma_{kn}^{\operatorname{Fan}}(\varepsilon_{kn}, T) + \operatorname{Re}\Sigma_{kn}^{\operatorname{DW}}(T).$$
(8)

As discussed in the Introduction, there are challenges in obtaining converged results for band energy renormalization for bands other than VBM and CBM using eqn (6), (7) and (8). The convergence with respect to energy level broadening parameter δ as $\delta \rightarrow 0$ is a slow linear convergence³² and hence one needs to use rather small δ , which in turn requires a large number of q-points in the summation. The broadening of the energy levels obtained from the imaginary part of the self-energy is on the order of 100 meV or more. It is therefore questionable if the $\delta \rightarrow 0$ limit is relevant at all. It is certainly more appropriate to self-consistently determine the renormalization and broadening of the energy levels. This can be achieved as follows. We note first that the terms $\frac{1}{\omega - \varepsilon_{k+qm} \pm \omega_{q\nu} + i\delta}$ in eqn (6) represent the retarded Green's function of a bare electron $G_{k+am}^{(0)}(\omega \pm \omega)$

 $\omega_{a\nu}$, while eqn (6) is the self-energy in the so-called Migdal approximation. A more accurate approximation is the selfconsistent Migdal approximation where the bare Green's function $G^{(0)}$ is replaced with the dressed Green's function G. Eqn (6) then takes the form

$$\Sigma_{kn}^{\text{Fan}}(\omega) = \frac{1}{N_q} \sum_{m,q\nu} \left| g_{nm,\nu}^{\text{Fan}}(\boldsymbol{k},\boldsymbol{q}) \right|^2 \\ \times \left[(n_{q\nu}(T) + 1 - f_{\boldsymbol{k}+\boldsymbol{q}m}) G_{\boldsymbol{k}+\boldsymbol{q}m}(\omega - \omega_{\boldsymbol{q}\nu}) + (n_{q\nu}(T) + f_{\boldsymbol{k}+\boldsymbol{q}m}) G_{\boldsymbol{k}+\boldsymbol{q}m}(\omega + \omega_{\boldsymbol{q}\nu}) \right].$$
(9)

One can in principle determine the Green's function, the selfenergy, the spectral function and hence the energy level renormalization and broadening by self-consistently solving eqn (9) and the Dyson equation. However, this requires evaluation of all these quantities at wave vectors throughout the whole Brillouin zone in each step of the self-consistent procedure, which is a highly demanding computational task. A significant simplification that decouples different kn states can be made as follows. We first note that the Green's function in eqn (9) is given as

$$G_{k+qm}(\omega) = \frac{1}{\omega - \varepsilon_{k+qm} - \Sigma_{k+qm}(\omega)}.$$
 (10)

We then make a replacement $\Sigma_{k+qm}(\omega) \rightarrow \Sigma_{kn}(\omega)$ in the previous equation (where $\Sigma_{kn}(\omega) = \Sigma_{kn}^{\text{Fan}}(\omega) + \Sigma_{kn}^{\text{DW}}$). This replacement is justified by the fact that the dominant contribution to the sum in eqn (9) comes from the terms in the sum that have m = n and a small value of **q**. For such terms $\Sigma_{k+qm}(\omega) \approx \Sigma_{kn}(\omega)$. It is therefore appropriate to replace the self-energy for all terms in the sum with the self-energy of the dominant terms. The expression for Σ_{kn}^{Fan} then reads

$$\Sigma_{kn}^{\text{Fan}}(\omega) = \frac{1}{N_q} \sum_{m,q\nu} \left| g_{nm,\nu}^{\text{Fan}}(\boldsymbol{k}, \boldsymbol{q}) \right|^2 \\ \times \left(\frac{n_{q\nu}(T) + 1 - f_{\boldsymbol{k}+\boldsymbol{q}m}}{\omega - \varepsilon_{\boldsymbol{k}+\boldsymbol{q}m} - \omega_{q\nu} - \Sigma_{kn}(\omega - \omega_{q\nu})} \right) + \frac{n_{q\nu}(T) + f_{\boldsymbol{k}+\boldsymbol{q}m}}{\omega - \varepsilon_{\boldsymbol{k}+\boldsymbol{q}m} + \omega_{q\nu} - \Sigma_{kn}(\omega + \omega_{q\nu})} \right).$$
(11)

It is important to note that eqn (11) does not contain the self-energies of the states other than kn, which is a consequence of the approximation used for $\Sigma_{k+qm}(\omega)$. The self-energy $\Sigma_{kn}^{\text{Fan}}(\omega)$ can now be obtained using a self-consistent procedure as follows. One starts with an initial guess for $\Sigma_{kn}(\omega)$ and evaluates $\Sigma_{kn}^{\text{Fan}}(\omega)$ using eqn (11) and the total self-energy as the sum of the Fan and the Debye-Waller term. A new value of $\Sigma_{kn}^{\text{Fan}}(\omega)$ is then calculated again using eqn (11) and the procedure is repeated until the convergence of $\Sigma_{kn}^{\text{Fan}}(\omega)$ is reached. The spectral function is then obtained as

$$A_{kn}(\omega) = -\frac{1}{\pi} \text{Im} \frac{1}{\omega - \varepsilon_{kn} - \Sigma_{kn}(\omega)}$$
(12)

and the renormalized energy E_{kn} is obtained as the energy ω_{max} at which the spectral function reaches a maximum. The spectral function $A_{kn}(\omega)$ represents the probability density that an

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electron of momentum k in band n has the energy ω . We note that our procedure for evaluation of renormalized energies is similar in spirit to the procedure suggested in ref. 50 (Eq. 166 therein), where approximations that also lead to decoupling of different kn states were used. The difference between these procedures is that we consider the full frequency dependence of self-energies rather than the energy of the renormalized state and its broadening only.

In Section 3, we will present the results obtained using both of the mentioned approaches. The results obtained from eqn (8) with self-energies given by eqn (6) and (7) will be referred to as OTMS results, while the results obtained using eqn (12) and self-consistent solution of eqn (11) will be referred to as the self-consistent procedure (SCP) results.

We note that it is rather challenging to treat the electronphonon interaction in real materials beyond the approximations mentioned. These approximations all contain the assumption that the electron-phonon interaction is not too strong. Full nonperturbative treatment of electron-phonon interactions has so far only been performed for model Hamiltonians, such as the Holstein or Fröhlich model. In a recent study of the Holstein model⁵² it was shown that for relatively weak electron-phonon coupling the spectral functions in the Migdal and self-consistent Migdal approximation are similar to the spectral functions obtained using more advanced approaches, such as the cumulant expansion method and the dynamical mean field theory. Moreover, self-consistent Migdal approximation performs overall only somewhat worse than the cumulant expansion method, which is not the case for the Migdal approximation that gives inaccurate results starting from moderate values of electronphonon coupling. Based on the knowledge gained from the Holstein model, we can infer about the accuracy of the OTMS and SCP results for real perovskite materials. It is expected that the SCP results which are based on the self-consistent Migdal approximation should in principle be more accurate than the OTMS results which are based on the Migdal approximation. On the other hand, it will be shown in Section 3 that OTMS and SCP results are not too different. This suggests that we are in the regime where electron-phonon coupling is relatively weak, where it is appropriate to apply either the Migdal or the selfconsistent Migdal approximation.

We also note that in both the OTMS and SCP approach, as typically done in the literature,⁵⁰ we were evaluating only the diagonal (intraband) self-energies $\Sigma_{knn}(\omega)$ and not the offdiagonal (interband) self-energies $\Sigma_{knnn}(\omega)$ (with $n \neq m$). In the case of the OTMS approach one is actually interested in diagonal self-energies only because they directly determine the band energy renormalization, see eqn (8). On the other hand, introduction of off-diagonal self-energies in the SCP approach would strongly increase the computational burden of the whole procedure. On physical grounds, it should be noted that band energy renormalization due to interband electron-phonon scattering processes is already described by the diagonal self-energies [*via* the $m \neq n$ terms in the sum in eqn (6)]. Hence, inclusion of non-diagonal self-energies would represent only a higher order effect.

2.2. The self-consistent phonon method

Since the standard approach based on the use of harmonic approximation and DFPT is not sufficient to describe phonons in cubic $CsPbX_3$ materials, a more sophisticated approach is needed. We therefore use the self-consistent phonon method following the methodology and the implementation of ref. 53. In this section, we briefly review the main ideas of the method and its implementation.

In the Born–Oppenheimer approximation, the dynamics of lattice ions is described by the Hamiltonian H = T + U, where *T* is their kinetic energy, while *U* is the potential energy which is a function of the displacements from the equilibrium position. The potential energy can be expanded as $U = U_0 + U_2 + U_3 + U_4 + \ldots$, where the term U_n is of *n*-th order with respect to atomic displacements and the term U_1 is missing because it contains forces which are zero in equilibrium. Keeping the terms U_0 and U_2 only is the standard harmonic approximation. In this case, phonon frequencies are obtained from diagonalization of the corresponding dynamical matrix.

To obtain the phonon frequencies in a general case when the terms beyond U_2 are included, one can make use of many body Green's function theory. The Hamiltonian is divided into $H = H_0 + H_1$ where $H_0 = T + U_0 + U_2$ is the harmonic part of the Hamiltonian whose solution is known, while the anharmonic terms $H_1 = U_3 + U_4 + ...$ constitute the interaction part. The phonon Green's function G_0 for the Hamiltonian H_0 is known, while the Dyson equation relates G_0 , the phonon Green's function *G* of the Hamiltonian *H* and the self-energy Σ . The Dyson equation has to be complemented with the equation for selfenergy. The self-energy is in principle given by a diagrammatic expansion involving an infinite number of Feynman diagrams.



Fig. 1 Comparison of experimental and theoretical results for the electronic gap for CsPbX₃ (X = Cl, Br or I) calculated without taking temperature effects into account. The line x = y represents the experimental results for the lowest temperature of the cubic structure. The symbols denote calculated values for the cubic structure using the PBE (PBEsol) functional for CsPbI₃ (CsPbCl₃ and CsPbBr₃) (inverted triangles) and PBE0 functional modified to satisfy the Koopmans condition (diamonds).

In practice one selects only the most relevant diagrams for the problem at hand. To obtain the renormalized phonon frequencies, it turns out that the most relevant diagram is the loop diagram originating from the quartic term U_4 (shown in Fig. 1(a) in ref. 53). The Green's function and the self-energy can then be found self-consistently and the renormalized phonon frequency is determined from the pole of the Green's function.

To perform the calculation within the SCPH method, one also has to obtain all relevant force constants that appear in the U_n terms in the expansion of U. The second order force constants are obtained from supercell density functional theory calculations and the finite displacement method. While the finite displacement method can in principle be used to obtain higher order force constants, a different strategy yields more stable results for the force constants. Namely, finite-temperature *ab-initio* molecular dynamics calculations are performed to obtain various atomic configurations and the corresponding total energy and forces in these configurations. The force constants that appear in anharmonic terms in U are then fitted to the data obtained, where great care has to be taken to avoid overfitting the data. Details of the full calculation protocol are reported in Section 3.4.

3. Results and calculation details

3.1. Density functional theory calculations with semilocal functionals

As a first step, we performed density functional theory calculations of the electronic structure of the CsPbX₃ materials using the semilocal PBEsol⁵⁴ functional in the case of CsPbCl₃ and CsPbBr₃, while the PBE functional⁵⁵ was used in the case of CsPbI₃. Calculations were performed using the plane-wave code Quantum Espresso.^{56,57} Norm-conserving fully relativistic pseudopotentials^{58,59} were used to treat the effect of core electrons. The effects of spin–orbit interaction were included. The wave functions were represented on a $4 \times 4 \times 4$ reciprocal space k- point grid with a kinetic energy cutoff of 50 Ry for CsPbCl₃ and CsPbBr₃ and a cutoff of 40 Ry for CsPbI₃. We note that a different functional was used for CsPbI₃ because the gap obtained using the PBEsol functional at the optimized lattice constant obtained from this functional is nearly zero, which prevents the use of this functional in further DFPT calculations.

The optimized lattice constants for the cubic structure obtained from the calculations are respectively 10.6 a_0 , 11.1 a_0 and 12.1 a_0 (in units of first Bohr radius a_0 for CsPbCl₃, CsPbBr₃ and CsPbI₃). We note that the lattice constants obtained for CsPbCl₃ and CsPbBr₃ are in excellent agreement with the experimental lattice constant at the lowest temperature where the material exhibits a cubic structure (which are 10.59 a_0 at 320 K for CsPbCl₃ and 11.10 a_0 at 403 K for CsPbBr₃, see ref. 42). This agreement is reasonable in the case of CsPbI₃ (experimental lattice constant is 11.67 a_0 at 300 K, see ref. 60) and would be better if the PBEsol functional, which gives the lattice constant of 11.8 a_0 , was used. However, as noted before, the use of PBEsol functional for CsPbI₃ closes the gap of the material and hence this functional was not used for CsPbI₃. While the agreements

obtained are somewhat fortuitous because standard DFT calculations are performed at zero temperature, the lattice constants obtained were used in further calculations because they are in good agreement with experimental lattice constants. The direct band gaps at the *R*-point obtained for CsPbCl₃, CsPbBr₃ and CsPbI₃ are respectively 0.59 eV, 0.22 eV and 0.21 eV. These gaps are well below the experimental band gaps, see Fig. 1. This is expected because it is well known that semilocal functionals underestimate the band gap.⁶¹

We also performed calculations for the orthorhombic structure of the CsPbX₃ material that is stable at zero temperature. The coordinates of the initial structure were taken from The Materials Project website⁶² as structures numbered 675 524, 567 629, and 1 120 768 for CsPbCl₃, CsPbBr₃ and CsPbI₃, respectively, and were further relaxed (cif files for the initial and relaxed structures are included in the ESI[†]). The CsPbCl₃ orthorhombic structure corresponds to space group number 38 (Amm2) with 10 atoms per primitive cell, while CsPbBr3 and CsPbI3 orthorhombic structures both correspond to space group number 62 (Pmna) with 20 atoms per primitive cell. The same density functionals, k-point grid dimension, and the plane wave kinetic energy cutoff were used as in the case of the cubic structure. We used the PBEsol functional for optimization of atomic coordinates and dimensions of the unit cell for all three materials (since the gap of orthorhombic CsPbI3 does not close when the PBEsol functional is used in the calculation). The calculations were performed using the Quantum Espresso code56,57 with variable cell relaxation option. The band gaps obtained for orthorhombic CsPbCl₃, CsPbBr₃ and CsPbI₃ are respectively 1.1 eV, 0.83 eV and 0.62 eV.

3.2. Hybrid functional calculations

To overcome the band gap problem of semilocal functionals, we performed the electronic structure calculation using a hybrid functional. In particular, we make use of the PBE0 functional^{63,64} whose parameter α is chosen to satisfy the Koopmans condition. We used the values of α for CsPbX₃ materials that were calculated in ref. 65. Hybrid functional calculations were also performed using the Quantum Espresso code.^{56,57,66} The calculation parameters common to standard semilocal DFT calculation were set to the same values. In addition, for cubic structures a $4 \times 4 \times 4$ reciprocal q- points grid was used to sample the Fock operator and the Gygi-Baldereschi method⁶⁷ was used to treat the singularity at $q \rightarrow 0$. For orthorhombic structures that have a larger unit cell than cubic structures, $3 \times 3 \times 2 k$ - and q-points grids were used in the case of CsPbBr₃ and CsPbI₃, while we used $4 \times 4 \times 4 \times 4 \times 4 k$ - and q-points grids for CsPbCl₃.

In hybrid functional calculations, we obtain the values of 2.4 eV, 1.5 eV and 0.96 eV for the band gap of cubic CsPbCl₃, CsPbBr₃ and CsPbI₃. These values are closer to experimental values than the values obtained from semilocal functionals. However, these values are still smaller than the experimental band gaps, see Fig. 1. This result indicates that temperature effects might play a significant role and that it is important to investigate them.

In the case of orthorhombic structures, we obtain band gaps of 3.0 eV, 2.4 eV and 1.5 eV, respectively for CsPbCl₃, CsPbBr₃

and CsPbI₃. These results are in good agreement with experimental gaps of the low-temperature orthorhombic structures, which are 3.056 eV for CsPbCl₃ (ref. 68), 2.25 eV for CsPbBr₃ (ref. 69) and 1.72 eV for CsPbI₃ (ref. 70).

3.3. Density functional perturbation theory calculations of the phonon band structure

To take into account the effect of temperature on the electronic band structure, it is necessary to calculate the phonon frequencies and eigenvectors and the electron–phonon coupling constants. For this reason, we perform DFPT calculations of phonons in harmonic approximation. The same density functional, kinetic energy cutoff and the reciprocal space *k*-point grid were used as in DFT calculations. The calculations were performed using the ABINIT code.^{71–74}

The phonon band structures obtained from calculations for cubic $CsPbX_3$ materials are presented in Fig. 2 (dashed line), where phonons with imaginary frequencies are presented using negative values. Since the cubic structure is not stable at zero temperature, there is a significant number of phonon modes with imaginary frequencies. It is therefore a challenge to include such modes in the calculation of phonon-induced band renormalization.

3.4. Calculation of phonon band structure within the self-consistent phonon method

Standard DFPT calculations of the phonon band structure assume zero temperature and the harmonic approximation. As discussed in Section 3.3, this leads to phonon modes with imaginary frequencies for the cubic structure. To overcome this issue, one has to take into account the anharmonic effects and the effects of temperature. This can be naturally accomplished using the self-consistent phonon method.^{53,75}

The calculations based on the SCPH method were performed using the following protocol. The calculations were performed using the ALAMODE code,53,76 while DFT calculations and ab-initio molecular dynamics simulations were performed using the Quantum Espresso code.^{56,57} One first has to obtain all relevant force constants. (i) Harmonic force constants were obtained by performing the DFT calculation of $2 \times 2 \times 2$ cubic supercells, where a shifted $4 \times 4 \times 4$ k-point grid was employed. Other parameters of the DFT calculation are the same as in Section 3.1. An atom is displaced by 0.01 Å in a certain direction and new atomic forces are calculated. The harmonic force constants are then obtained from these forces using a least squares fit implemented in the ALAMODE code. (ii) To obtain anharmonic force constants, we first generate representative atomic structures which will be used for evaluation of forces and subsequent force constant fitting. We perform 2000 steps of NVT ab-initio molecular dynamics at a temperature of 500 K with a timestep of 2 fs for a 2 \times 2 \times 2 cubic supercell. To gain computational speed in this calculation we reduce the kinetic energy cut-off to 30 Ry and we use the *k*-point grid consisting of the Γ point only. This is justified in this place, since the goal is only to obtain configurations where atoms are displaced from their equilibrium positions, rather than to extract physical quantities from the molecular dynamics

simulation. We then select 30 snapshots from the simulation which are equally spaced from timestep 500 to timestep 2000. (iii) For the snapshots obtained, we additionally displace each atom by up to 0.1 Å in each direction. For these 30 snapshots, we accurately compute the atomic forces from DFT by using 50 Ry kinetic energy cutoff and a shifted $4 \times 4 \times 4$ k-point grid. (iv) With the forces obtained we perform fitting of the force constants using the adaptive LASSO method, following ref. 53 and 77. In the fitting, we put a restriction that fourth order force constants are zero beyond third neighbor atoms, that the fifth and sixth order constants are nonzero for nearest neighbors only and that higher order constants are equal to zero. (v) The force constants obtained in the previous step are used as an input for the SCPH method calculation. In the SCPH method calculation, we neglect the off-diagonal elements of the self-energy and use a $4 \times 4 \times 4$ grid to represent the self-energy in reciprocal space.

The phonon band structure obtained from the SCPH method is presented in Fig. 2. We obtain phonon frequencies that are non-negative throughout the whole Brillouin zone. We also find that with an increase of temperature, a small but non negligible shift in frequencies is present. These shifts are negative for the three highest bands and positive for the rest. We will see in Section 3.5 that these shifts are large enough to have a significant contribution to the renormalization of electronic bands.

3.5. Band energy renormalization calculations using the OTMS approach

In this section, we present the results for band energy renormalization calculations of cubic $CsPbX_3$ materials obtained using the OTMS approach. The calculations, in this and in the following section, were performed using our own code which takes DFPT results from the ABINIT code.⁷¹ These results include variations of the Kohn–Sham potential with respect to ionic displacements and the interatomic force constants, that are then used to calculate first and second order matrix elements of electron–phonon interaction. In all band energy renormalization calculations bare band energies that appear in eqn (6) and (7) were taken from DFT calculations reported in Section 3.1.

To make sure that the results obtained are reliable one has to take enough *q*-points in the summations in eqn (6) and (7) and one has to check the sensitivity of the results to the value of the parameter δ in eqn (6). It has been shown in ref. 32 that the band energy renormalization for polar materials converges as $\frac{1}{N_q}$ with the number of points N_q and that a Lorentzian type convergence for CBM and VBM energies of polar materials is obtained while decreasing δ .

In ref. 22 phonon modes obtained within the harmonic approximation were used, however, the phonon modes with imaginary frequencies were simply disregarded. In this approach it remains unclear whether one should disregard only the phonons at certain *q*-points where their frequency becomes imaginary or one should disregard the whole phonon mode that produces an imaginary frequency in at least one



Fig. 2 Phonon dispersion (left column) and phonon density of states (in arbitrary units) for $CsPbX_3$ (X = Cl, Br or I, in rows from top to bottom) obtained using the SCPH method at T = 400 K (solid line) and T = 700 K (dot-dashed line), as well as using DFPT with harmonic approximation (dashed line).

point in the Brillouin zone. To understand whether the approach where imaginary phonon frequencies are discarded can provide reasonably good results, we performed the convergence tests with respect to N_q and δ in three cases: (i) assuming phonon frequencies from DFPT and disregarding the contribution from phonons with imaginary frequencies; (ii) assuming phonon frequencies from DFPT and disregarding the contribution from the whole phonon bands that exhibit imaginary frequencies at any *q*-point; (iii) assuming phonon frequencies obtained from the SCPH method. These three cases will be referred to as cases (i), (ii) and (iii) in what follows.

In Fig. 3 we present the results for band gap renormalization obtained using the OTMS approach in each of these cases. We see that in case (i) the behavior with respect to N_q is not convergent and one obtains unphysically large band gap renormalizations. In this case several phonon bands cross zero energy at several different points in the Brillouin zone (see the left column in Fig. 2), which leads to divergence of Fan matrix elements due to the $\omega_{q\nu}$ term in the denominator, see eqn (5). The convergence is better in case (ii) when such phonon bands are simply disregarded, however one obtains band gap renormalization which is underestimated with respect to case (iii). In case (iii), we obtain convergence with respect to δ and N_q .

In Fig. 4 we decompose the CBM and VBM renormalization into contributions from phonons of different energies. Most of the contributions come from the region where the density of phonon states is the highest and these contributions come mostly from lower bands. Lower energy phonons also tend to have larger electron-phonon coupling matrix elements due to the $\omega_{q\nu}$ term in the denominator in eqn (5). This fact also contributes to prevalent contribution of lower energy phonons to band energy renormalization. Since most of these lower energy phonons turn

into imaginary frequency phonons within the DFPT calculation, the results obtained in case (ii) are underestimated in comparison to the results in case (iii). We also analyzed the contributions of the first order Fan and second order Debye–Waller terms in eqn (8) to band energy renormalization. In line with previous literature results for other materials,^{29,78} we find that these two terms have opposite signs and that both of these terms have significant absolute values, see Fig. S22 in the ESI.† For these reasons, accurate calculation of each of these terms is necessary to obtain reliable final results for band energy renormalization.

Next, we discuss the linearity of the temperature dependence of the band gap renormalization. One can notice from eqn (8) [with self-energies given by eqn (6) and (7)] that the temperature dependence originates only from the Bose term in these equations. When phonon energies are small the temperature dependence of the Bose term is linear. As a consequence, the temperature dependence of band energy renormalization is also linear in case (ii), as can be seen in Fig. 4. On the other hand, in case (iii) the phonon frequencies also depend on temperature and the temperature dependence of the band gap is determined by the ratio of the Bose term (which contains temperature dependent phonon frequency) and the phonon frequency [which comes from the Fan matrix element, see eqn (5) and (6)]. The Bose term increases the gap with temperature as in case (ii), however, most of the temperature dependent frequencies (especially the ones where the density of phonon states is the largest) increase with temperature. They then tend to decrease the renormalization, which leads to nonlinear dependence in case (iii), as seen in Fig. 4.

Our final result for temperature dependence of the band gap of the investigated materials using the OTMS approach is among the results presented in Fig. 5. For the reasons



Fig. 3 Dependence of band gap renormalization obtained using the OTMS approach on the number of *q*-points N_q and on the small parameter δ (whose value is specified in the legend) for CsPbX₃ (X = Cl, Br or I, in rows from top to bottom) materials at T = 400 K. The column labeled as PHCUT0 denotes the result obtained assuming phonon frequencies from DFPT and disregarding the contribution from phonons with imaginary frequencies [case (i) discussed in the text], while the column labeled as PHCUT6 denotes the results obtained assuming phonon frequencies from DFPT and disregarding the contribution from the whole bands that exhibit imaginary frequencies at any *q*-point [case (ii) in the text]. The column labeled as SCPH denotes the result obtained by taking phonon frequencies from the SCPH method [case (iii) in the text].



Fig. 4 Contributions from phonons of different frequencies to VBM (left column) and CBM (middle column) renormalization at T = 400 K and temperature dependent gap renormalization (right column) for CsPbX₃ (X = Cl, Br or I, in rows from top to bottom) obtained using the OTMS approach. The results in case (ii) are shown as filled bins, while the results in case (iii) are shown as transparent bins. The value of each bin $b(\omega_i)$ represents the contribution of all phonons with frequencies from the range ($\omega_i - \Delta\omega/2$, $\omega_i + \Delta\omega/2$) to band energy renormalization, so that $\Delta E_{kn} = \Sigma_i b(\omega_i)$. Filled circles in the right column correspond to case (ii), while empty deltoids correspond to case (iii).

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Fig. 5 Temperature dependence of the calculated band gap of $CsPbX_3$ materials (X = Cl, Br or I, from top to bottom). The calculated band gap of orthorhombic structures at zero temperature is represented by hexagons, while the band gaps of the cubic structure calculated using the SCP (OTMS) approach are represented by full (dotted) lines and two color squares (circles). Experimental results are represented by single color squares with the values of 2.85 eV (ref. 79), 2.36 eV (ref. 80), and 1.67 eV (ref. 81) respectively, at temperatures of 320 K, 403 K and 300 K, respectively, for CsPbCl₃, CsPbBr₃ and CsPbI₃, respectively. Dashed lines are used as a guide to the eye to connect the zero temperature result for the band gap of the orthorhombic structure with the result at the lowest temperature where the material exhibits a cubic structure.

previously discussed, these results and all subsequent results were obtained by taking the phonon frequencies obtained from the calculation based on the SCPH method. In all calculations reported in this and the next section renormalized band energies were obtained by adding the phonon-induced renormalization to the band energies calculated using the hybrid functional as described in Section 3.2. The results at temperatures lower than the temperatures where the cubic structure exists are blurred.

The OTMS approach can be used in principle to determine the renormalization of bands other than the CBM and the VBM. As discussed in the introduction and Section 2.1, band renormalization for other bands exhibits a slow linear convergence with respect to δ when $\delta \rightarrow 0$ in contrast to Lorentzian convergence of CBM and VBM. As a consequence, one has to go to rather small values of δ to reach convergence. However, for small values of δ , large values of N_a are needed, which introduces a large computational burden. We illustrate this behavior in Fig. S1, Fig. S9 and Fig. S14 in the ESI,† for the cases of CsPbCl₃, CsPbBr₃, and CsPbI₃, respectively. For larger values of δ (100 meV and 50 meV in the figure) good convergence with respect to N_a is achieved but the result still depends on δ and one therefore needs to go to smaller δ to achieve convergence with respect to δ . However, for smaller values of δ (10 meV and 1 meV), convergence with respect to N_q could not be achieved with grids up to 20 \times 20 \times 20. As also discussed in the introduction and Section 2.1, it is questionable whether the limit $\delta \rightarrow 0$ of the energy level broadening parameter gives accurate results given the fact that the energy levels of higher bands can exhibit significant broadening. For all these reasons, it is more desirable to self-consistently determine the energy level broadening. These results are the subject of Section 3.6.

3.6. Band energy renormalization calculations using the SCP approach

We now present the results for band energy renormalization obtained using the SCP approach. The frequency dependence of the self-energy and the spectral function for several bands at the R point in the case of the CsPbBr₃ material at T = 400 K is presented in Fig. 6 (the same results for CsPbCl₃ and CsPbI₃ are presented respectively in Fig. S4 and S17 in the ESI†). We denote the bands in ascending order of energies at the R point as VBM4 $(2\times)$, VBM3 $(4\times)$, VBM2 $(2\times)$, VBM1 $(4\times)$, VBM $(2\times)$, CBM $(2\times)$, CBM1 (4 \times), CBM2 (2 \times), CBM3 (2 \times), and CBM4 (4 \times), where the numbers in brackets denote their degeneracy. The spectral functions of the CBM and VBM are relatively narrow and symmetric, while the spectral functions of other bands (CBM1 and VBM1 in Fig. 6 and CBM2-4 and VBM2-4 in Fig. S10 and S12 in the ESI[†] in the case of CsPbBr₃, see also Fig. S2, S4 and S6 (ESI[†]) for CsPbCl₃, as well as Fig. S15, S17 and S19 (ESI[†]) for the CsPbI₃ material) are wider and somewhat asymmetric. This result confirms that it was necessary to go beyond the OTMS approach in the $\delta \rightarrow 0$ limit to obtain accurate results for bands other than the CBM and VBM. There is even a difference between the OTMS and SCP result for CBM and VBM which leads to a band gap difference between the two approaches on the order of 100 meV at T = 400 K (see Section 3.7 for more details).

In Fig. 7 we demonstrate that convergence with respect to N_a was achieved with a $20 \times 20 \times 20$ grid. Convergence is achieved both for the real part of self-energy that corresponds to band energy renormalization and for the imaginary part of the selfenergy that is related to energy level broadening. As expected, it is easier to reach convergence for energy levels that exhibit larger broadening, that is, for states other than the CBM and VBM (Fig. 7 and Fig. S11 and S13 in the ESI,† see also Fig. S3, S5 and S7 (ESI[†]) for the CsPbCl₃ material, as well as Fig. S16, S18 and S20 (ESI[†]) for the CsPbI₃ material). The CBM and VBM states exhibit the lowest broadening due to the fact that single phonon emission processes from these states are not possible. Hence the total scattering rate from these states, which is related to energy level broadening, is determined by phonon absorption processes only. On the other hand, for bands higher than the CBM (lower than the VBM), there is always a nearby other band below (above) it to which phonon emission is also possible. Hence, these states exhibit higher electron-phonon scattering rates than the CBM and VBM, which leads to larger broadening of these states.

The final results for temperature dependence of band energies and the imaginary part of self-energies (that are related to energy level broadening) at the *R* point for the CsPbBr₃ material are presented in Fig. 8. The same results for CsPbCl₃ and CsPbI₃ are presented in Fig. 88 and S21, respectively, in the ESI.† The results indicate that the temperature dependence of band energies is most pronounced for the CBM and the VBM and that it is much weaker for the other bands. The energy level broadenings increase as the temperature increases and this dependence is nearly linear for most bands.

The temperature dependence of the band gap calculated within the SCP approach is presented in Fig. 5. The results



Fig. 6 The frequency dependence of the self-energy and the spectral function for bands VBM1, VBM, CBM and CBM1 at the R point in the case of the CsPbBr₃ material at T = 400 K.

suggest that the gap renormalization and the band gap are somewhat smaller in the SCP approach than in the case of the OTMS approach. The largest difference between the two approaches is at the highest temperatures. This difference originates from the fact that the spectral function within the SCP approach takes a relatively broad asymmetric shape at these temperatures, while the OTMS approach inherently assumes a narrow symmetric Lorentzian spectral function. A comparison of the temperature dependence of the band gap within the SCP approach with experiments will be discussed in Section 3.7.

To gain insight into the effect of temperature on band energies throughout the Brillouin zone, we also performed SCP calculations of the spectral function and band energy renormalization at points Γ , X and M in the Brillouin zone for the three investigated materials. The results are presented in Fig. S23–S85 in the ESI.† All energy levels at X and M points are twofold degenerate, while the degeneracy of the bands at Γ is as follows: VBM4 (4×), VBM3 (2×), VBM2 (4×), VBM1 (2×), VBM (4×), CBM (2×), CBM1 (4×), CBM2 (2×), CBM3 (2×), and CBM4 (4×). We can see (Fig. S29, S36, S43, S50, S57, S64, S71, S78, and S85 in the ESI†) that in most cases the real and the imaginary part of the self-energy are smooth and continuous when the temperature changes. The exceptions are VBM2 for CsPbCl₃ between T = 50 K and T = 100 K, and VBM1 for CsPbBr₃

and CsPbI₃ between T = 550 K and T = 600 K, all three at the X point (Fig. S50, S57, and S64 in the ESI,† respectively). In these cases, the spectral function has two competing maxima (see Fig. S87-S89 in the ESI[†]) that are well inside the range of its half-width and the change in temperature changes the dominant maximum. It should be noted that for all of the examined points, the changes in state energies are such that the band gap remains determined by the R point VBM and CBM. However, an increase in the temperature can change the ordering of the bands: at certain points in the Brillouin zone some neighbouring bands below (above) the VBM1 (CBM1) will swap places with respect to their order obtained from the PBE0 functional calculations. Nevertheless, for simplicity, we label the bands based on their ordering obtained from zero temperature PBE0 functional calculations. When it comes to energy level broadening, it turns out that it is lowest for the VBM and CBM bands (with the imaginary part of the self-energy well below 100 meV for these states and significantly above 100 meV for the other states), as in the case of the *R* point. The CBM and VBM states at these points are well separated in energy from the other bands (see the material band structures in Fig. S86 in the ESI[†]) which restricts the phase space for electron scattering. The exception to this behaviour is the VBM state at the Γ point which is rather broad. In this case, there are several bands that



Fig. 7 The dependence of the real and imaginary part of self-energy at the renormalized energy on the size of the q-points grid. The results are presented for the CsPbBr₃ material at T = 400 K for bands VBM1, VBM, CBM and CBM1 at the R point.



Fig. 8 Temperature dependence of the band energy and the imaginary part of the self-energy for VBM and VBMx (CBM and CBMx) bands (where x = 1, 2, 3, 4) calculated using the SCP approach. The results are shown for CsPbBr₃ at the *R* point. Vertical and horizontal dotted lines represent the temperature of the phase transition to cubic structure $T_c = 403$ K and band energy from PBE0 calculations, respectively.

are close in energy to the VBM state at Γ . The hole can scatter to these bands which contributes to the increase of energy level broadening.

3.7. Comparison of temperature dependence of the band gap with experiments

In this section, we compare the results for the band gap and its temperature dependence with available experimental results from the literature.

In the case of CsPbBr₃ we obtain the band gap of 2.08 eV and 2.20 eV from SCP and OTMS, respectively, at a temperature of 400 K. This result is close to the experimental value of 2.36 eV from ref. 80, obtained at 403 K. Our calculation gives the band gap of CsPbCl₃ of 3.01 eV and 3.07 eV from SCP and OTMS, respectively, at a temperature of 320 K. This result is in good agreement with experimental value of 2.85 eV from ref. 79. For the CsPbI₃ material we obtain the band gaps of 1.35 eV and 1.45 eV from SCP and OTMS, respectively, at a temperature of 300 K, which is in reasonable agreement with experimental values of 1.67 eV (ref. 81) and 1.73 eV (ref. 82).

Next, we discuss the slope of the temperature dependence of the band gap. In the range of temperatures where the material is in the cubic form, the calculated temperature dependence is nearly linear. Therefore, for the purpose of comparison with experiments, it is sufficient to discuss its slope. In the case of CsPbBr₃, we obtain the slope $\left(\frac{dE_g}{dT}\right)_{ph}$ of 0.50 meV K⁻¹ and 0.80 meV K⁻¹ from SCP and OTMS, respectively, in the temperature range from 400 K to 700 K. For CsPbCl₃, the calculation yields the slope of 0.68 meV K⁻¹ and 0.96 meV K⁻¹ from SCP and

OTMS, respectively, in the temperature range from 320 K to 700 K. Finally, for CsPbI₃ we obtain the slope $\left(\frac{dE_g}{dT}\right)_{ph}$ of 0.41 meV K⁻¹ and 0.77 meV K⁻¹ from SCP and OTMS, respectively, in the temperature range from 300 K to 700 K.

To compare the slope of the temperature dependence to experiments, one also has to take into account the effect of thermal expansion, which is not included in the calculation with a fixed lattice constant. The slope of the temperature dependence of the band gap from the effect of thermal expansion is given as

$$\left(\frac{\mathrm{d}E_g}{\mathrm{d}T}\right)_{\mathrm{TE}} = \left(\frac{\mathrm{d}E_g}{\mathrm{d}a}\right) \left(\frac{\mathrm{d}a}{\mathrm{d}T}\right),\tag{13}$$

where $\frac{dE_g}{da}$ is the slope of the dependence of the band gap on the lattice constant and $\frac{da}{dT}$ is the slope of the temperature dependence of the lattice constant, which is related to linear thermal expansion coefficient as

$$\alpha = \frac{1}{a} \frac{\mathrm{d}a}{\mathrm{d}T}.$$
 (14)

We estimate $\frac{dE_g}{dq}$ by calculating the gap dependence of the lattice constant using DFT with the same semilocal functional used in Section 3.1. We obtain respectively the values of 2.1, 2.4 and 1.1 eV Å⁻¹ for CsPbBr₃, CsPbCl₃ and CsPbI₃. Literature values of linear thermal expansion coefficients are respectively 0.26×10^{-4} K⁻¹, $(0.22-0.30) \times 10^{-4}$ K⁻¹ and $(0.39-0.40) \times 10^{-4}$ K⁻¹ for CsPbBr₃, CsPbCl₃ and CsPbI₃ (ref. 83). From eqn (13) and (14) we then obtain that $(dE_g/dT)_{TE}$ is respectively

equal to 0.32 meV K^{-1} , 0.35 meV K^{-1} and 0.29 meV K^{-1} for CsPbBr₃, CsPbCl₃ and CsPbI₃. The results suggest that the contribution from thermal expansion is smaller than the contribution from phonon-induced band gap renormalization for all the materials studied.

The total slope of the temperature dependence of the band gap can be estimated by adding contributions from phononinduced band gap renormalization and from thermal expansion

$$\frac{\mathrm{d}E_g}{\mathrm{d}T} = \left(\frac{\mathrm{d}E_g}{\mathrm{d}T}\right)_{\mathrm{TE}} + \left(\frac{\mathrm{d}E_g}{\mathrm{d}T}\right)_{\mathrm{ph}}.$$
 (15)

We then obtain $\frac{dE_g}{dT}$ of 0.81 meV K⁻¹ (1.12 meV K⁻¹), 1.02 meV K⁻¹ (1.31 meV K⁻¹), and 0.70 meV K⁻¹ (1.06 meV K⁻¹) from SCP (OTMS) results, respectively, for CsPbBr₃, CsPbCl₃ and CsPbI₃.

Experimental data for the temperature dependence of the band gap of the cubic structure and its slope are relatively scarce. In ref. 84 the slope of (0.85 \pm 0.05) meV K⁻¹ was reported for CsPbI3 based on the measurements in the temperature range from 570 K to 620 K. This value is in the range between our results from SCP and OTMS for the same material. The slope of 0.341 meV K⁻¹ was reported for CsPbBr₃ in ref. 27 in the temperature range from 380 K to 435 K where the material exhibits a phase transition from tetragonal to cubic structure. This slope is significantly smaller than our estimated slope. It is however questionable if the comparison of these slopes is meaningful given the fact that experimental data cover only a very small initial part of the temperature range where the material is cubic. For the CsPbCl₃ material, we are not aware of any literature data with temperature dependence of the band gap in the cubic phase. Overall, further experimental measurements of the temperature dependence of the band gap in a broader temperature range in the cubic phase are certainly desirable.

Finally, we briefly discuss the temperature dependence of the band gap at lower temperatures when the materials exhibit an orthorhombic or a tetragonal structure. Experimental results at these temperatures generally indicate that temperature dependence of the band gap is rather weak. For example, it was reported in ref. 70 that the band gap of $CsPbBr_3$ ($CsPbI_3$) increases by about 60 meV (80 meV) from 0 K to 300 K. In ref. 79 a similar result was obtained for CsPbBr₃, while in the case of CsPbCl₃ the changes in the band gap in this temperature range were smaller than 20 meV. In ref. 85-87, a comparably weak temperature dependence of the gap was observed for nanocrystals based on CsPbX₃ materials in the same temperature range. For all three materials, the band gap at zero temperature is only slightly (by less than 100 meV) lower or even slightly larger than at the lowest temperature where the materials exhibit a cubic structure, see the reference to the values of experimental band gaps at the end of Section 3.2 for the orthorhombic structure and the beginning of this section for the cubic structure. Our calculations of the band gap of the orthorhombic structure at zero temperature and of the cubic structure are in line with such behavior (see the dashed lines in Fig. 5). Since the orthorhombic and tetragonal structure have a larger unit cell than the cubic structure, we did not perform temperature dependent electronic structure calculations of these structures due to larger computational cost and the fact that experimental results indicate a rather weak temperature dependence in this range of temperatures.

4 Discussion and conclusions

Next, we discuss previous computational studies where the effects of temperature on the electronic structure of halide perovskites were investigated. In ref. 23, the effects of temperature were included by performing finite temperature ab-initio molecular dynamics with a sufficiently large supercell and by calculating the average band gap change from many molecular dynamics snapshots. Excellent agreement with experimental band gaps of cubic inorganic halide perovskites at the lowest temperature where the material exhibits a cubic structure was obtained. On the computational side, this approach is rather demanding as it would require a separate molecular dynamics simulation at each temperature to obtain the temperature dependence of the band gap. This approach inherently assumes classical phonons which is likely good approximation at room temperature because the dominant phonon modes that determine electronic structure renormalization have energies which are significantly smaller than thermal energy $k_{\rm B}T$ at room temperature. In ref. 45 and 88 the effects of temperature were also included by taking an average over many different configurations with atoms displaced from their equilibrium positions. In ref. 24 and 25 the authors exploited the special displacements method^{89,90} which enables calculation of the band gap at a given temperature from a single calculation of a large supercell with atoms displaced from their equilibrium positions in accordance with a particular pattern. In ref. 22, Allen-Heine-Cardona theory, the finite difference approach, as well as the approach with an average over many different atomic configurations sampled using a Monte Carlo approach were used to study the temperature dependence of the band gap of cubic methylammonium lead iodide perovskite. However, the Allen-Heine-Cardona theory was applied by simply excluding imaginary phonon modes, while we find that this procedure does not give reliable results in the case of the inorganic halide perovskites that we investigated.

We finally note several advantages, as well as shortcomings, of the approach based on the Allen–Heine–Cardona theory over other approaches. To obtain temperature dependence of the electronic structure, the most demanding steps of the procedure – DFPT calculations and extraction of force constants for application of the SCPH method – need to be performed only once, that is, they do not have to be repeated for each temperature. On the other hand, in all approaches based on atomic displacements (sampled either from molecular dynamics, Monte Carlo or using the special displacements) the whole computational procedure has to be repeated at each temperature. Within the Allen–Heine–Cardona approach it is straightforward to obtain

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renormalization of states other than the CBM or VBM, while in the methods based on supercell calculations this is either impossible or one has to exploit a certain type of unfolding procedure, such as the one used in ref. 89. It should be mentioned that the approach based on the Allen–Heine–Cardona theory certainly has its limitations. Being based on expansion up to second order terms with respect to atomic displacements, it is not expected to be highly accurate in conditions when this expansion is not sufficient. On the other hand, the approaches based on atomic displacements usually do not have such a limitation.

In conclusion, we performed *ab-initio* calculations of the temperature dependent electronic structure of inorganic halide perovskite materials CsPbX₃. The challenge that comes from the fact that cubic structure is not stable at zero temperature and that one obtains phonon modes with imaginary frequencies in a standard DFPT calculation was overcome by using the SCPH method that gives the phonon spectrum with real non-negative frequencies. The challenge of obtaining the energies of bands other than the CBM and the VBM in the calculations based on the Allen-Heine-Cardona theory was addressed by exploiting a selfconsistent procedure for evaluation of relevant self-energies and spectral functions. We obtain the band gaps at the lowest temperature where the materials exhibit a cubic structure in good agreement with experiments. We also find good agreement of calculated and experimental temperature dependence of the band gap for the CsPbI₃ material where reliable experimental data are available in the literature. Our results also suggest that the band gaps at the lowest temperature where the materials exhibit a cubic structure are similar to the band gaps at zero temperature where the materials exhibit an orthorhombic structure. This finding is consistent with experimental data that suggest a rather weak temperature dependence at lower temperatures where the materials exhibit an orthorhombic or a tetragonal structure. Finally, we find that the temperature dependence of band energies at the Rpoint is most pronounced for the CBM and the VBM, while it is less pronounced for higher and lower bands.

Conflicts of interest

There are no conflicts of interest to declare.

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