

Temperature Dependence of the Energy Levels of Methylammonium Lead Iodide Perovskite from First-Principles

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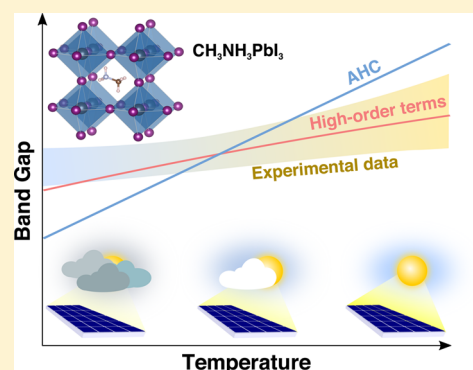
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Supporting Information

ABSTRACT: Environmental effects and intrinsic energy-loss processes lead to fluctuations in the operational temperature of solar cells, which can profoundly influence their power conversion efficiency. Here we determine from first-principles the effects of temperature on the band gap and band edges of the hybrid perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$ by accounting for electron–phonon coupling and thermal expansion. From 290 to 380 K, the computed band gap change of 40 meV coincides with the experimental change of 30–40 meV. The calculation of electron–phonon coupling in $\text{CH}_3\text{NH}_3\text{PbI}_3$ is particularly intricate as the commonly used Allen–Heine–Cardona theory overestimates the band gap change with temperature, and excellent agreement with experiment is only obtained when including high-order terms in the electron–phonon interaction. We also find that spin–orbit coupling enhances the electron–phonon coupling strength but that the inclusion of nonlocal correlations using hybrid functionals has little effect. We reach similar conclusions in the metal–halide perovskite CsPbI_3 . Our results unambiguously confirm for the first time the importance of high-order terms in the electron–phonon coupling by direct comparison with experiment.



Metal–halide hybrid perovskites are promising candidates as light absorbers for the next generation of solid-state hybrid photovoltaic devices.^{1–7} Their solar power conversion efficiency has reached 22.1%,⁸ an impressive achievement considering that the first perovskite-based solar cell was only made 7 years ago.¹ These light-absorbing materials belong to the perovskite family ABX_3 , where A is a cation located at the center of a cube formed from corner-sharing BX_6 octahedra.

Methylammonium lead iodide, MAPbI_3 , where MA represents the organic cation CH_3NH_3^+ , has an optimal band gap for light absorption of 1.6 eV and exhibits large electron and hole diffusion lengths, which make it a prime candidate for solar cell applications.^{3,4} Another factor determining the efficiency of a solar cell is the band alignment between the light absorber and its transport layers.⁹ As an example, a common electron transport layer is TiO_2 , which has a conduction band that is only 0.1 eV lower than that of MAPbI_3 .¹⁰

Solar cell devices are subject to significant temperature variations under normal operating conditions.¹¹ Ambient temperatures can oscillate between 250 and 310 K, and energy-loss mechanisms associated with the conversion of solar power to electric power can increase the operating temperature of the cell above 340 K.^{11–13} These temperature fluctuations can affect both the absorption onset and band alignment and

therefore the performance of the solar cell, as was demonstrated for MAPbI_3 -based solar cells, which showed an open-circuit voltage drop from 1.01 to 0.83 V as the temperature increased from 300 to 360 K.¹⁴ Recently, two experimental studies have investigated the temperature-dependent properties of MAPbI_3 and reported changes in the band gap reaching 40 meV in the temperature range of solar cell operation^{15,16} and even larger changes exceeding 100 meV in the individual band edges.¹⁵

While the properties of MAPbI_3 are well-characterized both theoretically and experimentally, there is an increasing research effort to find alternatives to this light absorber,^{17–20} with the aim of tuning the physical properties of the solar cells and moving toward lead-free devices. In this context, it would be desirable to accurately calculate the effects of temperature changes to aid in the computational design of novel perovskite solar cell materials under real working conditions. Unfortunately, the organic–inorganic nature of MAPbI_3 , together with the presence of heavy Pb atoms, makes it a challenging system to study from first-principles.^{21–28}

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In this Letter, we determine the temperature evolution of the band gap and band edges in MAPbI₃ using first-principles methods while accounting for both electron–phonon coupling and thermal expansion. Our results accurately reproduce the band gap opening observed experimentally in MAPbI₃ upon increasing temperature.^{15,16} We further show that the commonly used Allen–Heine–Cardona (AHC) theory,^{29,30} which successfully captures the low-order terms in electron–phonon coupling and can be used to explain the temperature dependence of band gaps in multiple systems, fails in MAPbI₃ because high-order terms in the electron–phonon interaction make significant contributions. Furthermore, we show that spin–orbit coupling (SOC) must be included to accurately describe the electron–phonon coupling strength of this system, while nonlocal correlation effects incorporated using a hybrid functional do not yield significant changes. Our final results are in excellent agreement with experimental data, thus verifying that thermal effects can be reliably computed using first-principles methods to design novel perovskite solar cells. Additionally, our demonstration that low-order treatment of the electron–phonon interactions fails for the band edges of perovskite solar cell materials raises the question of whether this would also be true for other electronic states in the Brillouin zone (BZ). Quantities such as electronic transport depend on the electron–phonon interaction averaged over the entire BZ, and therefore, it would be interesting to study whether the standard approach to these calculations based on a low-order treatment of electron–phonon coupling is valid.

Methodology. Our calculations are based on density functional theory (DFT)^{31–33} using the VASP^{34–37} and ABINIT³⁸ software packages. We use the semilocal Perdew–Burke–Ernzerhof (PBE)³⁹ exchange–correlation functional, as well as the hybrid Heyd–Scuseria–Ernzerhof (HSE)^{40,41} functional, with and without SOC. The computational details are provided in the [Supporting Information](#). To make our calculations tractable, we focus on the high-temperature cubic phase of MAPbI₃, but we expect that our results are also applicable to the tetragonal phase that is stable below 330 K^{23,42,43} as experimental results show that the band gap evolution with temperature transitions smoothly between the cubic and tetragonal phases.^{15,16} The cubic phase exhibits some unstable modes, and we have set their amplitudes to zero in the calculations reported. These modes can contribute to the strength of electron–phonon coupling,⁴⁴ but as they represent only a small fraction of all modes, we expect their contribution to the temperature dependence of the band gap to be small. Calculations in which these modes are allowed to have nonzero amplitudes indicate that neglect of the unstable modes leads to an error that is smaller than the statistical uncertainty in our calculations (see the [Supporting Information](#)).

Allen–Heine–Cardona Theory. The coupling between electronic states and nuclear vibrations due to quantum zero-point (ZP) motion and thermal motion renormalizes the electronic eigenenergies ϵ_{kn} as

$$\epsilon_{kn}(T) = \frac{1}{Z} \sum_s \langle \chi_s | \epsilon_{kn} | \chi_s \rangle e^{-E_s/k_B T} \quad (1)$$

where $|\chi_s\rangle$ is the vibrational eigenstate s with eigenvalue E_s , $Z = \sum_s e^{-E_s/k_B T}$ is the partition function, T is the temperature, and k_B is the Boltzmann constant. Evaluation of eq 1 is challenging and has only recently become fully amenable to first-principles methods.^{45–50} The vast majority of these

calculations rely on a low-order expansion of the electronic energy as a function of the atomic displacements, leading to a particularly convenient expression for the change in the electronic energy $\Delta\epsilon_{kn}(T) \triangleq \epsilon_{kn}(T) - \epsilon_{kn}(0)$ at temperature T

$$\Delta\epsilon_{kn}(T) = \frac{1}{N_q} \sum_{\mathbf{q}, \nu} \frac{a_{\mathbf{q}\nu}^{(2)}}{\omega_{\mathbf{q}\nu}} \left[\frac{1}{2} + n_B(\omega_{\mathbf{q}\nu}, T) \right] \quad (2)$$

where $\mathbf{q}$ and ν are the phonon quantum numbers, N_q is the number of points in the vibrational BZ, $a_{\mathbf{q}\nu}^{(2)}$ is the second-order electron–phonon coupling constant, $\omega_{\mathbf{q}\nu}$ is the harmonic frequency, and n_B is a Bose–Einstein factor. The coupling constants can be evaluated using finite displacements (FDs) in conjunction with supercells^{51,52} or using density functional perturbation theory (DFPT) by invoking the rigid-ion approximation, which leads to the so-called AHC theory.^{29,30} A description of the use of the rigid-ion approximation in the context of AHC theory can be found in ref 53. Further details of these methods are provided in the [Supporting Information](#).

The approximation in eq 2 is computationally tractable as it allows a fine sampling of the vibrational BZ because phonon modes can be treated independently. AHC theory within DFPT can be used to sample the vibrational BZ using very fine $\mathbf{q}$ -point grids, readily obtaining converged results.⁵⁴ The recent introduction of nondiagonal supercells has allowed calculations using the FDs method to reach levels of convergence approaching those of DFPT.⁵² In the [Supporting Information](#), we present a comparison of both approaches, which deliver similar results. We therefore infer that it is safe to apply the rigid-ion approximation in MAPbI₃ (See [Supporting Information](#), which includes refs 23–30, 34–41, and 51–67).

We apply AHC theory using DFPT in conjunction with the PBE functional³⁹ to compute the ZP and finite-temperature renormalization of the direct minimum gap of MAPbI₃, located at the BZ boundary point **R**. Figure 1 shows the temperature dependence of the band gap change obtained using different $\mathbf{q}$ -point grids to sample the vibrational BZ, and the inset shows the corresponding ZP corrections arising from quantum motion of the valence band maximum (VBM), conduction band minimum (CBM), and band gap. Appreciable convergence is

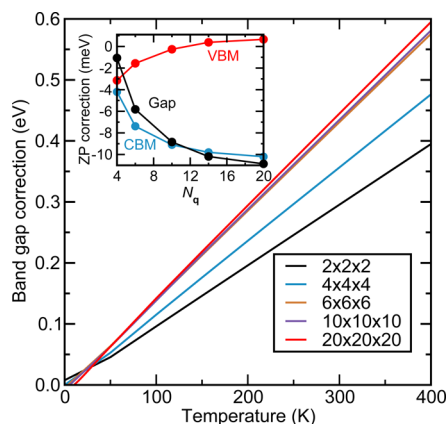


Figure 1. Temperature dependence of the band gap of MAPbI₃ evaluated using the AHC approach with different BZ grids of sizes N_q .³ The inset shows the convergence of the VBM, CBM, and band gap ZP corrections at the **R**-point as a function of the vibrational BZ grid linear size.

reached in the temperature range of 0–400 K with a $6 \times 6 \times 6$ q -point grid. However, as seen in the inset of Figure 1, the very small ZP correction needs a denser q -point grid of $20 \times 20 \times 20$ to be accurately converged in the meV range.

Figure 1 shows that the electron–phonon coupling widens the band gap with increasing temperature, which is opposite to the behavior of most materials where temperature reduces the size of the band gap.⁶⁸ We find that thermal expansion further widens the band gap by 50 meV as the temperature increases from 0 to 400 K, in agreement with earlier first-principles calculations.^{15,69} The band gap opening is in qualitative agreement with two recent experiments that also observed gap opening with increasing temperature.^{15,16} However, our calculated band gap change severely overestimates the one observed experimentally; calculations result in a band gap change of 120 meV between 290 and 380 K, while the experimentally observed increase is only 30–40 meV.^{15,16} Figure S5 in the Supporting Information shows the temperature dependence of the band gaps at other points in the BZ; all indicate that the large change with temperature is not limited to the R zone boundary point but rather is a general feature of AHC theory in MAPbI₃.

To better understand the large discrepancy between experiment and theory, we examine temperature effects on the individual band edges at the R point. Ignoring thermal expansion, in the temperature range from 290 to 380 K, the VBM decreases by 104 meV while the CBM increases by 43 meV. Experimentally, the VBM is observed to decrease by 110 meV, in agreement with our calculations but at variance with our calculations; the CBM also shifts down by 77 meV.¹⁵

The chemical character of the CBM is dominated by Pb atoms in MAPbI₃, and this suggests that the disagreement between theory and experiment might be due to the neglect of relativistic effects in our calculations so far. Indeed, SOC is needed to accurately calculate the static lattice band gap.^{25,28} To test the importance of SOC on our results, we have performed electron–phonon coupling calculations using the FD approach. Figure 2 compares the temperature dependence

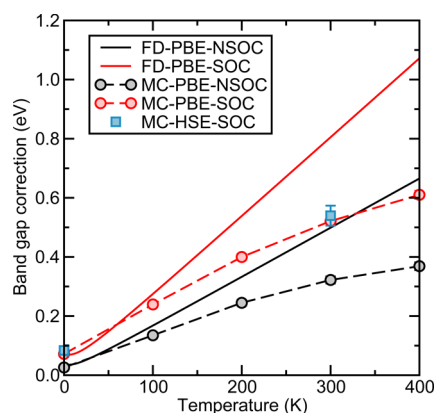


Figure 2. Temperature dependence of the band gap of MAPbI₃ evaluated using the PBE functional and the FD approach without (NSOC) and with (SOC) spin–orbit coupling and using the MC approach without and with SOC. Additional MC calculations are performed with the HSE functional and including SOC. The calculations are performed for the primitive cell, equivalent to sampling the Γ -point only. The statistical error bars in the MC results are included in all data points, but their size is smaller than the symbol size for some.

of the MAPbI₃ band gap without (FD-PBE-NSOC) and with (FD-PBE-SOC) spin–orbit coupling. In these calculations, we used the primitive cell (equivalent to sampling only the Γ -point of the vibrational BZ), and thus, they are not converged. Nevertheless, these results clearly demonstrate that SOC enhances the strength of electron–phonon coupling, almost doubling the band gap change with temperature. This shows that, although the proper description of electron–phonon coupling in MAPbI₃ requires SOC, its inclusion worsens the agreement between AHC theory and experiment.

Another possible explanation for the discrepancy between AHC theory and experiment is electron correlation, which can modify the strength of electron–phonon coupling in gapped systems.^{66,67} To test this, we performed additional calculations using the hybrid HSE functional.^{40,41} Our results show that the inclusion of nonlocal correlation does not significantly affect the electron–phonon coupling strength. As a consequence, in the rest of the Letter, all calculations are performed using PBE + SOC.

Our analysis suggests that neither the inclusion of SOC nor a better description of exchange–correlation effects in the DFT functional nor the rigid-ion approximation are responsible for the discrepancy between AHC theory and experiment. The only possibility left is that the commonly used low-order expansion of electron–phonon coupling fails in MAPbI₃. Despite the successes of AHC theory to describe the temperature dependence of the band structures of a wide range of materials,^{45,48,54,70} recent calculations question the validity of AHC theory in helium at terapascal pressures,⁶⁰ in molecular crystals at ambient conditions,⁶¹ in the perovskite CsSnI₃,⁶² and even (albeit moderately) in crystals like diamond.⁶³

To assess the importance of high-order terms in the evaluation of electron–phonon coupling in MAPbI₃, we compute eq 1 directly using a Monte Carlo (MC) method.^{47,60}

We show the results in Figure 2, obtained by sampling the vibrational BZ at the Γ -point only. The ZP quantum corrections to the band gaps are similar between the FD and MC approaches, but their temperature dependence differs substantially. For example, for the curves including SOC, at 400 K, the FD change in the band gap overestimates the MC change by 460 meV. Thus, in MAPbI₃, high-order terms in the electron–phonon coupling are important, and the commonly used eq 2, with either DFPT or FD, fails in this system. Interestingly, to the authors' knowledge, this is the first instance of the failure of AHC theory that can be verified by direct comparison to experimental data.

The MC method is a real-space method, and the convergence of the results with system size (equivalent to the convergence with respect to the BZ grid size) is particularly difficult. The computation of the electron–phonon coupling with cross-terms requires large diagonal supercells with sizes limited by the maximum number of atoms that can be realistically included in a DFT calculation. For MAPbI₃, the band gap correction in the temperature range of 290–380 K is sufficiently converged with $3 \times 3 \times 3$ primitive cells, containing 324 atoms. Finite size effects are discussed in the Supporting Information based on the convergence of the AHC method in Figure 1.

Figure 3 shows the temperature dependence of the MAPbI₃ band gap evaluated using the MC approach in conjunction with PBE+SOC in the temperature range from 290 to 380 K, relevant for solar cell applications. Thermal expansion effects

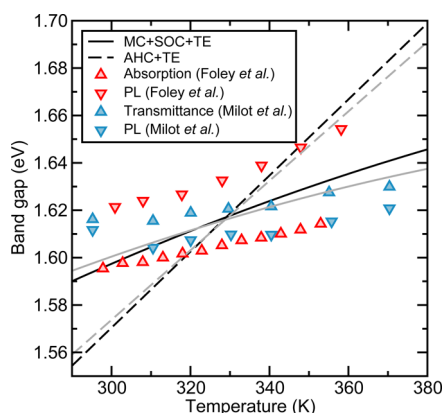


Figure 3. Temperature dependence of the band gap of MAPbI₃ from Foley et al.¹⁵ and from Milot et al.¹⁶ using various techniques (red and blue triangles respectively), compared to the theoretical prediction using the MC approach (black solid line) and AHC theory (dashed black line). Both theoretical lines include the effects of thermal expansion, but only the MC line includes SOC. The results neglecting thermal expansion are shown with gray lines.

on the results are also presented in the figure. For comparison, we show the results obtained from two experimental studies measured using optical absorbance or transmittance and photoluminescence spectroscopy.^{15,16} We only show the temperature range 290–380 K common to the two studies, and we do not distinguish between the tetragonal and cubic phases as argued before. The spread observed in the experimental data from the two measurement techniques is likely due to the presence of trap states below the band edges, but in both studies, the band gap variations with temperature are less sensitive to experimental uncertainty and range between 30 and 40 meV. To avoid any complications arising from well-known errors of DFT in computing absolute band gaps and to focus only on the band gap change with temperature, we shift the calculated temperature dependence such that at 329 K the value of the gap is 1.616 eV, given by the average of the experimental data.

The change in the experimental band gap of 30–40 meV in the temperature range of interest is in good agreement with the MC results that predict a change of 40 meV. Repeating the MC calculations using a $2 \times 2 \times 2$ supercell gives a change of 30 meV, also within the experimentally observed range. The change of the band gap originates from the VBM as the computed CBM correction is relatively flat in that temperature range, which is consistent with experiment.¹⁵ By contrast, AHC theory predicts a change of 120 meV in the band gap, severely overestimating the strength of electron–phonon coupling. These results are the first direct comparison of two leading first-principles methods to compute the temperature dependence of band gaps where higher-order terms dominate and for which an experimental measurement exists.

Although AHC theory fails to provide quantitatively accurate results for the strength of electron–phonon coupling in MAPbI₃, it is still useful in investigating the microscopic origin of the electron–phonon coupling strength as each normal mode ($\mathbf{q}, \nu$) appears independently in eq 2. Our results show that low-energy crystal modes dominate the coupling over the molecular high-energy modes. This is consistent with the fact that the VBM and CBM are formed by states whose character is dominated by Pb and I. It is interesting to note that the low-energy modes in MAPbI₃ also drive the tetragonal to cubic

phase transition as the temperature increases.⁶⁹ These results are also suggestive that the failure of AHC theory is not due to high-energy phonon modes associated with the organic molecule as these contribute the least to the energy renormalization. We have further investigated this point by calculating the temperature dependence of the band gap of the inorganic CsPbI₃ perovskite, where a similar picture emerges (see the Supporting Information).

Overall, our results show that temperature drives changes in the absolute value of the band gap of MAPbI₃, as well as in the shape of the band structure, from both electron–phonon coupling and thermal expansion. It has also been shown in previous work how the molecular orientation of the organic cation can modify these quantities,^{71,72} and it would be interesting in future work to explore the combination of both effects.

We have determined the temperature dependence of the band gap and band edges of the cubic phase of MAPbI₃ using first-principles methods. Our results show that the MAPbI₃ band gap opens by 40 meV as the temperature increases from 290 to 380 K due to thermal expansion and electron–phonon coupling, which is in excellent agreement with the experimental value of 30–40 meV. Furthermore, we demonstrate that the calculation of electron–phonon coupling is particularly intricate as we expose the limitations of the commonly used AHC theory, arising from the dominant contribution in the electron–phonon coupling of high-order terms. We have also found that the use of the HSE hybrid functional has little effect, but the presence of Pb atoms means that the spin–orbit interaction substantially modifies the strength of electron–phonon coupling.

Overall, our MC approach leads to good agreement between theory and experiment and unambiguously confirms for the first time the importance of higher-order terms in electron–phonon coupling. These results call for a revision of previous calculations of electron–phonon coupling and associated properties in these materials. We also hope that our findings will foster the design of new perovskite materials and the development of improved first-principles methods to efficiently tackle these challenging materials.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpclett.6b02560.

Computational details, methodology, convergence tests, Allen–Heine–Cardona theory results for high-symmetry $\mathbf{k}$ -points in the Brillouin zone, effects of temperature on band edges, and thermal band gap changes for CsPbI₃. (PDF)

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Notes

The authors declare no competing financial interest.

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REFERENCES

- (1) Kojima, A.; Teshima, K.; Shirai, Y.; Miyasaka, T. Organometal Halide Perovskites as Visible-Light Sensitizers for Photovoltaic Cells. *J. Am. Chem. Soc.* **2009**, *131*, 6050.
- (2) Kim, H.-S.; Lee, C.-R.; Im, J.-H.; Lee, K.-B.; Moehl, T.; Marchioro, A.; Moon, S.-J.; Humphry-Baker, R.; Yum, J.-H.; Moser, J. E. Lead Iodide Perovskite Sensitized All-Solid-State Submicron Thin Film Mesoscopic Solar Cell with Efficiency Exceeding 9%. *Sci. Rep.* **2012**, *2*, 591.
- (3) Lee, M. M.; Teuscher, J.; Miyasaka, T.; Murakami, T. N.; Snaith, H. J. Efficient Hybrid Solar Cells Based on Meso-Superstructured Organometal Halide Perovskites. *Science* **2012**, *338*, 643.
- (4) Burschka, J.; Pellet, N.; Moon, S.-J.; Humphry-Baker, R.; Gao, P.; Nazeeruddin, M. K.; Grätzel, M. Sequential deposition as a route to high-performance perovskite-sensitized solar cells. *Nature* **2013**, *499*, 316.
- (5) Snaith, H. J. Perovskites: The Emergence of a New Era for Low-Cost, High-Efficiency Solar Cells. *J. Phys. Chem. Lett.* **2013**, *4*, 3623.
- (6) Xing, G.; Mathews, N.; Sun, S.; Lim, S. S.; Lam, Y. M.; Grätzel, M.; Mhaisalkar, S.; Sum, T. C. Long-Range Balanced Electron- and Hole-Transport Lengths in Organic-Inorganic $\text{CH}_3\text{NH}_3\text{PbI}_3$. *Science* **2013**, *342*, 344.
- (7) Hodes, G. Perovskite-Based Solar Cells. *Science* **2013**, *342*, 317.
- (8) NREL Best Research-Cell Efficiencies Chart. www.nrel.gov/ncpv/images/efficiencychart.jpg (2016).
- (9) Marcus, R. A. On the Theory of Electron-Transfer Reactions. VI. Unified Treatment for Homogeneous and Electrode Reactions. *J. Chem. Phys.* **1965**, *43*, 679.
- (10) Schulz, P.; Edri, E.; Kirmayer, S.; Hodes, G.; Cahen, D.; Kahn, A. Interface energetics in organo-metal halide perovskite-based photovoltaic cells. *Energy Environ. Sci.* **2014**, *7*, 1377.
- (11) Sze, S. M.; NG, K. K. *Physics of Semiconductor Devices*; Wiley: New Jersey, 2007.
- (12) Emery, K.; Burdick, J.; Caiyem, Y.; Dunlavy, D.; Field, H.; Kroposki, B.; Moriarty, T.; Ottoson, L.; Rummel, S.; Strand, T.; et al. Temperature dependence of photovoltaic cells, modules and systems. *Photovoltaic Specialists Conference, 1996, Conference Record of the Twenty Fifth IEEE*; 1996; pp 1275–1278.
- (13) Skoplaki, E.; Boudouvis, A.; Palyvos, J. A simple correlation for the operating temperature of photovoltaic modules of arbitrary mounting. *Sol. Energy Mater. Sol. Cells* **2008**, *92*, 1393.
- (14) Zhang, H.; Qiao, X.; Shen, Y.; Moehl, T.; Zakeeruddin, S. M.; Grätzel, M.; Wang, M. Photovoltaic behaviour of lead methylammonium triiodide perovskite solar cells down to 80 K. *J. Mater. Chem. A* **2015**, *3*, 11762.
- (15) Foley, B. J.; Marlowe, D. L.; Sun, K.; Saidi, W. A.; Scudiero, L.; Gupta, M. C.; Choi, J. J. Temperature dependent energy levels of methylammonium lead iodide perovskite. *Appl. Phys. Lett.* **2015**, *106*, 243904.
- (16) Milot, R. L.; Eperon, G. E.; Snaith, H. J.; Johnston, M. B.; Herz, L. M. Temperature-Dependent Charge-Carrier Dynamics in $\text{CH}_3\text{NH}_3\text{PbI}_3$ Perovskite Thin Films. *Adv. Funct. Mater.* **2015**, *25*, 6218.
- (17) Kulkarni, S. A.; Baikie, T.; Boix, P. P.; Yantara, N.; Mathews, N.; Mhaisalkar, S. Band-gap tuning of lead halide perovskites using a sequential deposition process. *J. Mater. Chem. A* **2014**, *2*, 9221.
- (18) Mosconi, E.; Amat, A.; Nazeeruddin, M. K.; Grätzel, M.; De Angelis, F. First-Principles Modeling of Mixed Halide Organometal Perovskites for Photovoltaic Applications. *J. Phys. Chem. C* **2013**, *117*, 13902.
- (19) Filip, M. R.; Eperon, G. E.; Snaith, H. J.; Giustino, F. Steric engineering of metal-halide perovskites with tunable optical band gaps. *Nat. Commun.* **2014**, *5*, 5757.
- (20) Volonakis, G.; Filip, M. R.; Haghighirad, A. A.; Sakai, N.; Wenger, B.; Snaith, H. J.; Giustino, F. Lead-Free Halide Double Perovskites via Heterovalent Substitution of Noble Metals. *J. Phys. Chem. Lett.* **2016**, *7*, 1254.
- (21) Lindblad, R.; Bi, D.; Park, B.-w.; Oscarsson, J.; Gorgoi, M.; Siegbahn, H.; Odelius, M.; Johansson, E. M. J.; Rensmo, H. Electronic Structure of $\text{TiO}_2/\text{CH}_3\text{NH}_3\text{PbI}_3$ Perovskite Solar Cell Interfaces. *J. Phys. Chem. Lett.* **2014**, *5*, 648.
- (22) Mosconi, E.; Ronca, E.; De Angelis, F. First-Principles Investigation of the TiO_2 /Organohalide Perovskites Interface: The Role of Interfacial Chlorine. *J. Phys. Chem. Lett.* **2014**, *5*, 2619.
- (23) Baikie, T.; Fang, Y.; Kadro, J. M.; Schreyer, M.; Wei, F.; Mhaisalkar, S. G.; Grätzel, M.; White, T. J. Synthesis and crystal chemistry of the hybrid perovskite $(\text{CH}_3\text{NH}_3)\text{PbI}_3$ for solid-state sensitised solar cell applications. *J. Mater. Chem. A* **2013**, *1*, 5628.
- (24) Brivio, F.; Walker, A. B.; Walsh, A. Structural and electronic properties of hybrid perovskites for high-efficiency thin-film photovoltaics from first-principles. *APL Mater.* **2013**, *1*, 042111.
- (25) Even, J.; Pedesseau, L.; Jancu, J.-M.; Katan, C. Importance of Spin-Orbit Coupling in Hybrid Organic-Inorganic Perovskites for Photovoltaic Applications. *J. Phys. Chem. Lett.* **2013**, *4*, 2999.
- (26) Umari, P.; Mosconi, E.; De Angelis, F. Relativistic GW calculations on $\text{CH}_3\text{NH}_3\text{PbI}_3$ and $\text{CH}_3\text{NH}_3\text{SnI}_3$ Perovskites for Solar Cell Applications. *Sci. Rep.* **2014**, *4*, 4467.
- (27) Brivio, F.; Butler, K. T.; Walsh, A.; van Schilfgaarde, M. Relativistic quasiparticle self-consistent electronic structure of hybrid halide perovskite photovoltaic absorbers. *Phys. Rev. B: Condens. Matter Phys.* **2014**, *89*, 155204.
- (28) Filip, M. R.; Giustino, F. GW quasiparticle band gap of the hybrid organic-inorganic perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$: Effect of spin-orbit interaction, semicore electrons, and self-consistency. *Phys. Rev. B: Condens. Matter Phys.* **2014**, *90*, 245145.
- (29) Allen, P. B.; Heine, V. Theory of the temperature dependence of electronic band structures. *J. Phys. C: Solid State Phys.* **1976**, *9*, 2305.
- (30) Allen, P. B.; Cardona, M. Theory of the temperature dependence of the direct gap of germanium. *Phys. Rev. B: Condens. Matter Phys.* **1981**, *23*, 1495.
- (31) Hohenberg, P.; Kohn, W. Inhomogeneous Electron Gas. *Phys. Rev.* **1964**, *136*, B864–B871.
- (32) Kohn, W.; Sham, L. J. Self-Consistent Equations Including Exchange and Correlation Effects. *Phys. Rev.* **1965**, *140*, A1133–A1138.
- (33) Payne, M. C.; Teter, M. P.; Allan, D. C.; Arias, T. A.; Joannopoulos, J. D. Iterative minimization techniques for *ab initio* total-energy calculations: molecular dynamics and conjugate gradients. *Rev. Mod. Phys.* **1992**, *64*, 1045–1097.
- (34) Kresse, G.; Hafner, J. *Ab initio* molecular dynamics for liquid metals. *Phys. Rev. B: Condens. Matter Phys.* **1993**, *47*, 558.
- (35) Kresse, G.; Hafner, J. *Ab initio* molecular-dynamics simulation of the liquid-metal-amorphous-semiconductor transition in germanium. *Phys. Rev. B: Condens. Matter Phys.* **1994**, *49*, 14251.
- (36) Kresse, G.; Furthmüller, J. Efficiency of *ab-initio* total energy calculations for metals and semiconductors using a plane-wave basis set. *Comput. Mater. Sci.* **1996**, *6*, 15.
- (37) Kresse, G.; Furthmüller, J. Efficient iterative schemes for *ab initio* total-energy calculations using a plane-wave basis set. *Phys. Rev. B: Condens. Matter Phys.* **1996**, *54*, 11169.

- (38) Gonze, X.; Jollet, F.; Abreu Araujo, F.; Adams, D.; Amadon, B.; Applencourt, T.; Audouze, C.; Beuken, J.-M.; Bieder, J.; Bokhanchuk, A.; et al. Recent developments in the ABINIT software package. *Comput. Phys. Commun.* **2016**, *205*, 106.
- (39) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77*, 3865.
- (40) Paier, J.; Marsman, M.; Hummer, K.; Kresse, G.; Gerber, I. C.; Ángyán, J. G. Screened hybrid density functionals applied to solids. *J. Chem. Phys.* **2006**, *124*, 154709.
- (41) Paier, J.; Marsman, M.; Hummer, K.; Kresse, G.; Gerber, I. C.; Ángyán, J. G. Erratum: Screened hybrid density functionals applied to solids [J. Chem. Phys. 124, 154709 (2006)]. *J. Chem. Phys.* **2006**, *125*, 249901.
- (42) Poglitsch, A.; Weber, D. Dynamic disorder in methylammoniumtrihalogenoplumbates (II) observed by millimeter-wave spectroscopy. *J. Chem. Phys.* **1987**, *87*, 6373.
- (43) Stoumpos, C. C.; Malliakas, C. D.; Kanatzidis, M. G. Semiconducting Tin and Lead Iodide Perovskites with Organic Cations: Phase Transitions, High Mobilities, and Near-Infrared Photoluminescent Properties. *Inorg. Chem.* **2013**, *52*, 9019.
- (44) Whalley, L. D.; Skelton, J. M.; Frost, J. M.; Walsh, A. Phonon anharmonicity, lifetimes and thermal transport in $\text{CH}_3\text{NH}_3\text{PbI}_3$ from many-body perturbation theory. *arXiv:1609.00825*; 2016.
- (45) Giustino, F.; Louie, S. G.; Cohen, M. L. Electron-Phonon Renormalization of the Direct Band Gap of Diamond. *Phys. Rev. Lett.* **2010**, *105*, 265501.
- (46) Cannuccia, E.; Marini, A. Effect of the Quantum Zero-Point Atomic Motion on the Optical and Electronic Properties of Diamond and Trans-Polyacetylene. *Phys. Rev. Lett.* **2011**, *107*, 255501.
- (47) Patrick, C. E.; Giustino, F. Quantum nuclear dynamics in the photophysics of diamondoids. *Nat. Commun.* **2013**, *4*, 2006.
- (48) Monserrat, B.; Needs, R. J. Comparing electron-phonon coupling strength in diamond, silicon, and silicon carbide: First-principles study. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2014**, *89*, 214304.
- (49) Poncé, S.; Antonius, G.; Boulanger, P.; Cannuccia, E.; Marini, A.; Côté, M.; Gonze, X. Verification of first-principles codes: Comparison of total energies, phonon frequencies, electron-phonon coupling and zero-point motion correction to the gap between ABINIT and QE/Yambo. *Comput. Mater. Sci.* **2014**, *83*, 341.
- (50) Giustino, F. Electron-phonon interactions from first principles. *arXiv:1603.06965*; 2016.
- (51) Kunc, K.; Martin, R. M. *Ab Initio* Force Constants of GaAs: A New Approach to Calculation of Phonons and Dielectric Properties. *Phys. Rev. Lett.* **1982**, *48*, 406.
- (52) Lloyd-Williams, J. H.; Monserrat, B. Lattice dynamics and electron-phonon coupling calculations using nondiagonal supercells. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2015**, *92*, 184301.
- (53) Poncé, S.; Antonius, G.; Gillet, Y.; Boulanger, P.; Laflamme Janssen, J.; Marini, A.; Côté, M.; Gonze, X. Temperature dependence of electronic eigenenergies in the adiabatic harmonic approximation. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2014**, *90*, 214304.
- (54) Poncé, S.; Gillet, Y.; Laflamme Janssen, J.; Marini, A.; Verstraete, M.; Gonze, X. Temperature dependence of the electronic structure of semiconductors and insulators. *J. Chem. Phys.* **2015**, *143*, 102813.
- (55) Blöchl, P. E. Projector augmented-wave method. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1994**, *50*, 17953.
- (56) Kresse, G.; Joubert, D. From ultrasoft pseudopotentials to the projector augmented-wave method. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1999**, *59*, 1758.
- (57) Tkatchenko, A.; Scheffler, M. Accurate Molecular Van Der Waals Interactions from Ground-State Electron Density and Free-Atom Reference Data. *Phys. Rev. Lett.* **2009**, *102*, 073005.
- (58) Gonze, X.; Lee, C. Dynamical matrices, Born effective charges, dielectric permittivity tensors, and interatomic force constants from density-functional perturbation theory. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1997**, *55*, 10355.
- (59) Gonze, X.; Boulanger, P.; Côté, M. Theoretical approaches to the temperature and zero-point motion effects on the electronic band structure. *Ann. Phys.* **2011**, *523*, 168–178.
- (60) Monserrat, B.; Drummond, N. D.; Pickard, C. J.; Needs, R. J. Electron-Phonon Coupling and the Metallization of Solid Helium at Terapascal Pressures. *Phys. Rev. Lett.* **2014**, *112*, 055504.
- (61) Monserrat, B.; Engel, E. A.; Needs, R. J. Giant electron-phonon interactions in molecular crystals and the importance of nonquadratic coupling. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2015**, *92*, 140302.
- (62) Patrick, C. E.; Jacobsen, K. W.; Thygesen, K. S. Anharmonic stabilization and band gap renormalization in the perovskite CsSnI_3 . *Phys. Rev. B: Condens. Matter Mater. Phys.* **2015**, *92*, 201205.
- (63) Antonius, G.; Poncé, S.; Lantagne-Hurtubise, E.; Auclair, G.; Gonze, X.; Côté, M. Dynamical and anharmonic effects on the electron-phonon coupling and the zero-point renormalization of the electronic structure. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2015**, *92*, 085137.
- (64) Godby, R. W.; Schlüter, M.; Sham, L. J. Accurate Exchange-Correlation Potential for Silicon and Its Discontinuity on Addition of an Electron. *Phys. Rev. Lett.* **1986**, *56*, 2415–2418.
- (65) Godby, R. W.; Schlüter, M.; Sham, L. J. Self-energy operators and exchange-correlation potentials in semiconductors. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1988**, *37*, 10159–10175.
- (66) Antonius, G.; Poncé, S.; Boulanger, P.; Côté, M.; Gonze, X. Many-Body Effects on the Zero-Point Renormalization of the Band Structure. *Phys. Rev. Lett.* **2014**, *112*, 215501.
- (67) Monserrat, B. Correlation effects on electron-phonon coupling in semiconductors: Many-body theory along thermal lines. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2016**, *93*, 100301.
- (68) Cardona, M.; Thewalt, M. L. W. Isotope effects on the optical spectra of semiconductors. *Rev. Mod. Phys.* **2005**, *77*, 1173–1224.
- (69) Saidi, W. A.; Choi, J. J. Nature of the Cubic to Tetragonal Phase Transition in Methylammonium Lead Iodide Perovskite. *J. Chem. Phys.* **2016**, *145*, 144702.
- (70) Han, P.; Bester, G. Large nuclear zero-point motion effect in semiconductor nanoclusters. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2013**, *88*, 165311.
- (71) Mosconi, E.; Quarti, C.; Ivanovska, T.; Ruani, G.; De Angelis, F. Structural and electronic properties of organo-halide lead perovskites: a combined IR-spectroscopy and *ab initio* molecular dynamics investigation. *Phys. Chem. Chem. Phys.* **2014**, *16*, 16137.
- (72) Motta, C.; El-Mellouhi, F.; Kais, S.; Tabet, N.; Alharbi, F.; Sanvito, S. Revealing the role of organic cations in hybrid halide perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$. *Nat. Commun.* **2015**, *6*, 7026.