

Unraveling the Elastic Properties of (Quasi)Two-Dimensional Hybrid Perovskites: A Joint Experimental and Theoretical Study

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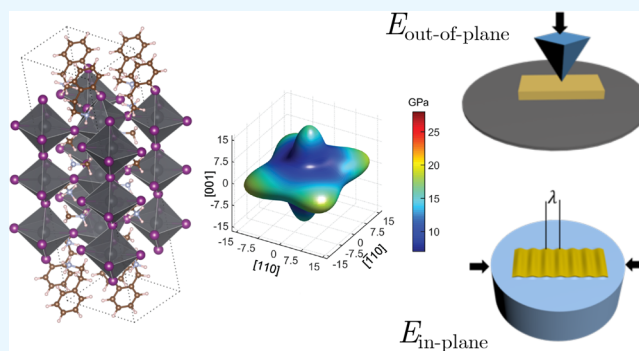
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ABSTRACT: The unique properties of hybrid organic–inorganic perovskites (HOIPs) promise to open doors to next-generation flexible optoelectronic devices. Before such advances are realized, a fundamental understanding of the mechanical properties of HOIPs is required. Here, we combine *ab initio* density functional theory (DFT) modeling with a diverse set of experiments to study the elastic properties of (quasi)2D HOIPs. Specifically, we focus on (quasi)2D single crystals of phenethylammonium methylammonium lead iodide, $(\text{PEA})_2\text{PbI}_4(\text{MAPbI}_3)_{n-1}$, and their 3D counterpart, MAPbI_3 . We used nanoindentation (both Hertzian and Oliver–Pharr analyses) in combination with elastic buckling instability experiments to establish the out-of-plane and in-plane elastic moduli. The effect of Van der Waals (vdW) forces, different interlayer interactions, and finite temperature are combined with DFT calculations to accurately model the system. Our results reveal a nonmonotonic dependence of both the in-plane and out-of-plane elastic moduli on the number of inorganic layers (n) rationalized by first-principles calculations. We discuss how the presence of defects in as-grown crystals and macroscopic interlayer deformations affect the mechanical response of (quasi)2D HOIPs. Comparing the in- and out-of-plane experimental results with the theory reveals that perturbations to the covalent and ionic bonds (which hold a 2D layer together) is responsible for the relative out-of-plane stiffness of these materials. In contrast, we conjecture that the in-plane softness originates from macroscopic or mesoscopic motions between 2D layers during buckling experiments. Additionally, we learn how dispersion and π interactions in organic bilayers can have a determining role in the elastic response of the materials, especially in the out-of-plane direction. The understanding gained by comparing *ab initio* and experimental techniques paves the way for rational design of layered HOIPs with mechanical properties favorable for strain-intensive applications. Combined with filters for other favorable criteria, e.g., thermal or moisture stability, one can systematically screen viable (quasi)2D HOIPs for a variety of flexible optoelectronic applications.

KEYWORDS: two-dimensional hybrid organic–inorganic perovskites, layered perovskites, elastic properties, mechanical properties, nanoindentation, wrinkling, density functional theory, flexible electronics



1. INTRODUCTION

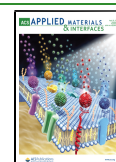
Thin-film electronic devices that are flexible and able to maintain performance while enduring different types of stresses (uniaxial, biaxial, hydrostatic) of varying magnitudes are technologically desirable.^{1–3} The quest to rationally search for and fabricate such thin films requires a detailed understanding of their mechanical properties, both in the elastic and plastic regimes. Hybrid organic–inorganic perovskites (HOIPs) are a class of materials that continues to revolutionize the field of photovoltaics, with power conversion efficiencies of solar cells comprising them surpassing 25%.^{4,5} Additionally, low-temperature production methods and high optical absorption over the visible spectrum make these materials good candidates for the next generation of optoelectronic devices.^{6,7} Three-dimensional (3D) HOIPs belong to a wider class of materials with composition ABX_3 , where the BX_6

groups form octahedral units that are connected through corner-sharing X atoms, and the A cations are engaged in the confined spaces formed by this network. Most of the work on perovskite materials for photovoltaic applications has focused on materials where $\text{A} = \text{CH}_3\text{NH}_3$ and/or Cs; $\text{B} = \text{Pb}$; $\text{X} = \text{I}$ and/or Br.⁸ Judiciously manipulating the stoichiometry of precursors and introducing bulkier cations result in controlled separation of the ABX_3 octahedra in the out-of-plane direction, with layers of the larger organic cations separating the

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octahedral layers. Specifically, the materials studied here belong to the Ruddlesden–Popper family of structures with the general form $A_2A_{n-1}B_nX_{3n+1}$.^{5,9,10}

Such two-dimensional (2D) hybrid perovskite materials have been shown to have increased ambient stability compared to their three-dimensional counterparts.^{11,12} Increasingly, these materials are attracting great attention as one can introduce functionalities to both the organic and inorganic layers to access a rich field of physical and optoelectronic properties arising from the combination of diverse organic and inorganic moieties.^{11,13} The relative ease of processing perovskite materials (both 3D and 2D) from solution promises their application in thin-film devices for flexible electronics and other strain-intensive applications.¹⁴ In order to effectively apply these materials in flexible devices and to understand their limitations, knowledge of their behavior under different mechanical conditions is necessary. Among the 2D HOIPs, it has been shown that systems that incorporate organic cations with aromatic rings yield better (moisture) stability. Here, for the first time, we study the elastic properties of such aromatic-based 2D HOIPs and reveal the interplay between their structure, mechanical properties, and chemical stability.

Recent efforts have contributed to the characterization of the mechanical properties of perovskite materials. DFT calculations performed by Feng have quantified the elastic constants of $\text{CH}_3\text{NH}_3\text{BX}_3$, where $B = \text{Sn}, \text{Pb}$ and $X = \text{Br}, \text{I}$ ¹⁵ from which the Young's moduli, shear, and bulk moduli for the cubic, tetragonal, and orthorhombic phases of each material were determined. Cheetham and co-workers conducted the first experimental study to measure the Young's modulus and hardness of HOIP single crystals by nanoindentation,¹⁶ revealing the role of different types of halides in dictating the HOIP elastic properties by changing the chemical nature of the Pb-halide bond. A subsequent nanoindentation study of HOIPs and CsPbBr_3 single crystals by Cahen and co-workers provided qualitative agreement with this work.¹⁷ Complementing these static elastic studies of HOIP single crystals, we recently reported on the dynamic mechanical properties of HOIP single crystals and found that the time and rate dependences of plastic deformation are directly controlled by their Pb-X framework structure.¹⁸ Mechanical studies have also been extended to polycrystalline HOIP films. Dauskardt and co-workers¹⁹ studied the fracture resistance of MAPbI_3 thin films. They found MAPbI_3 -based solar cells to exhibit low resistance to fracture, with fracture energies lower than 1.5 J/m² regardless of stoichiometry, precursor chemistry, processing conditions, and deposition techniques. This study implicates both perovskite active layers and organic charge transport layers as the main sources of global mechanical failure in solution-processed HOIP solar cells, rather than the ITO electrodes. Lin and co-workers²⁰ performed a study based on atomistic simulations that probed the ductility of single-crystalline and polycrystalline MAPbI_3 . Compared to inorganic optoelectronic materials, they found HOIPs to absorb more energy before fracture and, in the case of polycrystalline films, the ductility to increase with decreasing grain size. Thus, the HOIPs are resilient toward more global (extensive) deformations. Nevertheless, decreasing grain size renders the material softer and less resilient toward locally intensive strain, making it vulnerable to crack propagation. A recent joint experimental–theoretical study examined the out-of-plane elastic properties of several (quasi)2D layered alkylammonium lead iodide crystals.²¹ They report a monotonic increase in out-of-

plane elastic moduli with increasing number of inorganic layers, n , and a monotonic decrease in the elastic moduli when the alkyl chain length on the larger organic cation increases. However, their DFT-driven values are almost twice as great as the experimental ones, which was hypothesized to be due to defects in the samples and finite temperature effects.

Inspired by the increasing interest in (quasi)2D HOIPs,^{11,22–24} we determine and report the elastic properties of single crystals of these materials. Specifically, we focus on a series of phenethylammonium (PEA) methylammonium lead iodide crystals, with the general formula $(\text{C}_6\text{H}_5(\text{CH}_2)_2\text{NH}_3)_2(\text{CH}_3\text{NH}_3)_{n-1}[\text{Pb}_n\text{I}_{3n+1}]$, hereafter referred to as $(\text{PEA})_2\text{PbI}_4(\text{MAPbI}_3)_{n-1}$, with $n = 1, 2, 3$, and 4 (Figure 1a). Here, n represents the number of inorganic

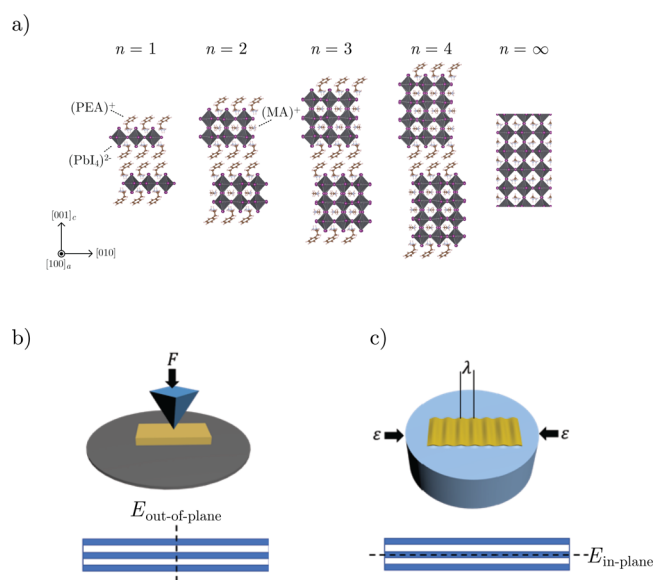


Figure 1. (a) Structure of two-dimensional perovskite crystals studied in this work as the number of inorganic layers, n , increases. (b) In nanoindentation, a diamond tip is pressed against the (001) surface of the crystal in a load-controlled experiment. This experiment yields the out-of-plane elastic modulus, E . (c) Schematic showing an exfoliated 2D crystals undergoing buckling instability as a uniaxial compressive strain is applied to the elastomeric substrate. Cylindrical PDMS substrates were used to facilitate directional control of the applied uniaxial strain. This experiment measures the in-plane elastic modulus.

layers between the larger PEA cation layers in the unit cell. The $(\text{PEA})_2\text{PbI}_4(\text{MAPbI}_3)_{n-1}$ system we study incorporates bulky PEA cations, which are known to have significantly greater moisture resistance than the alkylammonium-based systems.²⁵ These aromatic cations possess stronger interlayer π interactions and thus have a greater tendency for perfect interlayer stacking, reducing but not eliminating structural defects, e.g., missing ions, interlayer ripples, and the corresponding voids. Such favorable stacking, and the hydrophobic nature of bulky aromatic cations, not only enhance the ambient stability but can also change the mechanical properties of the material. In order to effectively apply these materials in strain-intensive applications, the interplay between the chemical stability and mechanical properties must be understood. For the first time, we (a) show a nonmonotonic n dependence of out-of-plane elastic properties in (quasi)2D HOIPs using nanoindentation experi-

ments, (b) introduce a procedure for first-principles DFT-based determination of the elastic properties of 2D HOIPs that yields a quantitative agreement with experimentally measured out-of-plane elastic moduli, and (c) measure the n dependence of the in-plane elastic response for this class of materials via elastic buckling instability experiments. We show vdW forces have a great effect on structural and mechanical properties of these 2D-HOIPs. Our DFT calculations benefit from the very accurate Grimme-D3 correction scheme, which includes the two- and three-body dispersion interactions, making it able to discern the chemical environment of the atoms in addition to their identity.¹⁷ Additionally, our DFT structural models are fully relaxed with no empirical structural constraints. Consequently, we do not use any symmetry arguments to have some elastic constants equal to zero, deriving the effective elastic moduli self-consistently within the framework of (zero temperature) DFT. We then combine such self-consistent approach with a final universal temperature correction to the Young's modulus that has been recently introduced by Zakarian et al.²⁷

The hybrid layered structure has two different types of interatomic interactions: first, the stronger chemical interactions that exist inside each 2D inorganic layer, and second, the weaker vdW and π interactions (in the case of aromatic cations). We will discuss how these two fundamentally different types of interactions dictate the anisotropy of the mechanical properties in these materials. Our diverse set of experimental and theoretical observations reveal that different types of multiscale deformations are responsible for the elastic properties of (quasi)2D HOIPs, in- and out-of-plane. This work bridges the gap between structural and chemical stability of HOIPs and points to the promising direction of new applications, which can be enabled by high-quality, water-resistant, and flexible photovoltaic devices based on (quasi)2D HOIPs.

2. METHODS

2.1. Crystal Growth. (PEA)₂PbI₄ (MAPbI₃) _{$n-1$} single crystals, with $n = 1, 2, 3$, and 4, were grown as previously reported.²⁸ Briefly, precursors containing lead oxide, methylammonium iodide, and phenethylamine with specific ratios, namely, 1.72:0:3.45 mmol ($n = 1$), 6:18:1 mmol ($n = 2$), 10:24:1 mmol ($n = 3$), and 10:30:1 mmol ($n = 4$), were dissolved in 30 mL of hydriodic acid (HI) solution (57% w/w in water) at $\sim 90^\circ\text{C}$. The solution was then slowly cooled to room temperature at a rate of 1°C/h . As-grown crystals were rinsed with diethyl ether and then dried under vacuum. X-ray diffraction data for the as-grown crystals can be found in Section 1 of the Supporting Information.

2.2. Nanoindentation Measurements. We measured the out-of-plane elastic modulus using nanoindentation (Figure 1b). Nanoindentation experiments were performed using a Triboscope Nano-mechanical Testing System (Hysitron Inc., Minneapolis, MN). For the nanoindentation, a $3\ \mu\text{m}$ radius conospherical tip was pressed against the (001) surface of the crystals in a load-controlled experiment with a maximum load of 2 mN at loading/unloading rate of $10\ \mu\text{N s}^{-1}$. The tip was held at maximum load for 30 s. All crystals were glued (Loctite 495) to stainless steel atomic force microscopy specimen discs. Crystal samples used for these measurements were approximately $500\ \mu\text{m}$ - to 1 mm-thick, while their lateral dimensions were millimetric. In addition, measurements were performed under ambient conditions, in the dark, after brief light exposure for crystal placement and tip-surface approach. While crystals were stored in a dark, inert environment, to reduce the effects from contamination or degradation, the surface of the crystals was exfoliated using adhesive tape prior to measurements in order to expose a fresh layer. From the load–displacement curve (Figure 2a),

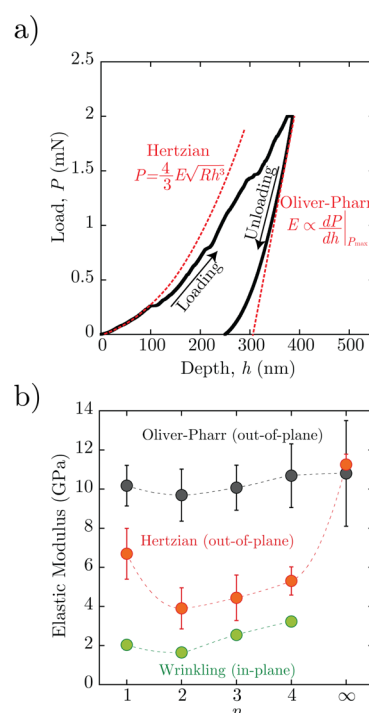


Figure 2. (a) Representative nanoindentation load–displacement curve obtained on an $n = 2$ crystal. Hertzian and Oliver–Pharr fittings used to calculate the elastic moduli are shown. (b) Comparison of the elastic moduli obtained from nanoindentation (using both Hertzian and Oliver–Pharr analyses) and elastic buckling instability analysis (wrinkling) as a function of n for 2D perovskites. Comparison between the elastic moduli for (quasi)2D HOIPs and the 3D MAPbI₃ crystal ($n = \infty$) is also shown. Error bars represent the standard deviation from at least three independent measurements.

we determined the out-of-plane elastic modulus ($E_{\text{out-of-plane}}$). The Hertzian analysis extracts the elastic modulus from the nanoindentation deformation curve on loading, prior to the occurrence of first pop-in (Figure 2a). Pop-ins are defined as sudden excursions in displacement with negligible change in measured force during nanoindentation loading. The first pop-in event observed for all materials tested was observed at a depth of less than 100 nm (Figure S2). In Oliver–Pharr analysis, the elastic modulus is calculated from the load–displacement slope on unloading (Figure 2a).

2.3. Elastic Buckling Instability (Wrinkling) Experiments. We measured the in-plane elastic modulus of each crystal via elastic buckling instability (wrinkling). Figure 1c shows a schematic of a 2D perovskite crystal attached to a polydimethylsiloxane (PDMS) substrate while undergoing wrinkling. As-grown crystals were picked up from a glass slide using adhesive tape and repeatedly transferred to fresh tape to produce increasingly thin crystals attached on the receiving tape. In the last exfoliation step, crystals are transferred to the final receiving substrate by manually attaching the tape on the PDMS surface and gently removing it. The resulting crystals used in the wrinkling experiments are thin (50–250 nm) two-dimensional crystal films. The crystal thickness was obtained by measuring the step heights (relative to the PDMS surface) through optical profilometry using a Leica DCM 3D Micro-optical system (Leica Microsystems GmbH, Germany). Polydimethylsiloxane (PDMS) substrates were prepared by mixing the Dow Corning Sylgard 184 polymer base and cross-linking agent at a 20:1 polymer base/cross-linking agent ratio by mass. The 20:1 mix was poured into cylindrical molds of 1.5 cm in diameter and 2 cm in height. The preparation was cross-linked for at least 4 h at 70°C . Tensile tests (Instron, Norwood, MA) were used to characterize the Young's modulus of PDMS dogbones prepared under the same conditions as the substrates, $\bar{E}_s = 0.4 \pm 0.05\ \text{MPa}$. A home-built, screw-driven, manual strain stage was used to apply uniaxial

mechanical compression to the elastomeric substrates. When the elastomeric substrate is uniaxially compressed in-plane, the attached crystal undergoes elastic buckling instability at a critical strain, defined as $\varepsilon_c = 1/4(3\bar{E}_s/\bar{E}_{\text{in-plane}})^{2/3}$, where $\bar{E} = E/(1 - \nu^2)$ is the plane-strain modulus, expressed in terms of the in-plane Young's modulus, E , and Poisson's ratio, ν . The subscript s refers to the elastic modulus of the substrate. The resulting wrinkled topography has a characteristic wavelength $\lambda = 2\pi t(3\bar{E}_s/\bar{E}_{\text{in-plane}})^{1/3}$. We measured the wrinkling wavelength (λ) and corresponding crystal thickness (t) using optical profilometry (Leica DCM 3D Micro-optical system). $\bar{E}_{\text{in-plane}}$ was extracted from the slope of λ versus t , as reported previously.^{29,30} λ versus t for wrinkling experiments on the (quasi)2D materials studied here are shown in Section 2 of the Supporting Information.

2.4. DFT Modeling. Our calculations were done using density functional theory (DFT) with a plane-wave basis set, as implemented in the Quantum Espresso software package.³¹ Ultrasoft GBRV pseudopotentials³² and the Perdew–Burke–Ernzerhof (PBE) exchange correlation (XC) functional have been used.³³ Only a small subset of calculations for determining reduced density gradient calculations were done using norm-conserving pseudopotentials.³⁴ Dispersion interactions were accounted for using the Grimme-D3 method²⁶ as the inclusion of dispersion interactions to accurately describe hybrid perovskite systems has been shown to be of great importance.³⁵ This is further reinforced by our findings here that show the importance of such interactions in capturing the elastic response of 2D HOIPs. Here, we computed all independent elastic coefficients of these materials using the stress–strain methodology.^{36–38} As shown in Figure 1a and Table S1, the relaxed DFT ground-state (PEA)₂PbI₄(MAPbI₃)_{*n*−1} structures for $n = 1, 2, 3$, and 4 are all triclinic, and MAPbI₃ ($n = \infty$) exhibits a tetragonal crystal structure ($a \approx b \neq c$, $\alpha, \gamma, \beta = 90^\circ$). The calculated elastic coefficients C_{ij} for different n values are shown in Section 5 of the Supporting Information. One should note that the elastic moduli defined in this work as E correspond to effective moduli, which take into account several elastic coefficients C_{ij} as defined in Section 5 of the Supporting Information. Our C_{ij} matrices satisfy the generic necessary and sufficient elastic stability condition that all eigenvalues of the matrix are positive.³⁹ Due to its tetragonal crystal structure, coefficients C_{11} and C_{22} for MAPbI₃ are almost the same (Table S2), and the off-diagonal moduli from C_{14} to C_{56} are almost zero (Table S3). Using these coefficients, the effective Young's moduli, E_V and E_R , are obtained from the Voigt (continuous strain)⁴⁰ and Reuss (continuous stress)⁴¹ averaging methods. The Voigt and Reuss averages are the upper and lower bounds for elastic moduli, respectively. The detailed procedure used to calculate the effective Young's moduli and the Poisson's ratio is described in Section 5 of the Supporting Information. Furthermore, we estimate the temperature dependence of our DFT-derived elastic moduli, using a universal relation, proposed to interpret and extend first-principles results and experimentally confirmed for a wide class of materials, that has been recently developed by Zakarian et al. (for more details, see Section 6 of the Supporting Information).²⁷

3. RESULTS AND DISCUSSION

3.1. Out-of-Plane Elastic Properties. To study the out-of-plane deformation in the elastic regime, we measured the elastic modulus of each crystal by nanoindentation. The structures of the 2D hybrid perovskite single crystals in this study, with $n = 1–4$, are shown in Figure 1a. The nanoindentation load–displacement curves of layered perovskite crystal ($n = 2$) in Figure 2a show multiple sudden excursions in penetration depth with minimal variation in load. These events are known as pop-ins.⁴² In three-dimensional perovskite crystals, pop-ins represent the onset of plastic deformation through nucleation and propagation of slip dislocations.¹⁸ Representative load–displacement curves for all tested crystals are shown in Section 2 of the Supporting Information. The observation of multiple pop-in events is

common in layered crystals, such as muscovite.⁴³ In contrast to their three-dimensional counterparts, pop-ins in two-dimensional materials are usually attributed to stress localization in the form of kink-bands,^{44,45} interlayer delamination,⁴⁵ or fracture.

Figure 2b shows the out-of-plane modulus obtained through two approaches, Hertzian⁴⁶ and Oliver–Pharr⁴⁷ analyses, of nanoindentation data. Different from the results of Tu et al.,²¹ our analyses yield elastic moduli that are nonmonotonically dependent on n , with the magnitude of the moduli obtained from the Oliver–Pharr analysis being greater than those extracted from the Hertzian. In Oliver–Pharr analysis, it is assumed that the elastic responses under the tip before and after nanoindentation are the same. To understand why the Oliver–Pharr and Hertzian out-of-plane moduli are different in magnitude, we need to understand the deformation mechanisms during nanoindentation and the assumptions made in these analyses. During nanoindentation, a sharp diamond tip penetrates the sample perpendicular to the surface. The stress involved is very high and concentrated to the small sample volume around the sample–tip contact zone. The stress field is triaxial, with the main component perpendicular to the surface, underneath the tip. The stresses are mainly compressive, but tension and shear are also present around the contact zone. The differences between the results from Hertzian and Oliver–Pharr analyses suggest that significant structural change takes place during nanoindentation. Pop-ins and the hysteresis in elastic recovery measured during unloading are strong indications that the sample structure no longer corresponds to the as-grown two-dimensional perovskite crystal. As we will elucidate later, we conjecture that pop-in events reduce the effect of some of the entropy-driven structural defects present in the as-grown samples. Such structural defects can dominate (and soften) the elastic response of the material, as witnessed in the Hertzian regime. Consequently, after compressing those defects (leading to pop-ins) by the load introduced by the diamond tip, the material is rendered stiffer and the elastic response becomes closer to intrinsic values that correspond to perfect layered HOIPs. To gain a better understanding of the deformation mechanisms and elastic properties of (quasi)2D HOIP crystals in response to uniaxial mechanical stresses, we perform *ab initio* calculations of (PEA)₂PbI₄(MAPbI₃)_{*n*−1} for $n = 1, 2, 3$, and 4, as well as the 3D counterpart ($n = \infty$), MAPbI₃. Figure 3a depicts the trend of Young's modulus versus n . Table S4 and Figure 3 show that as n increases, the bulk, shear, and Young's moduli become larger due to an increase in the ratio of (stiffer) inorganic octahedra to (softer) long organic cations. However, this is not the only factor influencing the elastic properties; the ductility and distortions of these structures are also important, especially when comparing computational to experimental results. In Figure 3a, the effective Young's moduli, E_V and E_R , are obtained from the Voigt (continuous strain) and Reuss (continuous stress) averaging methods, respectively.^{37,41} Compared to E_V , E_R is more strongly influenced by the shear components of the stiffness matrix (Table S3).⁴¹ For a specific structure, values in the range between the upper bound E_V and lower bound E_R are expected. In nanoindentation, the measured elastic properties can be described as an effective Young's modulus containing contributions from both normal and shear stresses due to the shape of the indenter.^{16,47} Comparing the computed elastic moduli to the experimentally measured values, we deduce that the Oliver–Pharr analysis provides the best representation of

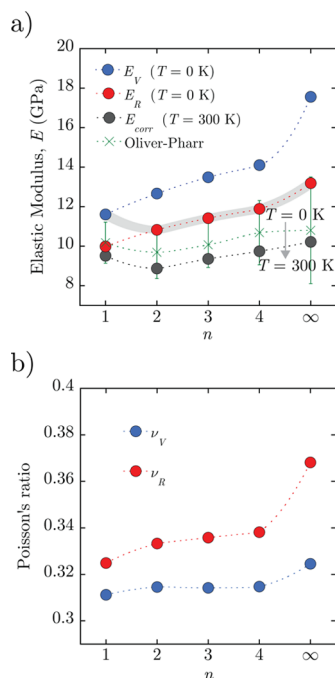


Figure 3. (a) Young's moduli of the $(\text{PEA})_2\text{PbI}_4(\text{MAPbI}_3)_{n-1}$ ($n = 1, 2, 3, 4$ and ∞) system, as a function of n . One can see both the Voigt (blue) and Reuss (red) limits at $T = 0$ K. Considering the effect of Poisson's ratio and octahedral distortions, the effective Young's moduli of $n = 1$ and $n > 1$ structures are closer to E_V and E_R , respectively. Thus, here, we use the shaded area in gray to represent the theoretically predicted effective Young's moduli directly comparable to the experiments (in green). The finite-temperature corrected values for the shaded area are shown in black. (b) Poisson's ratio in both Voigt and Reuss limits as a function of n .

the elastic properties of defect-free single-crystal samples. A noticeable difference between either the Voigt or Reuss DFT-derived numbers (Figure 3a) and the experiment (Figure 2b) is the nonmonotonic behavior of the experimental elastic moduli. Such nonmonotonic behavior is not reflected in either the Voigt or Reuss limits. Nevertheless, as will be discussed below, a deeper look into the structure of the material reveals the possible reasons behind this discrepancy.

Here, we rationalize why in Figure 3a, the nonmonotonic gray curve resembling the experimental trend is achieved by appropriately combining Voigt (for $n = 1$) and Reuss (for $n > 1$) limits. Figure 3b shows the Poisson's ratio as a function of n . The larger the Poisson's ratio, the more ductile a material is. As a result, during nanoindentation of a ductile material, shear deformations can play a dominating role.¹⁵ The Poisson's ratio is nearly stable from $n = 1$ to $n = 4$, but it increases for $n = \infty$. Hence, a higher proclivity toward shear deformations renders the effective Young's modulus of MAPbI_3 ($n = \infty$) closer to the (softer) Reuss (E_R) limit (Figure 3a). As will be discussed below, this should be contrasted with the case of $n = 1$ for which shear deformations play a less significant role and result in values closer to the E_V . The $n > 1$ structures, similar to $n = \infty$, are also closer to E_R . In short, the reason behind this is that the $n = 1$ structure, due to the lack of short cation groups, has a more ordered structure (relative to $n > 1$ layered structures) and thus hosts less interlayer voids and ripples (structural defects). Additionally, the structures with finite n have a greater formation energy, being maximal at $n = 1$.⁹ Thus the $n = 1$ structure is the most thermodynamically stable, while the $n =$

∞ is the least stable and most prone to point and stoichiometric defects. As for the $n = \infty$ case, there is no interlayer voids or ripples as the structure is not layered. Nonetheless, as mentioned above, the large ductility, the disorder introduced by the shorter (MA) cations, and smaller thermodynamic stability render the material closer to the (softer) Reuss (E_R) limit.

A first-principles measure to quantify order in the $n = 1$ structure is provided by comparing the degree of octahedral distortions in the $n = 1 - 4$ structures, as shown in Figure 4.

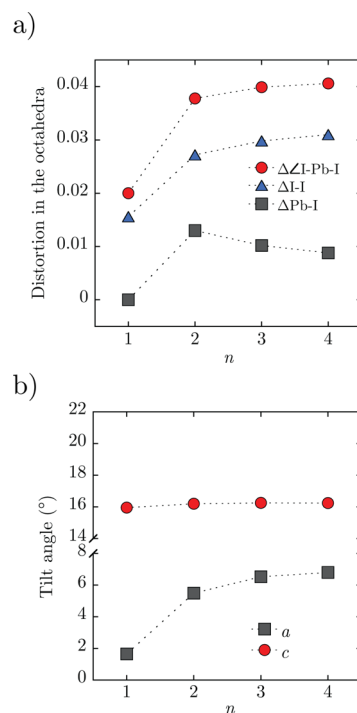


Figure 4. (a) Distortions in a single octahedron of $(\text{PEA})_2\text{PbI}_4(\text{MAPbI}_3)_{n-1}$ ($n = 1, 2, 3, 4$), as quantified by the relative change in the average I–Pb–I angle (red), I–I distance (blue), and Pb–I bond length (black). (b) Tilt angles of adjacent octahedra around the a and c axes. For detailed definitions, see Section 7 of the Supporting Information.

The octahedral distortions are associated with (a) changes in the bond lengths and angles in a single octahedron and (b) the tilting between consecutive layers of octahedra. For these layered structures, the out-of-plane distortions in each octahedron and the tilting around the in-plane axis (the a axis) dictate the large-scale order of the layered structure. As evident from Figure 4a,b, increasing the presence of MA^+ cations in the layered perovskite structure ($n \geq 2$) boosts the octahedral distortions. The small MA^+ cations (relative to the octahedral cage size) distort the structure to achieve optimal interaction with the I^- anions. Although such distortions are ordered (with a short period) in a small and periodic simulation slab, the real octahedral distortions depend on the thermal orientation of MA^+ cations across many unit cells. The greater degree of octahedral rotations in structures with MA^+ then can lead to a more distorted layered structure that can host ripples over many unit cells, and the less perfect stacking promotes more structural defects.²⁰ Such structural defects are softer in nature, and their shear response to nanoindentation could dominate the initial elastic response of the material (see

Section 8 of the Supporting Information), which results in an effective Young's modulus that is closer to E_R for $n = 2, 3$, and 4.^{48–50} In contrast, the structure without MA^+ ($n = 1$) has better odds of staying as a perfect layered structure; consequently, its elastic moduli are closer to the (stiffer) Voigt limit. We propose the disorder that originates from the presence of MA^+ to be the root cause for the nonmonotonic trend of the Young's modulus as a function of n , as observed in the experiments (highlighted region of Figure 3a).

Our DFT-derived results at $T = 0$ K are in good agreement with the Oliver–Pharr values (see shaded gray area in Figure 3a). We can further improve the agreement by introducing the finite temperature effect on Young's modulus.²⁷ The close agreement this procedure yields with experimental values is a significant improvement upon previous literature on similar (quasi)2D perovskite materials in which the DFT-derived and experimental values differ by almost a factor of 2.²¹ Additionally, our computational results indicate that the arrangement of π interactions can fine-tune the mechanical response of the stacked (quasi)2D HOIPs (see Figure 5a). The

of π interactions in the organic bilayer. We find that the small remaining discrepancy after finite temperature correction (see Figure 3a) is due to a slight underestimation of the π interactions in our original model. The model structures, shown in Figure 1a, were made with minimal number of possible atoms in a supercell to establish a viable protocol that can yield good estimates and understanding of the mechanical properties of HOIPs (in the Oliver–Pharr regime) with minimal computational cost. These structures show parallel π – π interaction and can be classified as an nRP stacking. It turns out that a larger supercell (more computationally expensive) that can capture a more intricate network of π interactions can further improve the quantitative predictive power of the model (such structure can also be classified as nRP).⁵¹ The π interactions can be visualized by the noncovalent index (NCI) based on reduced density gradient ($s = \frac{1}{2(3\pi^2)^{1/3}} \frac{|\nabla\rho|^2}{\rho^{4/3}}$).⁵² In our original model, π – π interactions (where the phenyl rings are parallel), in addition to vdW, were responsible for the interlayer interactions (see Figure 5c). The calculations we have performed with a larger supercell (see Figure 5b) indicate that a more energetically favorable stacking pattern includes T-shaped π interactions in the organic bilayer (see Figure 5d). Such structure is approximately $1 k_B T$ (per PEA) lower in energy than the one with parallel π – π interaction and consequently is slightly stiffer. Figure 5a indicates how the DFT-derived modulus for the $n = 1$ structure in the larger supercell with T-shaped π interactions can perfectly match the experimental data. Along similar lines of reasoning, we have quantified the effect of vdW interactions on the HOIP's mechanical response (see Figure 5a). The change in stacking energy and mechanical response due to the vdW interactions is considerably larger than the change due to π interactions. Considering the fact that including the vdW interactions comes at almost no additional computational cost, we propose that our original protocol with vdW interactions, temperature correction, and minimal model structures can be a computationally viable procedure to study the most important aspects of the HOIP's mechanical properties.

In addition to improvements in the computational protocol, our experimental samples are carefully stored in the dark under an inert atmosphere and only exposed to ambient conditions for short periods of time while performing the experiments. These procedures, in addition to using a phenyl-based HOIP allow us to deconvolute the effect of defects on the mechanical response from the intrinsic properties, to the best of our abilities. It has been hypothesized²¹ that the previously reported disagreement between the theory and experiment is partially due to the presence of defects in experimental samples. Here, we focus on PEA-based (quasi)2D perovskites in order to minimize the presence of moisture-driven degradation and defects as it is known that the PEA-based (quasi)2D perovskites are more stable in the presence of moisture than the alkyl-based layered ones.²⁵ Consequently, we believe our measured out-of-plane elastic moduli values are, so far, the closest to the elastic properties of ideal defect-free (quasi)2D perovskite structures. Our findings (both for aromatic and straight-chain alkyl-based systems) indicate that layered HOIPs are intrinsically stiffer than what has been previously reported²¹ (see Section 10 of the Supporting Information for more details).

The special characteristic of $n = 1$ structures, preferring a more perfectly layered structure, is also consistent with

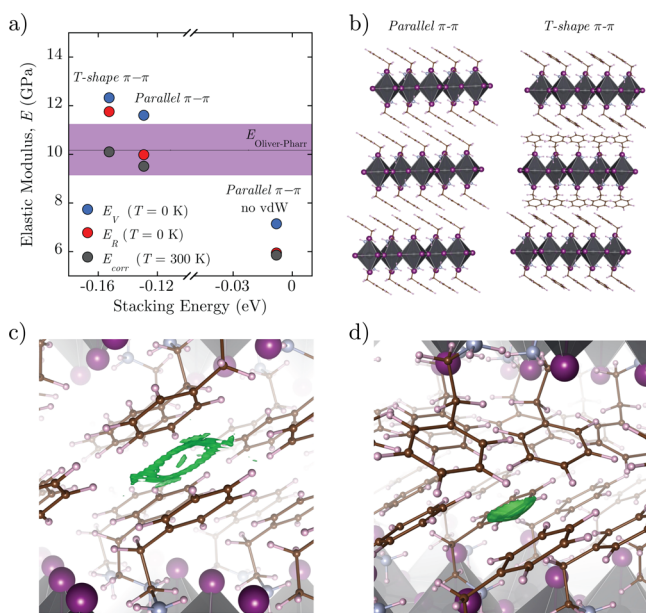


Figure 5. (a) For $(PEA)_2PbI_4$ ($n = 1$ structure), Young's moduli and stacking energy are compared for three types of interlayer interactions: parallel π – π interlayer interactions with and without vdW correction, and T-shaped π interactions with vdW correction. The experimentally measured value and the associated error bar (shaded area in magenta) are also depicted. In (b), side views of the structures with parallel and T-shaped interlayer stacking are depicted. (c, d) Noncovalent π interactions (in green) using the NCI index (isovalue = 0.4). The parallel π – π interaction is shown in (c), while the T-shaped interaction is shown in (d). In (d), one should note that there is effectively more than one region for the T-shaped interactions that each PEA cation experiences, but for visual clarity, only one of these is shown.

2D HOIP layers can stack in different orderings. The Dion–Jacobson (DJ) and Ruddlesden–Popper (RP) are the most well-known 2D stacking arrangements. Nevertheless, as described in the literature,⁵¹ other orders in between these two also exist, namely, “near-DJ” (nDJ) and “near-RP” (nRP) (for more details, see Section 9 of the Supporting Information). Different stacking orders can change the nature

disparate previous observations in the literature. For example, it has been shown that the perfectly layered $n = 1$ (PEA-based) structure has the most negative (favorable) formation energy.⁹ This means that the $n = 1$ system has the greatest driving force to form perfect layers with minimal defects. Recently, it has also been shown that exposing methylammonium lead tribromide single crystals to benzylamine creates a thermodynamically stable two-dimensional (2D) benzylammonium lead bromide perovskite, $(\text{BA})_2\text{PbBr}_4$, on the surface of the three-dimensional counterpart, protecting the underlying 3D perovskite from degradation.⁵³ Previously, it has been demonstrated that the bulk 3D hybrid perovskites are permeable to water, and such material can undergo a transition to a super-hydrous state and further degrade to non-perovskite phases.⁵⁴ The detection of $n = 1$ structure on such stable layered 2D–3D samples with greatly enhanced stability agrees with our theoretical results showing the $n = 1$ structure having the most favorable formation energy. More importantly, as interfacial defects have been identified as the initiating nuclei for water degradation of bulk 3D perovskites,⁵⁴ an effective 2D protection layer should host as few defects as possible. Consequently, the experimentally observed enhanced stability of such mixed-dimension systems⁵³ implies that the ($n = 1$) shell structure is almost perfect, with minimal defects and voids, blocking water entrance and inhibiting the water nanodroplets nucleation.

It is worthwhile to interpret the difference between the Hertzian and Oliver–Pharr measurements in Figure 2b. One can note that for $n = \infty$, both measured values overlap. For $n = 1$, the difference is also small. However, for finite $n > 1$ measurements, there are considerable differences between the Hertzian and Oliver–Pharr values. We interpret this behavior as evidence for the existence of interlayer structural defects (e.g., ripples and voids) in the (quasi)2D materials. Such defects can lower the material stiffness, especially in the Hertzian regime, as nanoindentation takes place on as-grown crystals hosting soft defects. We hypothesize that loading past the Hertzian region during nanoindentation fills or compacts such structural defects so that their effect on the material stiffness is less important when analyzing the unloading curve in the Oliver–Pharr analysis. Based on this premise, the number of voids and soft structural defects in the as-fabricated samples has a determining role in the gap between the Hertzian and Oliver–Pharr values. Based on Figure 2b, such voids are minimal in the 3D ($n = \infty$) sample due to the nonlayered structure. Nevertheless, the (quasi)2D samples consist of layers separated by much weaker vdW interactions. Creating voids between layers brings a much smaller energy penalty (than creating gaps in a 3D ionically bound material) and can be more easily favored by the gain in entropy. For the special case of $n = 1$, as mentioned above, the lack of short cations (MA^+) leads to less octahedral distortion (and consequently less disorder) and the growth of more perfectly layered crystals. That is why among the (quasi)-2D samples, the $n = 1$ has a considerably smaller discrepancy between the Oliver–Pharr and Hertzian data.

Finally, it has been reported that for (quasi)2D HOIPs with $n > 3$, the number of inorganic layers becomes polydisperse.^{55–57} This is due to a relative small difference in the formation energy between similar n values for the $n > 3$ regime.⁹ Consequently, due to finite temperature effects, a mixed (higher entropy) phase can possess a lower Gibbs free energy. In a mixed n structure, having inorganic layers with

different n values within the same layer (passivated by the longer cations) can lead to the creation of interlayer voids. Therefore, a more polydisperse sample should possess more of these voids and is expected to be softer in the out-of-plane direction. Although this mixture of layer numbers is expected, particularly in our $n = 4$ sample, it is not taken into account in simulations. The lack of polydispersity for $n = 1$ can perhaps contribute to its tendency to be closer to the stiffer (Voigt) limit than $n > 3$.

3.2. In-Plane Elastic Properties. Here, we discuss the response of 2D HOIPs to in-plane elastic deformation and the associated elastic moduli. Figure 6a contains optical micro-

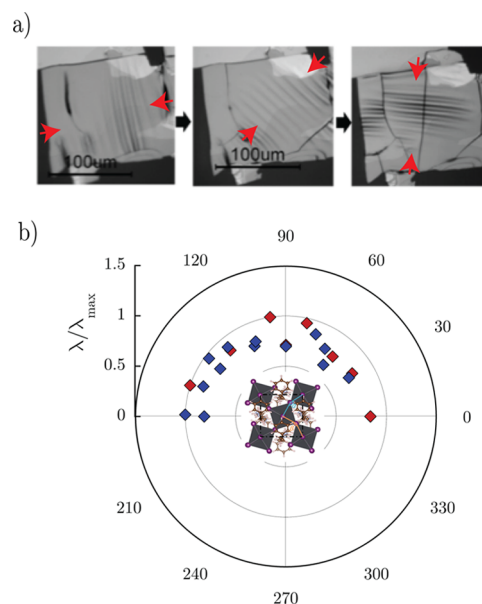


Figure 6. (a) Optical micrographs of an $n = 3$ crystal as it wrinkles along different directions, red arrows indicate the direction of uniaxial compression of the substrate. (b) Polar plot illustrating the change in wrinkle wavelength as a function of azimuthal angle, indicating an apparent in-plane mechanical isotropy. Red and blue markers represent different crystal samples.

graphs of a representative $n = 3$ crystal as it undergoes wrinkling along different in-plane loading directions. A polar plot (Figure 6b) illustrates the in-plane isotropy of the elastic moduli of two representative $n = 3$ crystals as they are uniaxially compressed along different crystallographic directions in-plane, quantified by the azimuthal angle, during wrinkling instability measurements. The elastic moduli extracted from the wrinkling instability measurements (Figure 1c), which correspond to the in-plane moduli, are also shown in Figure 2b. The elastic moduli from wrinkling analysis also show a nonmonotonic n dependence, where the modulus of $(\text{PEA})_2[\text{PbI}_4]$ ($n = 1$) is slightly higher than that of $(\text{PEA})_2(\text{MA})[\text{Pb}_2\text{I}_7]$ ($n = 2$). In contrast to the nanoindentation experiments, in-plane elastic mechanical measurements through wrinkling instability involve very low stresses, usually well within the elastic regime. The stresses act parallel to the surface of the 2D crystal uniaxially. The stress gradients are low, going from tension to compression across the crystal thickness. Our results show that the elastic moduli determined using wrinkling instability are smaller than those extracted from the out-of-plane measurements. The out-of-plane anisotropy is expected and observed in layered systems. In

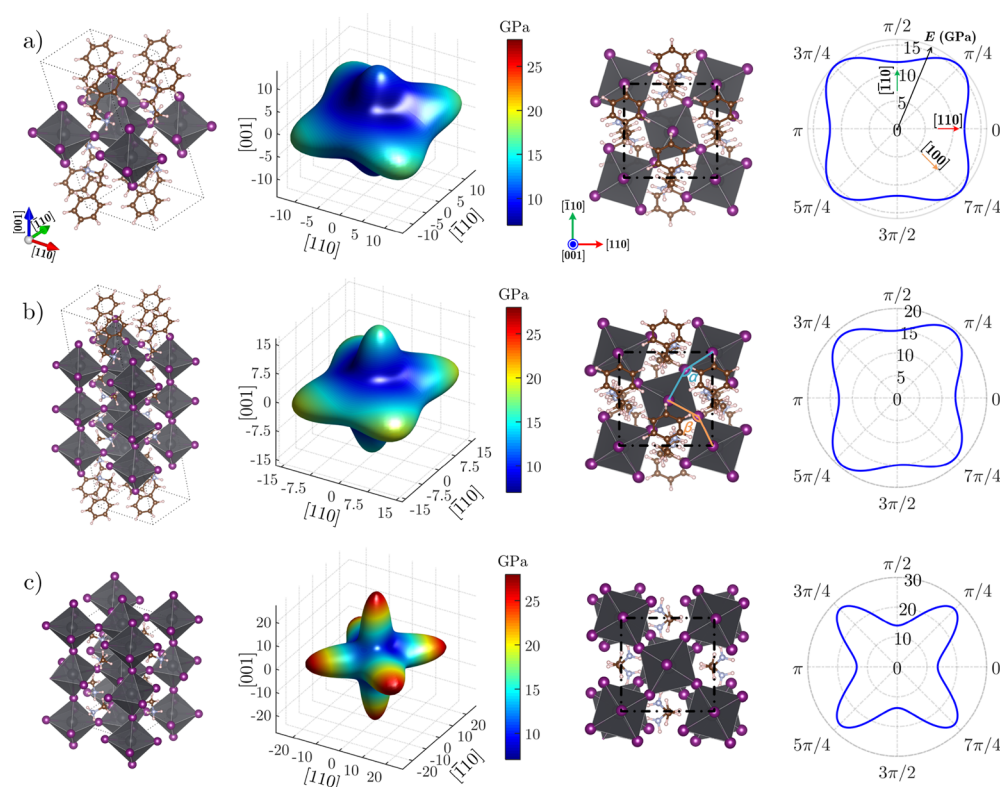


Figure 7. Directional dependence of Young's modulus (E) and E as a function of crystallographic orientations, plotted in the (001) plane under rotation about the [001] axis. (a) $n = 1$; (b) $n = 3$, where α and β represent Pb–I–Pb angles, equal to 152.1 and 149.5°, respectively. The difference between α and β yields a small difference of E along [100] and [010] crystallographic axes; (c) MAPbI₃ ($n = \infty$). In the polar plots, blue lines show directional dependence of the calculated in-plane E . This can be understood as the elastic response of the material when squeezed (or pulled) in a specific in-plane direction.

the plane, the elastic modulus appears independent of the crystallographic direction, as evidenced in the polar plot. The two-dimensional geometry of these crystals mandates an anisotropy in their mechanical properties, with in-plane elastic response different from the out-of-plane. Such elastic anisotropy is observed in other stacked (quasi)2D materials, such as mica⁵⁸ and clay composites,⁵⁹ and is summarized for these perovskite 2D crystals in Figure 2b. Additionally, a previous study has proposed to use the ratio between the in-plane and out-of-plane elastic moduli as a universal index to quantify the ease of mechanical exfoliation for 2D materials.⁶⁰

To better understand the directional dependence of the elastic properties of (PEA)₂PbI₄(MAPbI₃) _{$n-1$} , we derive the directional dependence of Young's moduli for $n = 1, 3$, and ∞ , as shown in Figure 7. This reveals that the direction of highest stiffness is along the Pb–I–Pb chains. Such directional dependence in the in-plane stiffness has also been computationally shown for the case of metal-free perovskites.⁶¹ Increasing n renders the Pb–I–Pb bonding network more interconnected and further strengthens the Pb–I–Pb chains, gradually enhancing the anisotropy of Young's modulus. In essence, pulling or pushing on a Pb–I–Pb bond perturbs the equilibrium bond distances in the direction of the strain. Consequently, the material bonding structure in the orthogonal direction relaxes to accommodate this perturbation. In materials with greater connectivity of the Pb–I–Pb network (higher n), exerting an in-plane strain in the direction of Pb–I–Pb bonds results in an out-of-plane relaxation, which affects a larger number (per material's volume) of Pb–I–Pb bonds. Thus, that direction appears stiffer, creating a higher degree of

anisotropy. Comparing the theoretical and experimental results, we notice the following differences: (a) the magnitude of the theoretical in-plane Young's moduli are generally much greater than the wrinkling results (Figure 2b), and (b) the theoretical values show clear in-plane anisotropy (polar plots in Figure 7), while the measured in-plane elastic constants appear more isotropic (Figure 6b). These differences can help us better understand the nature of in-plane deformations induced by the uniaxial strain in our wrinkling experiments.

We believe that the reason behind the almost 5-fold difference in elastic moduli between the wrinkling results and DFT-derived values stems from the different nature of deformations. In the out-of-plane nanoindentation experiments, the applied strain drives changes in the shape of the HOIP unit cell, i.e., compressing the inorganic layer (in concert with organic bilayer), along with atom-scale compression of interlayer defects. In contrast, for such layered (quasi)2D structures, the in-plane elastic response measured by wrinkling can be dominated by more macroscopic deformation phenomena, including sliding of entire 2D sheets and changes in their interlayer rippled structures (happening over relatively long distances).⁶² The hybrid layered structure has two different types of interatomic interactions: (a) the stronger chemical interactions that exist inside each 2D inorganic layer and (b) the weaker vdW and π interactions (in the case of aromatic cations). If the layered HOIP is subjected to in-plane purely uniaxial strain, the dominant factor will be the stronger chemical interactions (within the inorganic 2D sheets). In contrast, in a wrinkling experiment, where a uniaxial stress delivered to the bottom of the substrate induces

shear stress in the crystal, the dominant factor will be the weaker interlayer interactions as the material can respond to the applied stress with interlayer displacements given their smaller energy penalties. Consequently, the elastic moduli measured via wrinkling are influenced by shear, and consequently, they are lower, more isotropic, and of a different origin than the out-of-plane ones. One should note that the in-plane response measured here by the wrinkling experiment is fundamentally different than experiments in which the in-plane elastic constants are measured by uniaxial tensile tests. In the latter, the atomic bonds have to stretch, while for the former, as explained above, the interlayer degrees of freedom comply with the wrinkling-generated strain. Consequently, our measured in-plane elastic moduli are orders of magnitude smaller than those measured for layered materials like graphite by applying uniaxial tension on macroscopic samples.^{63,64} For more details, see Section 3 of the Supporting Information.

4. CONCLUSIONS

Using DFT modeling, nanoindentation, and wrinkling experiments, we performed a comprehensive study on the elastic properties of (quasi)2D single crystals of phenethylammonium methylammonium lead iodide $(\text{PEA})_2\text{PbI}_4(\text{MAPbI}_3)_{n-1}$ and their 3D counterpart, MAPbI_3 . Using carefully designed experiments, we probed the intrinsic elastic properties of our samples. By comparing our DFT-derived and experimental nanoindentation values (in both Hertzian and Oliver–Pharr regimes), we infer that defects play a significant role in dictating the measured in-plane and out-of-plane elastic properties. We learn that the Oliver–Pharr elasticity values best represent their intrinsic out-of-plane elastic properties because the compressive stress during loading removes the effect of (environment- or growth-induced) soft defects. In contrast, the Hertzian measurements best reflect the elastic properties of as-synthesized samples. We report a virtually perfect agreement between experimental and DFT-derived values for the elastic moduli of this class of HOIPs and illustrate how first-principles theory can be used to rationalize their elastic properties. We also reveal the effect of vdW interactions and different types of π stacking on the elastic properties (quasi)2D HOIPs. We demonstrate that the number of inorganic layers (n) strongly influences the elastic properties of two-dimensional hybrid perovskite single crystals. For the first time, we show that the n dependence is nonmonotonic due to the unique structural characteristics of $n = 1$. We trace this anomalous behavior back to $n = 1$ having an intrinsically more ordered and homogeneous layered structure than $n > 1$.

We have shown that the DFT modeling can have quantitative predictive power for the elastic properties of (quasi)2D HOIPs. It is possible to envisage natural extensions that can be explored building upon the results of our current study. One can explore the role of different families of organic (short or long) cations and the impact of anion (halide) substitution and search for rules that can control the elastic behavior of 2D HOIPs. In addition, for in-plane elastic moduli, the control of interlayer sliding is crucial. The energy barrier to interlayer sliding is dictated by the chemical structure of the organic bilayer. One can envision tuning the structural properties of organic bilayers to engineer the ease of interlayer sliding as required by different applications. We have created the foundations for concurrent design of stable light-absorbing materials with desired mechanical responses. Based on the

knowledge gained here, there are sweet spots to search for in such multidimensional optimization space. Examples include the possibility of (a) improving the charge transport properties or chemical stability through interlayer cross-linking of organic cations without greatly affecting the in-plane flexibility of the material or (b) inducing controlled type and number of interlayer structural defects to render the material more flexible out-of-plane while still possessing acceptable charge transport properties.

We emphasize that for the effective application of these materials in flexible optoelectronic devices, the mechanical behavior beyond the elastic regime should also be characterized. Moreover, the impact of elastic and plastic deformation on the optoelectronic properties of perovskite devices can be the focus of future studies. Our study now paves the way for such future necessary extensions.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsami.0c02327>.

XRD characterization of 2D crystals; representative load–displacement curves from nanoindentation experiments; wrinkling wavelength-crystal thickness fits; note on additional techniques to aid in the direct characterization of in-plane elastic properties and computational details; discussions on the effects of defects on elastic properties; relation of stacking structures and energy vs elastics properties; and the elastic properties of benzylammonium lead iodide perovskite layered structure (PDF)

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[†]M.A.R.-M., P.T., and A.K. contributed equally to this work. Y.-L.L. conceived the project. M.A.R.-M. designed and performed all the experimental measurements and analyses. A.K. and P.T. designed and executed the theory with guidance from A.M.R. S.B. helped with investigating the role of interlayer interactions theoretically.

Notes

The authors declare no competing financial interest.

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