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Broad Tunability of Carrier Effective Masses in Two-Dimensional Halide Perovskites

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ABSTRACT: The effective mass of charge carriers is a crucial parameter for the design of any optoelectronic device. The estimated values of the effective mass of 2D halide perovskites currently span a broad range, providing an unwelcome source of confusion in this promising material system. Here we highlight how the distortion imposed by the organic spacers, and orbital hybridization effects by the metal cation, govern the effective mass. As a result, the effective mass in 2D halide perovskites can be easily tailored over a wide range. To demonstrate this, we have directly measured the reduced effective mass of charge carriers in phenethylamine (PEA)-based 2D halide perovskites. Combining the experimental results with electronic band-structure calculations, we propose a scaling diagram for the effective mass value versus the distortion of the octahedra imposed by the organic cations.

The carrier effective mass is one of the most fundamental parameters characterizing any semiconductor. It plays a dominant role in charge-transport and optical absorption phenomena that are both of fundamental and practical relevance to semiconductor physics and is intimately connected to key semiconductor characteristics such as the carrier mobility, exciton binding energy, and diffusion length. Consequently, many crucial parameters of semiconductor devices, including integrated circuits, lasers, and solar cells are affected by this fundamental quantity. Moreover, because it can be straightforwardly calculated from the electronic band dispersion, it provides a practical benchmark for electronic-structure theories. Consequently, knowledge of the effective mass is of paramount importance for the in-depth understanding of any semiconductor. Although the effective mass is crucial for the device performance, tuning its value is conventionally restricted to alloying and strain engineering, which have many drawbacks, notably a significant deterioration of crystal quality. Here, we show that two-dimensional (2D) halide perovskites constitute a unique material system, in which the effective mass can be tuned over a broad range by means of ionic compositions that control the octahedral distortion and orbital hybridization without any deterioration of the crystal quality.

2D halide perovskites are attracting renewed interest,^{1–5} essentially driven by their increased environmental stability^{6–9} with respect to their 3D counterparts¹⁰ and their performance in photovoltaic devices^{7,11–13} and light-emitting diodes.^{14,15} In 2D halide perovskites, organic spacers together with the metal cation provide particularly tempting degrees of freedom for

tuning their optoelectronic properties. Organic spacers provide control over the dielectric confinement^{2,5,16–18} as well as the crystal and band structure.^{1,2,19,20} Furthermore, recent studies showed that in 2D halide perovskites the effective mass can be substantially modified by the quantum well thickness¹⁸ or structural changes associated with phase transitions.²¹ Moreover, the substitution of the commonly employed lead cation by tin strongly reduces the effective mass of excitons in 3D perovskites.²² These findings raise the natural question to what extent templating and substitution of the metal cation can be used to engineer the effective mass. To date, there are no direct experimental measurements of the reduced mass in 2D halide perovskites. Currently, the only available experimental values are based on combining excitonic transition spectroscopy in high magnetic fields with advanced exciton modeling or by making assumptions concerning the effective dielectric screening.^{18,23}

Here, we demonstrate, for the first time, a direct experimental determination of the effective mass in 2D (PEA)₂PbI₄ and (PEA)₂SnI₄ perovskites (PEA = phenethylamine). Using high magnetic field spectroscopy we observe interband Landau level transitions. The energy separation of

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Figure 1. (a) Transmission spectra of $(\text{PEA})_2\text{PbI}_4$ at 2 K for different magnetic field strengths. σ^+ and σ^- label right- and left-handed circular polarizations. The inset shows the second derivative, highlighting the equal magnitude of the energy shift of the excitonic features. (b) $T(B)/T(0)$ ratio transmission spectra at selected field strengths. Arrows indicate the equally spaced absorption minima corresponding to interband Landau level transitions. (c) Schematic showing the allowed optical transitions between the Landau states in the conduction (CB) and valence (VB) band as a function of the magnetic field. (d) False-color plot of the $T(B)/T(0)$ ratio transmission spectrum showing the energy shift of the first two Landau level transitions in extreme magnetic fields obtained in single-turn coil experiment.

the Landau levels provides a direct handle for the reduced effective mass of the charge carriers, μ , in 2D halide perovskites. Combining our measurement results with first-principles calculations, we find that μ can be tuned from a very low value of 0.05 to 0.15 by metal composition, which is a much wider range than that previously reported in 3D perovskites.^{22,24–26} Furthermore, we observe that the effective mass in 2D halide perovskites can be even lower than in the corresponding bulk material, which is in striking contrast to what is known for *classic* epitaxial quantum wells.^{27–31} Our direct experimental approach to determine the effective mass together with our theoretical calculations render a broader perspective on the available ways to modify effective mass in this fascinating material system.

To determine the reduced effective mass of charge carriers, μ , we have performed transmission (absorption) measurements in high magnetic fields in order to resolve transitions between Landau levels in the valence and conduction band. The spectra have been measured for two circular polarizations, σ^- (dashed) and σ^+ (solid), with the magnetic field applied in the Faraday configuration. Figure 1a shows typical transmission spectra, at selected magnetic fields up to 65 T, of a thin film of $(\text{PEA})_2\text{PbI}_4$ measured at $T = 2$ K. The spectra can be divided into two distinct energy ranges. The low-energy region is dominated by a strong absorption with a minimum starting at 2.348 eV (black arrow in Figure 1a), corresponding to the 1s excitonic transition, accompanied by series of phonon replicas on the higher-energy side.^{32–34,34} Each of these transitions exhibit the same energy shift ΔE in magnetic field as confirmed by the second derivative of the σ^+ and σ^- spectra at 65 T (inset to Figure 1a). Such a behavior clearly demonstrates the common origin of these transitions reinforcing the phonon replica assignment.³² Similar transmission spectra, at selected magnetic fields, for $(\text{PEA})_2\text{SnI}_4$ are presented in Figure S1. At energies, around ~ 2.6 eV, the spectra exhibit a characteristic

step-like feature, which is related to the band-to-band absorption in agreement with previous assignments.¹⁶

We now focus on absorption between valence and conduction band Landau levels in $(\text{PEA})_2\text{PbI}_4$. We analyze the ratio spectra, i.e., spectra measured at a high magnetic field divided by the zero-field spectrum (see Figure 1b). In the presence of a magnetic field, several equally spaced absorption minima are clearly observed that gain in intensity and shift their energy position with increasing magnetic field. Remarkably, this finding shows that the energy of electrons and holes in the 2D halide perovskites in the presence of a magnetic field is quantized into Landau levels with an orbital quantum number N , as schematically depicted in Figure 1c. The minima observed in the ratio spectra correspond to the transitions between the valence and conduction band Landau levels with the same quantum number N .³⁵ Further confirmation of this result is provided by absorption measurements in magnetic fields up to 156 T, shown as a false-color map in Figure 1d.

The energy of interband Landau levels transition (assuming a parabolic band dispersion) is given by

$$E_N(B) = E_g + \left(N + \frac{1}{2}\right)\hbar\omega_c \quad (1)$$

where E_g is the band gap; $N = 0, 1, 2, \dots$ represents the Landau orbital quantum number in the conduction and valence band; $\hbar\omega_c = eB/\mu$ is the combined (electron + hole) cyclotron energy and $\mu^{-1} = m_e^{-1} + m_h^{-1}$ is the exciton reduced mass (m_e and m_h are the effective masses for electrons and holes, respectively). Panels a and b of Figure 2 shows the $E_N(B)$ energy of the Landau level transitions for $(\text{PEA})_2\text{SnI}_4$ and $(\text{PEA})_2\text{PbI}_4$, respectively.

To determine a global value for the reduced effective mass μ , we analyze the energy difference between consecutive Landau level transitions. Data points in Figure 2c show the experimental $\Delta E(B) = E_{N+1} - E_N$ for all the transitions as a

Figure 2. Fan chart showing the measured energy of the interband Landau transitions as a function of the applied magnetic field strength at 2 K for (a) $(\text{PEA})_2\text{SnI}_4$ and (b) $(\text{PEA})_2\text{PbI}_4$. Stars indicate data points obtained in the *megaGauss* facility. Solid lines indicate fits to the Landau levels according to eq 1. (c) Energy difference between consecutive Landau levels as a function of the magnetic field for $(\text{PEA})_2\text{SnI}_4$ (diamonds), $(\text{PEA})_2\text{PbI}_4$ (squares), and FASnI_3 (circles) along with the fitted curves (solid lines).

function of the applied magnetic field for each sample. The solid lines are fits using the relation $\Delta E(B) = \hbar\omega_c = eB/\mu$, from which we directly determine the value of μ , without any further *a priori* assumptions concerning the value of any material parameter. The extracted reduced effective mass (in the units of electron mass) are 0.055 and 0.091 for $(\text{PEA})_2\text{SnI}_4$ and $(\text{PEA})_2\text{PbI}_4$, respectively. To the best of our knowledge, this is the first time such an approach has successfully been applied to determine the effective mass in 2D halide perovskites. Using the same methodology, we have determined the effective mass μ of 0.102 for the 3D FASnI_3 compound (Figure S4).

Having determined μ , we fit the experimental points in panels a and b using eq 1 to accurately extract the band gap for each compound. Because the $E_N(B) \rightarrow E_g$ as $B \rightarrow 0$, the fits to the experimental points intersect at E_g at zero magnetic field. The number of observed Landau level transitions (up to $N = 6$) imposes a tight constraint on the determined band gap energy E_g , with a standard error lower than ± 5 meV. The obtained band gap energies of 2.084 and 2.608 eV for $(\text{PEA})_2\text{SnI}_4$ and $(\text{PEA})_2\text{PbI}_4$ are higher than those reported previously^{33,34,36,37} (Figure S2). Because the higher excitonic states are merging with the band gap transition into a broad spectral feature (step-like feature at 2.56 eV in Figure 1a, section 2 of the Supporting Information), any attempt to determine the band gap from an optical density plot might lead to spurious values for the band gap. Having the precise value of E_g and energy of the 1s excitonic transition, we determine the exciton binding energy E_b . All values of μ , E_g , and E_b are summarized in Table 1.

Surprisingly, the reduced effective mass in $(\text{PEA})_2\text{PbI}_4$ ($\mu = 0.091$) is very small, close to the μ reported for 3D halide

Table 1. Material Parameters Determined in This Work^a

compound	μ (m_0)	E_g (eV)	E_b (meV)	source
$(\text{PEA})_2\text{SnI}_4$	0.055(0.001)	2.084(0.002)	174	this work
FASnI_3	0.102(0.001)	1.173(0.001)		this work
MAPbI_3	0.104	1.652		25
FAPbI_3	0.09	1.501		25
$(\text{PEA})_2\text{PbI}_4$	0.091(0.001)	2.608(0.002)	260	this work
$(\text{C}_{10}\text{H}_{21}\text{NH}_3)_2\text{PbI}_4$	0.15	~ 2.9		23, 38

^aFrom left: reduced effective mass, band gap energy, exciton binding energy, together with literature data for a temperature of 2 K.

perovskites FAPbI_3 (0.09) and MAPbI_3 (0.104). Remarkably, in the case of $(\text{PEA})_2\text{SnI}_4$ the value μ is further reduced to 0.055 and is clearly even less than in the tin-based 3D perovskite FASnI_3 (0.102). Such low effective masses for PEA-based 2D halide perovskites is in contrast to what is known for fully inorganic epitaxial quantum wells, where quantum confinement effects lead to an enhanced effective mass due to both the nonparabolicity of the conduction band and the wave function penetration into the barrier material.^{27–31} Our results show that the mechanism controlling the in-plane band dispersion in 2D halide perovskites is different and strongly depends on the ionic composition of the material, thus allowing for a broad tunability of the effective mass.

To investigate the microscopic origins of tunable carrier effective masses in 2D halide perovskites, we have performed first-principles calculations based on density functional theory (DFT) at the PBE+SOC level (see Methods section for details). Panels a, b, and c of Figure 3 show the electronic band-structure of $(\text{PEA})_2\text{PbI}_4$, $(\text{BA})_2\text{PbI}_4$ (LT) (BA = n-butylamine; LT refers to low-temperature structure), and $(\text{PEA})_2\text{SnI}_4$, respectively. We determined carrier and reduced exciton masses (see inset of Figure 3a–c,e) along high-symmetry directions of the relevant 2D reciprocal space at the Γ -point. Comparing the results for the three materials, we generally find lower masses for electrons than holes, which reflects the different atomic-orbital hybridization that involves I p–Pb/Sn p and I p–Pb/Sn s orbitals for the conduction and valence band, respectively. Along the series, we find pronounced modulations in the carrier masses that, notably, are stronger for holes than electrons. Specifically, the change of organic spacer cation from BA to PEA reduces μ from 0.15 to 0.11 (inset of Figure 3). Generally, these findings are in reasonable agreement with our experimental data (cf. Table 1). Furthermore, changing the metallic cation from Pb to Sn further reduces μ in the PEA-based 2D halide perovskites to 0.08, in good agreement with the trend in our experimental findings. The high-temperature structural motif of $(\text{BA})_2\text{PbI}_4$ is denoted as $(\text{BA})_2\text{PbI}_4$ (HT), for which $\mu = 0.106$ (inset of Figure 3e). It is also noted that our calculated data for the carrier masses in $(\text{BA})_2\text{PbI}_4$ disagree with theoretical estimates from the literature.¹⁸

We highlight two important effects that allow for a broad tunability of μ in 2D halide perovskites. Both involve the lone-pair s orbital of the metal cation and also explain the larger changes in the aforementioned hybridization of the valence-band states. First, we find that the carrier masses correlate with octahedral distortions in the perovskite layer, which is expected because these affect hybridization between I p and Pb s states.

Figure 3. DFT-computed electronic band-structure of (a) $(\text{PEA})_2\text{PbI}_4$, (b) $(\text{BA})_2\text{PbI}_4$ (LT), and (c) $(\text{PEA})_2\text{SnI}_4$. In all panels, the valence-band maximum (VBM) is set to zero, and the computed hole and electron masses (m_h and m_e) are reported as insets. (d) Schematic representation of octahedral distortions in 2D halide perovskites due to changes in the out-of-plane distortion angle, β , and in-plane distortion angle, δ . (e) DFT-computed map of the effect of δ and β distortion angles on the reduced effective mass, μ , in a set of constrained $(\text{BA})_2\text{PbI}_4$ (LT) geometries (see text for details). Symbols report μ of various fully relaxed 2D halide perovskite structures (see inset). Electronic density of states (DOS) projected onto selected iodine and metal cation (tin or lead) orbitals in the vicinity of the VBM of $(\text{PEA})_2\text{SnI}_4$ (panel f) and $(\text{PEA})_2\text{PbI}_4$ (panel g).

For example, while the distortion angle β (see Figure 3d) is approximately 15° for $(\text{PEA})_2\text{PbI}_4$ and 13° for $(\text{BA})_2\text{PbI}_4$ (LT), their distortion angles δ differ by 10° (smaller than 2° for $(\text{PEA})_2\text{PbI}_4$ and approximately 12° for $(\text{BA})_2\text{PbI}_4$ (LT)).

Therefore, the octahedral layers in PEA-containing compounds are much less corrugated than those of the BA-based perovskite in its low-temperature phase.³⁹ Building on this observation, we construct a set of $(\text{BA})_2\text{PbI}_4$ (LT) structures, in which we tune the distortion angles, β and δ (see Figure 3d), to then compute μ without further ionic relaxation. The resulting map, $\mu(\beta, \delta)$, highlights the wide range of μ values that are in principle accessible within the 2D iodide perovskite family (see Figure 3e), spanning values between approximately 0.05 and 0.30. We superimpose our calculated data of fully relaxed structures to the map and find that trends in the Pb-based 2D halide perovskites largely follow the map, but that the very low μ value of $(\text{PEA})_2\text{SnI}_4$ apparently cannot be explained by octahedral tilting effects alone (see purple diamond in Figure 3e).

Therefore, the second important effect allowing for tunability of carrier masses in 2D halide perovskites must stem from interaction effects due to the change from Pb to Sn. In Figure 3f, we compare the DFT-calculated density of states (DOS) projected onto selected atomic orbitals of $(\text{PEA})_2\text{SnI}_4$ and $(\text{PEA})_2\text{PbI}_4$ in the vicinity of the valence band maximum. The more balanced distribution of DOS between I p and Sn s

compared to I p and Pb s shows that the hybridization between I p and Sn s states is stronger than that between I p and Pb s states. This can be rationalized by the known decrease in stability of the lone-pair s orbital in Sn compared to Pb, resulting in a more favorable alignment with I p states and, thus, increased hybridization and smaller carrier masses.⁴⁰

We now consider the behavior of the 1s excitonic transition (Figure 1a) in magnetic field as it provides an alternative route to estimate the effective mass from magneto-optical measurements.²³ Despite the application of very high magnetic fields, the overall shift of the optical transitions is relatively small because of the large exciton binding energy exceeding 260 meV for $(\text{PEA})_2\text{PbI}_4$ (Table 1). In such a material system, when the interactions are governed by the Coulomb attraction, the magnetic field B can be treated as a perturbation.³⁵ The total shift of the 1s excitonic transition $\delta E_{\sigma\pm}$ as a function of the applied magnetic field is given by the sum of the spin-dependent Zeeman splitting and the diamagnetic shift of the exciton

$$\delta E_{\sigma\pm} = \pm \frac{1}{2} g \mu_B B + c_0 B^2 \quad (2)$$

in which g is the Landé g-factor, μ_B the Bohr magneton, and c_0 the diamagnetic coefficient of the transition.

In order to precisely extract the small shifts in magnetic field we employ an approach which is described in detail in our

preceding works^{21,41} and in section 4 of the Supporting Information. Figure 4a shows the energy shift of the σ^- and σ^+

Figure 4. (a) Magnetic field-induced energy shift of the 1s exciton state for σ^+ and σ^- polarization for (PEA)₂PbI₄ (green) and (PEA)₂SnI₄. (b) Extracted diamagnetic shift for the same materials fitted with eq 2.

components extracted from the fitting procedure (Figure S5). Having the σ^+ and σ^- from the fitting procedure, we decomposed the total shift $\delta E_{\sigma\pm}$ into its individual components: the spin-dependent Zeeman splitting (Figure S6) and diamagnetic shift (Figure 4b). The solid lines in Figure 4b are fits using eq 2 from which we determine the diamagnetic coefficient c_0 for both samples ($c_{\text{Sn}} = 0.68 \mu\text{eV T}^{-2}$ for (PEA)₂SnI₄; $c_{\text{Pb}} = 0.36 \mu\text{eV T}^{-2}$ for (PEA)₂PbI₄).

The diamagnetic coefficient of the excitonic transition can be expressed as

$$c_0 = \frac{e^2}{8\mu} \langle r \rangle^2 \sim \frac{e^2}{\mu^3} \quad (3)$$

in which e is the elementary charge, μ the reduced exciton mass, and $\langle r \rangle^2$ the squared expectation value for the radial extension of the exciton wave function. The latter parameter scales with the reduced exciton mass such that the diamagnetic coefficient c_0 is proportional to $\frac{e^2}{\mu^3}$ within the framework of a 2D hydrogen model for the exciton.³⁵ To support our determination of effective masses from the Landau level spectroscopy, we analyzed the ratio of diamagnetic shift of the 1s excitonic transition of both materials, giving access to the $\frac{\mu_{\text{Pb}}}{\mu_{\text{Sn}}}$

ratio. From Landau level spectroscopy we obtain a $\frac{\mu_{\text{Pb}}}{\mu_{\text{Sn}}}$ ratio of 1.63, whereas from the diamagnetic coefficient we calculated a similar but slightly lower $\frac{\mu_{\text{Pb}}}{\mu_{\text{Sn}}}$ value of 1.24. The latter value, however, is a lower limit as we have not taken the dielectric constant into consideration (see eq 3). Taking an ϵ_{eff} of the 3D Pb- and Sn-based counterparts (~ 9.4 and ~ 8 , respectively)^{22,42} to account for the lower dielectric constant of the SnI₄ layer, the mass ratio increases by at least 12%, approaching the mass ratio obtained from Landau levels. It is worth noting that the dielectric screening in 2D halide perovskites (as well as in other layered semiconductors) is a complex problem requiring good structural modeling.^{18,43,44} Thus, our intention is to provide an intuitive picture rather than to report strict values of ϵ . Because the efficiency of the dielectric screening in 2D halide perovskites is determined by the contrast between the dielectric constants of the inorganic layer and that of the organic spacers,⁵ the higher dielectric constant of PEA (and almost 2-fold reduction in μ with respect

to (BA)₂PbI₄) with respect to BA reduces the efficiency of the dielectric confinement and facilitates the penetration of the exciton wave function into the organic spacer layer.

We have demonstrated the broad tunability of carrier effective masses in 2D halide perovskites through the choice of the organic templating layer and metal cation. We have analyzed the spectral position of equally spaced above band gap absorption features that were identified as optical transitions between the Landau levels in the valence and conduction band. The determined reduced effective mass μ for (PEA)₂SnI₄ ($0.055m_0$) and (PEA)₂PbI₄ ($0.091m_0$) are very close to or even lower than that of their 3D analogues, which is atypical when quantum confinement plays a role. Our first-principles calculations demonstrated that the amount of octahedral distortion in the inorganic lattice can be controlled via the choice of the organic templating layer, which crucially impacts the carrier mass. Furthermore, the choice of metallic cation was shown to additionally modify the carrier mass through enhanced hybridization within the inorganic layer. Taken together, these findings highlight the 2D halide perovskites as a unique material system, in which the effective mass can be broadly tuned through ionic composition. Because the effective mass is a crucial parameter defining the performance of any optoelectronic device, our work implies that targeted ionic composition can be applied to design 2D halide perovskites specific to a given application. For example, in photovoltaics the lower effective mass can be beneficial providing enhanced carrier mobility and reduced exciton binding energy. On the other hand an enhanced effective mass and exciton binding energy can be attractive for light-emitting devices.

METHODS

Optical Spectroscopy Setup. Transmission spectra as a function of magnetic field were measured in a pulsed field magnet with maximum field $B = 68$ T and pulse duration of ~ 500 ms. Broad-band white light was provided by a tungsten halogen lamp. The magnetic field measurements were performed in the Faraday configuration, with the c -axis of the sample parallel to the magnetic field and incident light. The circular polarization was resolved *in situ* using a quarter wave-plate and a polarizer. Measuring in both directions of the magnetic field provides access to the σ^+ and σ^- polarized states. The light is sent to the sample using an optical fiber. The transmitted signal is collected by a lens and coupled to another fiber. The signal is dispersed using the grating of a monochromator and detected using a liquid-nitrogen-cooled CCD camera. The sample is placed in a liquid helium cryostat, and photoluminescence spectra are acquired in the same geometry.

Crystal Synthesis Details. Glass substrates were ultrasonically cleaned sequentially in detergent solution, deionized water, acetone, and isopropanol. Afterward, the substrates were dried in an oven at 140°C for at least 10 min and were subsequently treated with ultraviolet ozone for 20 min. After the cleaning procedure, the substrates were immediately transferred into a nitrogen-filled glovebox for film deposition.

A stoichiometric precursor solution was prepared by dissolving PEA₂I (98.0% TCI) and PbI₂ or SnI₂ at a molar ratio of 2:1 in a mixed solvent of DMF and DMSI (4:1 volume ratio, 0.5 M concentration). The solutions were stirred for at least 3 h at room temperature prior to deposition to homogenize the solutions. A spin-coating process with antisolvent treatment was used to deposit the precursor

solution onto the cleaned substrates. A rotation speed of 2000 rpm was used for the first 10 s of the spin-coating process and was ramped up to 8000 rpm for the remaining 30 s. Five seconds prior to the end of the spin coating cycle the antisolvent (chlorobenzene) was added to the substrate. The films were immediately annealed at 100 °C in a nitrogen atmosphere for 10 min. FASnI₃ was synthesized as reported in ref 45.

Band Structure Calculations. Density functional theory calculations were performed using the VASP code⁴⁶ applying a plane-wave basis set and projector augmented wave potentials.⁴⁷ For describing exchange–correlation, we used the PBE functional⁴⁸ and dispersive corrections with the Tkatchenko–Scheffler method.⁴⁹ Unless otherwise noted, all calculations accounted for the effect of spin–orbit coupling (SOC). The plane-wave kinetic energy cutoff was set to 500 eV, and a 4 × 4 × 1 Γ -centered k-point grid was used for self-consistently calculating the charge density. The experimentally determined crystal structures of BA₂PbI₄³⁹ was taken as a starting point to optimize the lattice parameters and atomic positions, in calculations without accounting for SOC, until the force on each atom was smaller than 0.01 eV/Å^{−1}. In this way, we obtained a unit cell with lattice constants of $a = 8.70$ Å, $b = 8.53$ Å, and $c = 28.28$ Å for the high-temperature phase and $a = 8.36$ Å, $b = 8.97$ Å, and $c = 26.14$ Å for the low-temperature phase, which agree well with the experimental result of $a = 8.88$ Å, $b = 8.69$ Å, and $c = 27.60$ Å and $a = 8.43$ Å, $b = 8.99$ Å, and $c = 26.23$ Å, respectively. Similar steps were performed on PEA₂PbI₄ and PEA₂SnI₄. For PEA₂PbI₄, the DFT optimized lattice constants $a = 8.66$ Å, $b = 8.63$ Å, $c = 32.32$ Å also agree reasonably well with the experimental data:⁵⁰ $a = 8.74$ Å, $b = 8.74$ Å, and $c = 33.03$ Å. However, the experimentally determined structure with two Sn atoms in the unit cell⁵¹ does not sufficiently describe distortions of SnI₆ octahedra in the calculation; hence, a supercell with four Sn atoms was adapted, where $a = 8.61$ Å, $b = 8.58$ Å, and $c = 32.22$ Å. The supercell can be transformed to a unit cell with $a = 6.11$ Å, $b = 6.04$ Å, and $c = 32.22$ Å, which agreed with the experimental structure of $a = 6.10$ Å, $b = 6.14$ Å, and $c = 32.30$ Å.

The color map in Figure 3e was interpolated by choosing 20 structures spanning the octahedral distortions of angles $\delta = 0, 5, 10, 15$ and $\beta = 0, 5, 10, 15, 20$. As shown in Figure 3d, β and δ are bond angles that involve an iodine atom and two neighboring lead atoms projected onto the (100)–(010) plane and (001)–(010) plane, respectively. The set of data points are calculated based on the BA₂PbI₄ (LT) structure, for which I atoms were moved according to β and δ angles, while the lattice constants and positions of Pb atoms and BA molecules were kept frozen.

The electronic band structure calculations were performed nonself-consistently, using an equally spaced k-grid of 30 points on each path between two high-symmetry points ($\Delta k \approx 0.002$ Å^{−1}); the numerical convergence with respect to Δk was verified. Electron and hole masses, m_e^* and m_h^* were calculated around Γ toward the X-point (0.5, 0, 0) in the Brillouin zone, because the fundamental gap occurs at the Γ -point. We note that the effective masses calculated with PBE + SOC hardly depend on the specific high-symmetry direction being probed in the 2D reciprocal space of dispersive bands. The effective masses were obtained using a finite difference method following the equation $m^* = \hbar^2(\partial^2 E / \partial^2 k)^{-1} \approx \hbar^2((E(k_\Gamma + 2\Delta k) + E(k_\Gamma) - 2E(k_\Gamma + \Delta k)) / \Delta k^2)^{-1}$. The exciton total effective mass M_X was then obtained according to

$M_X^{-1} = m_e^{-1} + m_h^{-1}$. To test the reliability of our PBE-based results, we have also performed HSE calculations, from which we obtained an essentially identical result for the reduced exciton mass compared to the PBE data.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsnenergylett.0c01758>.

Transmission spectra of (PEA)₂SnI₄ in magnetic field, band gap determination for (PEA)₂SnI₄ and (PEA)₂PbI₄, reflection spectra of FASnI₃ in magnetic field, and temperature dependence of transmission spectra of (PEA)₂SnI₄ and (PEA)₂PbI₄ (PDF)

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The authors declare no competing financial interest.

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