# Coupling of organic cation and inorganic lattice in methylammonium lead halide perovskites: Insights into a pressure-induced isostructural phase transition

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Organic-inorganic hybrid metal-halide perovskite (OIHP) materials provide a tunable platform for engineering their optoelectronic properties. Although several high-pressure studies have been conducted from the OIHP family of single crystals and films, the exact nature of the dynamic coupling of the CH<sub>3</sub>NH<sub>3</sub> (MA) cation with the octahedral lattice framework and the mechanisms responsible for the structural phase transformation under pressure are not well captured. By combined photoluminescence (PL), synchrotron-based x-ray diffraction, and Raman-scattering studies as a function of pressure from methylammonium lead bromide (MAPbBr<sub>3</sub>), we shed light on an isostructural phase transition due to the coupling of the MA cation and the PbBr<sub>6</sub> lattice through hydrogen bonding. The sharp discontinuities at  $\sim 1$  GPa and  $\sim 3$  GPa in the PL peak positions correlate with the structural changes observed in high-pressure XRD and Raman-scattering studies. The electronic band edge as a function of pressure is calculated within density-functional theory. The PL peak position, intensity and width of the excitonic peak show significant changes at 2 GPa, which corroborate the changes observed in high-pressure Raman-scattering studies. The frequencies of the lattice modes and the C-H/N-H bending and stretching modes of the MA cation show anomalous changes and other nuances at 2 GPa. The suppression of rotational and orientational disorder of the organic moiety is initiated at 2 GPa and the ordering is completed by 3.0 GPa, leading to an order-disorder type cubic II  $(Im\bar{3})$  to orthorhombic (*Pnma*) phase transition. Along with the revelation of an isostructural transformation at 2 GPa, this paper highlights the impact of molecular vibrations on the electronic properties of MAPbBr3 under pressure.

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## I. INTRODUCTION

Alkali-halide perovskite crystal structures adopt complex structural landscapes that can be tuned with temperature, pressure, and electric field. Organic-inorganic hybrid perovskites (OIHP) with their outstanding optoelectronic properties [1] have revolutionized the fields of photovoltaics with power conversion efficiencies exceeding 25% [2] and lightemitting diodes (LEDs) with external quantum efficiency exceeding 21% [3]. Among OIHPs, the structural properties of methylammonium (MA) hybrid organic-inorganic perovskites, MAPbX<sub>3</sub> (MA<sup>+</sup> = CH<sub>3</sub>NH<sub>3</sub><sup>+</sup> and X<sup>-</sup> = Cl<sup>-</sup>, Br<sup>-</sup>, or I<sup>-</sup>) were deciphered more than 40 years ago [4] although at that time their optoelectronic properties were not explored. Applications of MAPbX<sub>3</sub> in photovoltaics and LEDs are typically in the form of thin films [5].

A rapid crystal-growth method utilizing inverse temperature crystallization (ITC) of MAPbX<sub>3</sub> single crystals [6] has opened the path toward fundamental transport, structural, and optical studies. Such crystals have low trap densities with controllable shape and size by changing the growth parameters. Single crystals of MAPbX<sub>3</sub> grown using ITC and other methods have allowed detailed linear and nonlinear optical studies [7–13], application in lasing [14], observing spin-dependent phenomena [15–17], determination of elastic and vibrational properties using resonant ultrasound spectroscopy and neutron diffraction [18,19], and investigation of pressure-induced structural phase transformations [20–23]. The structural flexibility of MAPbX<sub>3</sub> provides a platform to engineer their optoelectronic properties by tuning the band-gap energies with external stimuli such as pressure, temperature, and chemical pressure; the latter is often achieved by means of compositional engineering [24].

In this paper, we use hydrostatic pressure as a probe to tune the structural, vibrational, and optical properties of MAPbBr<sub>3</sub> single crystals. Not only does this study highlight the structural phase transitions under pressure, it provides insight into an isostructural phase transition at 2 GPa, which is accompanied by a suppression of the orientational and rotational disorder of the MA cation.

The optical and vibrational properties of MAPbX<sub>3</sub> correlate with the crystal structure; hence, an understanding of the structural tunability as well as stability of these materials when exposed to various conditions of temperature and pressure are required prior to any device applications. Under ambient conditions, MAPbBr<sub>3</sub> adopts an aristo-type disordered cubic (space group [S.G.]:  $Pm\bar{3}m$ ) structure with Glazer tilting:  $a^0b^0c^0$  owing to the orientational disorder of the MA molecule [25]. Upon reducing the temperature, MAPbBr<sub>3</sub>

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undergoes a symmetry-lowering structural phase transition to an ordered orthorhombic phase (S.G: *Pnma*) with Glazer tilting:  $a^-b^+a^-$  at 148 K through an intermediate tetragonal phase (S.G: *I4/mcm*) with Glazer tilting:  $a^0a^0c^-$  at 235 K [25–27]. Interestingly, an incommensurate phase is seen at 150 K in MAPbBr<sub>3</sub> due to the coupling of structural dynamics of the organic cation with the inorganic framework [28].

As compared to chemical pressure, hydrostatic pressure is a clean and effective way to continuously tune the band gap, and thereby the structural, vibrational, electronic, and optical properties of materials. Pressure induces tilting and rotations of the PbX<sub>6</sub> octahedra along with tuning the interaction between the organic molecular cation and the inorganic framework, leading to several pressure-induced structural phase transitions. With pressure, the ambient cubic (S.G:  $Pm\bar{3}m$ ) phase of MAPbBr<sub>3</sub> transforms to an orthorhombic (S.G: *Pnma* and Glazer notation:  $a^+b^-b^-$ ) phase at 2.9 GPa via an intermediate cubic (S.G:  $Im\bar{3}$  and Glazer notation:  $a^+b^+b^+$ ) phase at  $\sim 1$  GPa [21,22]. A partial amorphization has also been noticed after 4 GPa [20,24]. High-pressure Raman scattering, infrared, and x-ray absorption spectroscopic studies from MAPbBr<sub>3</sub> show that the dynamic motion of the MA<sup>+</sup> cation induces a dynamic disordered liquidlike phase at ambient pressure to a static disorder amorphous-like phase via an intermediate static-order crystal-like phase [23].

Under ambient conditions, MAPbI3 deviates from the cubic phase and is mainly in the tetragonal phase (S.G: *I*4/*mcm*). The distortion from the cubic phase is attributed to the size of the *I* ion [29]. Although the chloride analog, MAPbCl<sub>3</sub>, is in the cubic phase (S.G.:  $Pm\bar{3}m$ ) under ambient conditions, the transition sequence under pressure is different from MAPbBr<sub>3</sub> [30]. The halogen atom, therefore, plays a large role in dictating the structural properties, including pressure-induced changes. In this paper, our focus is on the role of the organic cation in structural phase transformations under pressure. The interaction of the organic cation and the inorganic lattice tends to lower the symmetry, so it is best to begin with a system of high (cubic) symmetry, which immediately rules out MAPbI<sub>3</sub>. In the following, we choose MAPbBr<sub>3</sub> over MAPbCl<sub>3</sub> due to its high stability and high photoluminescence (PL) quantum vield.

The inorganic framework is formed by corner sharing of PbX<sub>6</sub> octahedra with the MA<sup>+</sup> occupying the cages formed by the octahedra, and is coordinated to 12 adjacent halide X<sup>-</sup> anions [31,32]. Theoretical and experimental studies unveil the coupling between the dynamical motion of the MA cation and the PbBr<sub>6</sub> lattice [33,34]; the hydrogen bonding between the organic cation and the PbBr<sub>6</sub> lattice plays a crucial role in tilting the octahedra of the OIHP [35]. It has been further shown that in the cubic and tetragonal phases, the predominant hydrogen bonding is between the NH<sub>3</sub> end of the MA cation to Br<sup>-</sup>, whereas in the low-temperature orthorhombic phase, the hydrogen bonding is due to both entities, i.e., NH<sub>3</sub> and CH<sub>3</sub> of the MA cation both play a role [25].

Here, we unravel the origin and evolution of an isostructural phase transition of MAPbBr<sub>3</sub> at 2 GPa by detailed highpressure PL, Raman scattering, synchrotron x-ray diffraction (XRD), and theoretical studies. The Raman frequencies from both the lattice and the MA cation show anomalous changes at 2 GPa, which suggests coupling of the MA cation and the inorganic framework. The position, intensity, and the width of the PL peaks show slope changes around 2 GPa. The coupling of the inorganic lattice and the MA cation initiates an ordering of the molecular cations at 2 GPa; the completion of this ordering is accompanied by an order-disorder structural phase transition from the cubic II ( $Im\bar{3}$ ) to the orthorhombic (Pnma) phase. The systematic changes observed both in the Raman spectrum and PL under pressure highlight the coupling of the molecular vibrations to the electronic properties.

## **II. EXPERIMENTAL AND THEORETICAL DETAILS**

#### A. Synthesis of MAPbBr<sub>3</sub> single crystals

Lead bromide ( $\geq$  98%), methylammonium bromide, and anhydrous dimethylformamide (DMF) were purchased from Sigma Aldrich and used without any further purification. The synthesis of the MAPbBr<sub>3</sub> single crystals was achieved as described in Ref. [6]. A one molar solution of PbBr<sub>2</sub> and MABr was prepared in DMF at room temperature. The solution was stirred vigorously with a vortex mixer until all solid particles were dissolved and the solution appeared homogenous. After stirring, the solution was filtered through a 0.22 micron PTFE filter and the resultant filtrate was placed in vials in 2-ml portions. The vials were then placed into a bath of 80 °C silicone oil with the entire bath covered by aluminum foil to trap heat and maintain the 80 °C growth temperature. After three hours, the vials were removed from the bath and the synthesized crystals were extracted from each individual vial.

## **B.** Optical characterization

Merrill-Bassett-type diamond anvil cells (DACs) with a culet size of  $600 \,\mu\text{m}$  were used for PL studies under pressure. A stainless steel gasket was preindented to a thickness of 60  $\mu$ m and a hole diameter of approximately 200  $\mu$ m was drilled at the center. The pressure-transmitting medium used was silicone oil. The pressure was determined using the fluorescence of a ruby chip. The PL measurements were carried out in a reflection geometry using the 457-nm line of an argon-ion laser as the excitation source with laser power on the sample being < 10 mW. The PL spectra were collected with an Ocean Optics USB 2000 spectrometer. The low-temperature measurements were conducted using a closed-cycle APD refrigerator. The pressure was determined by a Renishaw inVia spectrometer using a 514 nm Ar<sup>+</sup> ion laser or a UV lamp as the excitation source. The spectral resolution of the instrument is lower than  $0.2 \text{ cm}^{-1}$ ; hence, the pressure uncertainties are lower than 0.05 GPa. The twophoton PL spectrum was measured by exciting the sample with 800 nm, 100 fs, and 80 MHz repetition rate laser pulse from a Ti-sapphire oscillator (MaiTai from Spectra Physics). The high-pressure Raman-scattering measurements from a MAPbBr3 single crystal were conducted using a Merrill Bassett DAC with sodium chloride as the pressure transmitting medium. The Raman spectra were measured with a Renishaw inVia spectrometer affixed to a confocal microscope with a long working distance objective (50 x). A 785-nm excitation source along with a low wave-number edge filter, rejecting the Rayleigh scattered light down to  $50 \text{ cm}^{-1}$ , was used.



FIG. 1. (a) PL spectrum of MAPbBr<sub>3</sub> single crystal under ambient conditions with an excitation wavelength of 457 nm. The shaded regions show the fit to the spectrum with two Gaussian peaks. The red dotted line is the two-photon PL spectrum with an excitation wavelength of 800 nm (100 fs). The inset shows the process of two-photon (TP) PL. (b) Temperature dependence of the two PL peaks. The inset shows the PL spectrum and the deconvolution of the two peaks at 160 K.

## C. High-pressure synchrotron XRD

The high-pressure XRD measurements were conducted at sector 13-BMD, GSECARS, at the Advanced Photon Source (APS) in Argonne National Laboratory using a symmetric DAC. The x-ray source utilized a 0.3344 Å beam for all measurements. Ne gas was used as a pressure-transmitting medium and was loaded at GSECARS in sector 13 of the APS. The XRD data was analyzed using methods outlined in Ref. [36]. The lattice parameters of the cubic I phase were extracted using the Rietveld method and that of high-pressure cubic II and orthorhombic phases were extracted using the Le Bail method. The peak shape was modeled using a pseudo-Voigt function, and the profile parameters,  $R_B$ ,  $R_P$ ,  $R_{wp}$ , and  $\chi^2$  served as quantitative measures for the goodness of fit.

## **D.** Theory

We performed first-principles density-functional theory (DFT) calculations of MAPbBr<sub>3</sub> under pressure, implemented in the QUANTUM ESPRESSO code [37]. Using the Perdew-Burke-Ernzerhof (PBE) functional [38], the plane-wave cutoff was set as 75 Ry with optimized norm-conserving Vanderbilt pseudopotentials [39,40]. To include the effect of the van der Waals dispersive interactions, we performed structural relaxations with Grimme's D3 method [41]. Spin-orbit coupling was included in all the calculations, including structural relaxation. All geometry structures were relaxed until an energy convergence of  $10^{-9}$  Ry and a force convergence on atoms of  $10^{-3}$  Ry/Bohr. The **k** grids were set as  $10 \times 10 \times 10$  and  $4 \times 4 \times 4$  for the  $R\overline{3}m$  ( $Pm\overline{3}m$ ) cells and  $Im\overline{3}$  cells, respectively.

The geometry structures were determined following a twostep strategy. For a structure with a chosen lattice constant, we first relaxed the  $Pm\bar{3}m$  or  $Im\bar{3}$  unit cell of CsPbBr<sub>3</sub> to determine the inorganic framework. Subsequently, with the relaxed PbBr<sub>3</sub><sup>-</sup> framework, we replaced the Cs<sup>+</sup> ions with MA<sup>+</sup> ions oriented along (111). We then fixed the inorganic framework and fully relaxed the MA<sup>+</sup> until the energy was minimized. It should be pointed out that the so-obtained structures are not exactly in  $Pm\overline{3}m$  or  $Im\overline{3}$  symmetry within the small cells involved in our calculations. When the MA<sup>+</sup> is substituted in the  $Pm\overline{3}m$  ( $Im\overline{3}$ ) framework, the initial phase is rather in the  $R\overline{3}m$  (R3) symmetry. We refer to them as pseudo- $Pm\overline{3}m$ ( $Im\overline{3}$ ) structures, where the inorganic framework is in the correct symmetry of  $Pm\overline{3}m$  ( $Im\overline{3}$ ). However, if the framework is also relaxed, the resulting structure in exact  $R\overline{3}m$  symmetry is energetically more stable than the pseudo- $Pm\overline{3}m$  structure (see Supplemental Material) [42]. Therefore, we adopt  $R\overline{3}m$ structures as the theoretical ambient pressure phase before transition, instead of the pseudo- $Pm\overline{3}m$  structures. In addition, the pseudo- $Im\overline{3}$  structure turns into P1 symmetry after relaxation, though the framework is kept in  $Im\overline{3}$  symmetry.

#### **III. RESULTS AND DISCUSSIONS**

### A. Temperature-dependent PL

The PL spectrum of MAPbBr<sub>3</sub> under ambient condition shows a strong emission peak at 540 nm with a shoulder at 570 nm, depicted by the shaded regions in Fig. 1(a). This is similar to other reports in the literature where the PL spectrum of MAPbBr<sub>3</sub> single crystals is characterized by at least two excitonic peaks [9-11,43]. However, in contrast with other studies [44,45], we do not observe any defect emission at longer wavelengths. As a function of MAPbBr<sub>3</sub> dispersions for different concentrations, Shi et al. identified the two excitonic peaks in their absorption spectrum with binding energies of  $\sim 20$  meV and  $\sim 75$  meV for the high- and low-energy peaks, respectively; thus, referring to them as free and bound excitons [45]. From reflectance and PL studies on MAPbBr<sub>3</sub> single crystals, Do et al. [9] find the excitonic binding energies to be 20 meV and 90 meV for the low- and high-energy peaks, respectively.

The measurement geometry, i.e., whether the PL is measured in reflection or transmission, and the thickness of the crystal play a role in the observation of both or only one of the peaks in the PL spectrum [10]. The PL measurements in



FIG. 2. (a) PL spectra of an MAPbBr<sub>3</sub> single crystal at various pressures. (b) PL peak positions of peak 1 and 2 as a function of pressure. The blue arrows depict the discontinuities in the peak positions. (c) PL peak position and intensity of peak 1 between 1.2 GPa and 2.6 GPa. (d) FWHM of peak 1 as a function of pressure.

this paper were all performed in a reflection geometry. Here, we refer to the 540-nm and 570-nm peaks as peak 1 and peak 2, respectively. The PL process due to two-photon absorption is also shown in Fig. 1(a) as the red dotted line, where the incident wavelength was 800 nm (100 fs pulses). In the twophoton PL process, only peak 2 at 570 nm is observed, similar to other reports [11]. It has been suggested that the difference in the PL due to one-photon and two-photon absorption may originate from the spatial distribution of the photocarriers [46]. In the two-photon process, due to the high excitation intensity, the laser beam is focused in the bulk of the sample. This also suggests that the two-photon PL could be more sensitive to defect or trap states. No additional low-energy peaks are observed in the two-photon PL, indicating a lack of vacancies or other defects in the sample. More recently, detailed PL measurements from MAPbI3 conclusively show that the origin of peak 1 is mainly from the surface whereas peak 2 is from the bulk [47]. Further, the origin of peak 2 is attributed to extreme self-absorption effects due to internal reflections. This brings up the question whether temperature and pressure will result in different trends for the two excitonic peaks.

The temperature dependence of the PL peaks is plotted in Fig. 1(b). The inset shows a representative PL spectrum at 160 K with a fit to two Gaussian peaks. With increase in temperature, the two peaks diverge; peak 2 is seen to decrease in energy whereas peak 1 increases in energy with temperature. We note that the peak positions plotted here are in nm and not in eV. The temperature dependence of peak 1 (see Supplemental Material) [42] exhibits obvious slope changes at ~ 230 K and 125 K, indicating a cubic ( $Pm\bar{3}m$ ) to tetragonal (I4/mcm) and tetragonal to orthorhombic (Pnma) structural phase transition, respectively [25]. Additionally, the PL linewidth is seen to increase with temperature, reflecting exciton-phonon scattering in MAPbBr<sub>3</sub> [48]. The temperature response of the two excitonic peaks has been attributed to their differences in origin: peak 1 at 540 nm has been attributed to carriers at the Pb-Br antibonding states in the conduction and valence bands, whereas peak 2 is influenced by the bonds between MA<sup>+</sup> and Br<sup>-</sup> [9].

## **B.** Pressure-dependent PL

Figure 2(a) shows the PL spectra from a MAPbBr<sub>3</sub> single crystal for various values of pressure. Although the absolute PL intensity was not measured, the incident power and measurement geometry were not changed between measurements; hence, the PL intensities at different pressure values may be compared with each other. It can be seen that the PL peak position and intensity change with pressure. The individual spectra were fitted with two Gaussian peaks as discussed in

the previous section. The PL peak positions of both excitonic emissions display similar trends up to 3.4 GPa [Fig. 2(b)], beyond which peak 2 is very weak. What distinguishes this work from prior high pressure PL studies of MAPbBr<sub>3</sub> single crystals [20,21] is that both excitonic peaks with pressure could be tracked. Figures 1(b) and 2(b) contrast their behavior as a function of temperature and pressure. Although the exact origin of the differences in the trends in the shift of peaks 1 and 2 under temperature and pressure are not clear, our results depict that the factors influencing the blue-shift of peak 1 and red-shift of peak 2 as a function of temperature clearly do not play a role under pressure. In light of the experiments on MAPbI<sub>3</sub>, where peak 2 originates from self-absorption and multiple internal reflection, it is seen that temperature affects the reabsorption process, resulting in opposite trends for peaks 1 and 2 [47]. However, pressure uniformly impacts the bulk and the surface of the crystal; the two excitonic peaks are therefore expected to show the same trend.

The PL peak positions exhibit discontinuous change at 0.7 GPa, followed by a sharp change in slope at ~1 GPa. The PL intensity also reaches a maximum at 0.7 GPa [42]. Thus, the observed discontinuity in the PL peak position at 0.7 GPa may be attributed to a rearrangement of the MA, followed by a structural phase transition at ~1 GPa. Changes in the PL peak position at 1 GPa have been observed in other high-pressure studies of MAPbBr<sub>3</sub> single crystals and nanoplates [20,24]. Another sharp discontinuity is observed at 2.7 GPa, which correlates with a structural phase transition, observed in XRD and Raman spectroscopy (see below).

There are several other nuances, in addition to the changes associated with the two structural phase transitions observed in the PL data. There is an overall decrease in the PL intensity beyond the first structural phase transition at 1 GPa, followed by an enhancement in the intensity, starting at 2 GPa, and reaching a maximum at 2.6 GPa [Figs. 2(c) and S3] [42]. These observations may indicate a change from a direct to an indirect band gap, as predicted theoretically, albeit at higher pressures [49]. Our DFT calculations, presented in the next section, however, rule out this possibility; the band-edge calculations till 2 GPa maintain the band gap to be direct. The full width at half maximum (FWHM) of peak 1 shows a distinct change at 2 GPa [Fig. 2(d)]. We note that the XRD data under pressure (see Sec. III D) shows no evidence of any structural transition around this pressure. To investigate the origin of the changes occurring at 2 GPa in the PL, we have conducted detailed Raman scattering under pressure (see Sec. III E).

## C. DFT calculations

Van der Waals-corrected DFT shows that the orientation of the MA<sup>+</sup> groups plays a fundamental role in the dynamical change of the band structure, which may be responsible for carrier recombination in photovoltaic applications [50]. Firstprinciples band-edge calculations of the highly symmetric cubic phase of MAPbX<sub>3</sub> pose a challenge due to the dynamic motion of the MA<sup>+</sup> cation. For simplification, several approaches such as replacing MA<sup>+</sup> with Cs<sup>+</sup> [21], using the orthorhombic MAPbBr<sub>3</sub> (*Pnma*) structure [20], and orienting the MA molecules along the  $\langle 111 \rangle$  direction [49] have been considered in theoretical calculations. As explained in



FIG. 3. The band-gap energy shift obtained from DFT calculations as a function of pressure is shown in blue. The pressure-induced PL energy shift of peak 1 is shown in red. Inset: Total energy of the  $Pm\bar{3}m$  and  $Im\bar{3}$  phases as a function of unit cell volume obtained from theory.

Sec. II D, we have used pseudo- $Pm\bar{3}m$  and  $Im\bar{3}$  structures for the calculations here.

A lattice constant of a = 6.015 Å for MAPbBr<sub>3</sub> yields the lowest energy configuration for the  $Pm\bar{3}m$  ( $R\bar{3}m$ ) phase, which we take as the zero pressure point. The lattice constants were changed according to the experimental values determined from high-pressure XRD (Sec. III D). The total energies of the structures were calculated to predict the pressure-induced transition from the  $Pm\bar{3}m$  to the  $Im\bar{3}$  phase. The results are shown in the inset of Fig. 3. When the volume of the unit cell reaches  $210 \text{ Å}^3/\text{f.u.}$ , the  $Im\bar{3}$  phase is seen to have a lower energy compared to the  $Pm\bar{3}m$  phase, in agreement with experiments.

The band-gap energies obtained from our DFT calculations will be well below the experimental values, which is a wellknown feature of the PBE functional. However, the absolute band-gap energies are not important for our analysis: We are interested in the trends in band-gap changes and the transition pressures, and therefore plot the calculated band-gap energy shift (between the zero and other pressure values) in Fig. 3 and compare it with the corresponding experimental PL energy shift. The changes in the theoretical lattice constants were compared with the XRD data to determine the pressure values. The DFT calculations capture the initial redshift in the  $Pm\bar{3}m$ phase quite well. However, the blueshift in the PL energies when the MAPbBr<sub>3</sub> crystal is in the second  $Im\bar{3}$  phase is not reproduced in our DFT calculations. We note that inorganic perovskites such as CsPbBr3 nanocrystals do not show a blueshift in PL energies at low pressures [36], suggesting that the coupling of the MA cation with the PbBr<sub>6</sub> lattice (as shown in Sec. III E) may affect the PL energies.

It should be pointed out that the discrepancies in the shift of the band-gap energies between experiment and first-principles DFT calculations using the PBE functional at pressures below 5 GPa are seen in other perovskites such as MAPbI<sub>3</sub> [51]. The performance of PBE has been carefully tested for structural phase transitions of simple solids under pressure [52]. It was



FIG. 4. High-pressure synchrotron XRD of MAPbBr<sub>3</sub>. (a) The XRD pattern of MAPbBr<sub>3</sub> for representative pressure values for the first sample (run 1). The \* symbol represents additional peaks that may be due to impurities. The thick red circles at 1 GPa denote the appearance of new peaks. Different phases are indicated with different colors. The (200)<sub>c</sub> and (101)<sub>o</sub> peaks denote the first peak of cubic II and orthorhombic phases, respectively. (b) The XRD pattern of MAPbBr<sub>3</sub> for selected pressure values for another sample (run 2). The thick red circles at 1.5 GPa denote the appearance of new peaks. (c) Pressure dependence of the  $2\theta$  position of the first peak of the orthorhombic phase ((101)<sub>o</sub>). The vertical dotted line separates the orthorhombic phases are shown as an inset. A vertical dotted line separates the cubic II and orthorhombic phases. (d) Pressure dependence of the volume per formula unit (volume/Z, Z = 1, 8, and 4 for phases I, II, and III, respectively) of the cubic I, cubic II, and orthorhombic phases. The different phases are separated by vertical dotted lines.

found that transition pressures are reproduced quite accurately by PBE, and an accurate fundamental gap is not necessary for this. Nevertheless, more sophisticated DFT approaches such as SCAN or hybrid functionals would be preferable for describing the properties of materials under pressure [53] but, due to the increase in computational cost, such approaches are beyond the scope of this paper.

# D. Pressure-dependent XRD

High-pressure synchrotron powder XRD studies have been carried out from MAPbBr<sub>3</sub> to comprehensively discern the changes seen in the PL data. In particular, the questions we seek to answer are: What is the origin of the changes observed at 2 GPa in the PL data? Is there a correlation between the observed discontinuities in the PL peak positions with structural phase transitions? High-pressure XRD measurements of MAPbBr<sub>3</sub> for two sample loadings (referred to as run 1 and run 2) were carried out up to 13.3 GPa and 1.5 GPa,

respectively, as shown in Fig. 4. The XRD pattern at 0.2 GPa fits well with a cubic lattice of S.G.  $Pm\bar{3}m$  (phase I, Glazer tilt:  $a^0b^0c^0$ ) (see Supplemental Material) [42]. Upon compression, two weak reflections emerge at the  $2\theta$  positions of 5.2° and 6.2°, respectively; these peaks become stronger upon applying further pressure. The appearance of additional peaks indicates a symmetry-lowering structural phase transition. A detailed XRD analysis has been carried out at 1.5 GPa [42], which reveals that the observed high-pressure phase is another cubic lattice with a doubling of the unit cell. The group-subgroup relation suggests the symmetry of the doubled unit cell is  $Im\bar{3}$  (phase II, Glazer tilt:  $a^+b^+c^+$ ) due to the tilting of the PbBr<sub>6</sub> octahedral cage. These observations are in agreement with other reports [21,22,24,54].

The XRD pattern fits well with the cubic lattice of  $Im\bar{3}$  symmetry up to 2.7 GPa, beyond which a large change is noticed. A preliminary analysis of the XRD pattern reveals discontinuities in the pressure versus  $2\theta$  positions of several peaks. To explore these changes, the  $2\theta$  position of the first

peak at around  $3.2^{\circ}$  is plotted as a function of pressure from 1 to 13 GPa in Fig. 4(c). The change in slope at 3 GPa (inset) hints at an occurrence of another structural transition at this pressure. Detailed Raman-scattering studies, presented in Sec. III E, highlight a symmetry-lowering structural transition at 3.2 GPa. We note that in inorganic perovskites such as CsPbBr<sub>3</sub>, hydrostatic pressure induces a higher symmetry from the *Pnma* phase to the *Pm*3m phase at 1.7 GPa [36]. This further highlights the importance of the coupling of the MA cation to the inorganic lattice with pressure in MAPbBr<sub>3</sub>.

By invoking the group-subgroup relationship and also comparing with previous reports, we interpret the XRD pattern above 2.7 GPa to be orthorhombic with S.G. Pnma (phase III, Glazer tilt:  $a^+b^-c^-$ ) corresponding to the lattice parameters a = 7.58 Å, b = 11.24 Å, and c = 8.06 Å at 3.7 GPa [19,22,23]. The XRD pattern may be fitted with the orthorhombic lattice up to 6.5 GPa, beyond which a drastic reduction of the *c* value makes the fitting highly unreliable. To gauge this problem, the first XRD peak,  $(101)_0$  of the orthorhombic lattice, is plotted as a function of pressure in Fig. 4(c). Moreover, we observe a considerable peak broadening above 6.5 GPa and an obvious change in slope of peaks is discerned at 6.7 GPa. By comparing these changes with the Raman-scattering results (see below), we interpret the transition at 6.7 GPa to the loss of a long-range ordering of the perovskite structure (disordered phase, phase IV). Upon release of pressure, the sample reverts back to the ambient cubic I phase.

The cubic I (S.G:  $Pm\bar{3}m$ ) to cubic II (S.G:  $Im\bar{3}$ ) transition is accompanied by a volume change of about 2%, suggesting a first-order structural phase transition. Similarly, the cubic II to the orthorhombic phase is accompanied by a volume change of about 4% [Fig. 4(d)]. The group-subgroup relationship suggests that the  $Im\bar{3}$  to the *Pnma* symmetry to be of first order. By comparing the volume changes observed at 2.7 GPa with the observed discontinuity in the PL peak positions at the same pressure, we interpret the cubic II to orthorhombic phase transition as first order. This resolves a long-standing puzzle of the order of structural phase transitions in MAPbBr<sub>3</sub> [22,54] under high pressure. The bulk modulus  $(B_0)$  and its first derivative  $(B'_0)$  of the cubic I and cubic II phases are calculated by fitting the pressure versus volume/Z data with the second-order Birch-Murnaghan and the third-order Murnaghan equation of states, respectively, using EOSFIT7 software [55]. The calculated bulk moduli and their derivatives are  $B_0 = 21.8$  and  $B'_0 = 4$  for the cubic I phase and  $B_0 = 10.4$  and  $B'_0 = 5.2$  for the cubic II phase, which is comparable to the previous report of  $B_0 = 17.6(4)$  for the cubic I phase and  $B_0 = 12.6(6)$  for the cubic phase II [20]. The unusual decrease in the bulk modulus of the high-pressure cubic II phase suggests that it is softer than the cubic I phase.

#### E. Pressure-dependent Raman scattering

High-pressure Raman-scattering studies have been carried out on MAPbBr<sub>3</sub> to decipher the origin of the changes in the PL spectra at 2 GPa. Complementing the information obtained from XRD, Raman scattering is a powerful tool to probe the subtle changes in the octahedral tilt due to the coupling of the MA<sup>+</sup> molecular vibrations. The vibrational frequencies of MAPbBr<sub>3</sub> may be categorized as low frequency modes below  $350 \text{ cm}^{-1}$  that originate from the local Pb-Br vibrations (region 1) and the modes associated with MA which lie between 900 and 3000 cm<sup>-1</sup> (regions 2-4). As the MA cation resides in the cavities formed by the lattice of PbBr<sub>6</sub> octahedra, MAPbBr<sub>3</sub> possesses a lower symmetry ( $C_{3v}$ ) compared to the experimentally observed cubic symmetry [31]. To satisfy the average cubic site symmetry ( $O_h$ ) in MAPbBr<sub>3</sub>, the organic cation is forced to carry out complex rotational and orientational motion, leading to a dynamic disorder may lead to structural fluctuations due to the interaction of the organic cation in the octahedral cages with the PbBr<sub>6</sub> lattice, and results in local symmetry breaking (although by maintaining global cubic symmetry).

A detailed description of the mode assignments and ambient Raman spectrum of MAPbBr3 are provided in the Supplemental Material [42]. The Raman spectrum of MAPbBr<sub>3</sub> under ambient conditions in region 1 shows a featureless mode centered around 150 cm<sup>-1</sup>, which becomes more structured after a small compression. There has been some controversy in the assignment of the 325  $cm^{-1}$  Raman peak, which was previously assigned to the MA torsional mode. Considering that this peak is observed both in allinorganic CsPbBr<sub>3</sub> as well as in MAPbBX<sub>3</sub>, Guo et al. attribute this mode to the halide motion of the perovskite octahedral framework [28]. We denote the MA molecular vibrational modes as 600-1400 cm<sup>-1</sup> (region 2), 1400- $1800 \text{ cm}^{-1}$  (region 3), and  $2700-3200^{-1}$  (region 4). The 917  $cm^{-1}$ , 969  $cm^{-1}$ , and the 1250  $cm^{-1}$  peaks in region 1 are the CH<sub>3</sub> rocking, C-N stretching, and NH<sub>3</sub> rocking modes, respectively. The Raman peaks at 1427 cm<sup>-1</sup>, 1455 cm<sup>-1</sup>, 1480 cm<sup>-1</sup>, and 1591 cm<sup>-1</sup> in region 3 arise from C-H and N-H bending modes, and the three peaks in region 4 (2831  $cm^{-1}$ , 2896  $cm^{-1}$ , and 2971  $cm^{-1}$ ) are from C-H and N-H stretching vibrations [25,42,56,57].

Figure 5 shows the pressure dependence of the low frequency Raman modes. In the cubic I phase  $(Pm\bar{3}m)$ , a broad structureless feature at  $150 \text{ cm}^{-1}$  is observed [Fig. 5(a)], similar to what was seen by Capitani et al. [23] A weaker mode around 130  $\text{cm}^{-1}$  appears at 0.8 GPa (shown by the blue arrow) and another mode at 70 cm<sup>-1</sup> appears at 1.3 GPa. By comparing with the XRD and PL results, we attribute the emergence of these additional Raman modes to a symmetrylowering structural phase transition from cubic I (phase I,  $Pm\bar{3}m$ ) to cubic II (phase II,  $Im\bar{3}$ ) as confirmed from highpressure XRD studies. Upon further compression, another lattice mode around 58  $cm^{-1}$  appears at 3.2 GPa, which becomes more pronounced at 4 GPa, suggesting another symmetry-lowering structural phase transition from the cubic II to the orthorhombic phase (Pnma) at 3.2 GPa, in agreement with previous reports [23].

Figure 5(b) presents the vibrational frequencies in the lowfrequency region as a function of pressure. The 325 cm<sup>-1</sup> and the 175 cm<sup>-1</sup> modes are seen throughout the pressure range up to 5 GPa [Fig. 5(c)]. For a detailed assignment of these vibrations, which arise due to the vibrations of the Pb-Br bonds, we refer to Ref. [58]. The frequency of the 325 cm<sup>-1</sup> mode [Fig. 5(d)] shows a dramatic change in slope at 1 GPa indicating that that cubic I to cubic II transition is



FIG. 5. (a) Raman spectra of MAPbBr<sub>3</sub> for selected pressures below 500 cm<sup>-1</sup>. The red arrows denote the emergence of the 50 cm<sup>-1</sup> mode beyond 3 GPa and the 70 cm<sup>-1</sup> mode as it starts shifting with pressure. (b) Raman peak positions of the low-frequency modes seen in (a) as a function of pressure. (c) Close up of the 300 cm<sup>-1</sup> region for different pressure values. (d) Peak position of the 325 cm<sup>-1</sup> Raman mode as a function of pressure. The inset shows the peak position of the 70 cm<sup>-1</sup> mode as a function of pressure. The inset shows the peak position of the 70 cm<sup>-1</sup> mode as a function of pressure. The black dashed line is a guide to the eye. The red arrows denote discontinuity and slope change.

driven by a tilt of the octahedra, which further confirms that this Raman mode belongs to the lattice (bromide motion). Frequencies related to the bromide motion and the 70 cm<sup>-1</sup> mode exhibit an anomalous change in slope at 2 GPa. Since high-pressure XRD does not show any evidence of a structural phase transition around 2 GPa, we attribute these changes to an isostructural phase transition.

In addition to the vibrations associated with the perovskite octahedral framework, the vibrations associated with the MA cation are reflective of both structural and isostructural phase transformations. The pressure dependence of the Raman spectra in regions 2–4 are shown in Figs. 6(a)–6(c). The individual peaks were fitted with Lorentzian line shapes and their pressure dependencies are shown in Figs. 6(d)-6(f). The peak position of the 2830 cm<sup>-1</sup> mode softens, whereas the N-H stretch mode at 2970 cm<sup>-1</sup> hardens with pressure [Fig. 6(f)]. Above 3.5 GPa, a new peak below 2980  $\text{cm}^{-1}$  is observed, similar to what was reported by Capitani et al [23]. Such peak splittings are also observed in the C-N stretch region [Fig. 6(d)], C-H bend, and N-H bend and stretch modes due to the reorientation of the MA ion in the *Pnma* phase, lifting mode degeneracies. These observations correlate with the symmetry-lowering structural phase transition from cubic II to the orthorhombic (*Pnma*) phase at 3.2 GPa. Above 5.8 GPa, all the Raman peaks become broad, indicating a disordered phase. Upon releasing the pressure, the high pressure disordered phase is found to be stable up to 0.2 GPa [42]. We note that the cubic II to the orthorhombic transition manifests itself due to the ordering of the MA cation.

Along with the changes observed in the Raman modes at the structural phase transitions (1 GPa and 3 GPa), sharp changes in the phonon frequencies, FWHM, and changes in the intensity ratio at 2 GPa are observed (see Supplemental Material) [42]. The frequencies of the CH<sub>3</sub> rocking, C-N, and C-H stretching modes all exhibit sharp changes at 2 GPa. Notably, a dramatic enhancement in the intensity ratio of C-N stretch/C-H rock and N-H/C-H bend modes are observed around 2 GPa (Fig. S10), which correlates with the onset of MA cation ordering. By comparing the changes in the Raman spectra with the changes in the PL peak intensity, peak position, and FWHM at 2 GPa (Fig. 2), we assign these observations to an isostructural phase transition.

To understand the nature of the isostructural transition at 2 GPa and how it initiates the structural phase transition at 3.0 GPa, it is instructive to look into the evidence for coupling of the organic cations with the  $PbBr_6$  lattice under high



FIG. 6. (a)–(c) Raman spectra of MAPbBr<sub>3</sub> for selected values of pressure in regions 2, 3, and 4, respectively. The red arrows indicate the splitting of phonon modes during cubic II to the orthorhombic phase transition. (d)–(f) Frequencies of the various Raman modes, corresponding to regions 2–4, as a function of pressure. The red symbols denote the frequencies of new Raman modes that emerge with pressure. The red arrows denote discontinuity in the frequencies and the emergence of new modes.

pressure. The coupling of the organic cations with the lattice via hydrogen bonding in MAPb $X_3$  (X = Cl, Br or I) perovskites is well documented in the literature. These studies, which include Raman scattering, solid-state nuclear magnetic resonance, two-dimensional terahertz-infrared-visible spectroscopy, and high-resolution neutron scattering all reveal that the amine (NH<sub>3</sub>) end of the MA organic cation dynamically couples with the PbX<sub>6</sub> lattice [19,28,57,59-61]. The organic-inorganic interaction is mediated via H-bonding and is responsible for locking of the MA ions at high pressures, which is otherwise dynamically disordered under ambient conditions [23,25]. It is apparent from Fig. 6 that the CH<sub>3</sub> rocking mode shows an obvious change at 2 GPa and that the C-H and N-H stretching modes shift in opposite directions with a sharp softening of C-H stretching mode and hardening of N-H stretching mode at 2 GPa. These results suggest the role of H bonding between the NH<sub>3</sub> end of the MA cation to the Br<sup>-</sup> ion of PbBr<sub>6</sub> lattice for pressures lower than 2 GPa. The H bonding between the CH<sub>3</sub> end to Br<sup>-</sup> appears to be weak till 2 GPa. Around 2 GPa, the strength of the H bonding between CH<sub>3</sub> and Br<sup>-</sup> is enhanced, as evident from the strong softening of the C-H stretch mode and the CH<sub>3</sub> rocking mode. Thus, the anomalous changes observed both in the lattice and molecular vibrational modes along with the dramatic increase in the intensity ratios (N-H/C-H bend and C-N stretch/CH rock) and changes in FWHM suggest a strong coupling of the MA cation with the PbBr<sub>6</sub> lattice via H bonding. The DFT calculations also show a change in the H-Br<sup>-</sup> distances with pressure, as discussed in Sec. III F.

The discontinuity in the C–N stretching mode and splitting of the MA vibrational modes confirm the first-order cubic II

to an orthorhombic phase transition upward of 3.0 GPa. The hardening of the molecular vibrational modes above 3.6 GPa hints at the weakening of the hydrogen bonding before finally transforming to the disordered phase. The isostructural transition observed at 2 GPa therefore acts as a precursor for the cubic II to the orthorhombic structural phase transition. Since no major changes are observed in the molecular vibrational modes during the cubic I to cubic II transition (at 1 GPa), this transition is induced by the octahedral changes of the PbBr<sub>6</sub> lattice. The softening of the C–H stretching mode at  $\sim$  0.8 GPa correlates with the discontinuity in PL peak position observed at 0.7 GPa [Figs. 2(b) and 6(e)].

## F. Discussion

There is a striking similarity of the features and trends observed in the PL and the Raman scattering data. The structural transitions at 1 GPa and 3 GPa are reflected as sharp changes in the band-gap energy in the PL and as the appearance of new modes in the Raman spectrum due to lifting of the mode degeneracies as a result of lowering of the symmetry. What is perhaps even more surprising are the systematic changes observed at 2 GPa both in the PL and the Raman spectra. The XRD shows no structural phase transition at 2 GPa. In this region, the PL energies blueshift with sharp changes in intensity and FWHM at 2 GPa. Similarly, the Raman frequencies belonging to the inorganic cage and the MA vibrations show anomalies at this pressure. These observations further suggest a strong coupling of the electronic states of the perovskite to the vibrations of the PbBr<sub>6</sub> framework and the MA cation, which could then impact the details of the band structure. It is worth noting that our DFT calculations, which do not consider any electron-phonon interactions, fail to predict the experimental blue-shift in band-gap energies between 1 and 2 GPa. Moreover, the theoretical dielectric function is seen to have similar values across this pressure range, implying that there are other factors such as electron-phonon interactions and the dynamical motion of the organic cation that may be responsible for the discrepancy between theory and experiment.

The shifts of the Raman C-H and N-H stretching modes in opposite directions with steeper change in the slope beyond 2 GPa give us clues about the nature of the hydrogen bonding, which is known to play a role when the crystal lattice undergoes a phase transformation at low temperatures [25]. The softening of the C-H stretch mode suggests an enhancement in the interaction of the CH<sub>3</sub> end of MA and Br<sup>-</sup> with pressure. The DFT calculations show a similar trend in the  $Pm\bar{3}m$  phase (see Supplemental Material) [42]; the Br<sup>-</sup>-H-C separation is seen to decrease with decreasing lattice constant (increasing pressure), whereas the Br<sup>-</sup>-H-N separation increases with increase in pressure. It is worth emphasizing that the equilibrium geometry which corresponds to a = 6.015 Å shows the minimum separation for Br<sup>-</sup>-H-N. This isostructural phase transition at 2 GPa is accompanied by a locking of the rotational and orientational motion of the MA cation, which leads to an ordering of the molecular cation. Around 3 GPa, the dynamic motion of the MA cation is completely locked, resulting in an order-disorder cubic II to an orthorhombic phase transition.

# **IV. CONCLUSION**

In conclusion, high-pressure PL, synchrotron-based XRD, and Raman-scattering investigations from MAPbBr<sub>3</sub> reveal an isostructural phase transition at 2 GPa in addition to the structural phase transitions observed at 1 GPa (from cubic I to cubic II) and at 3 GPa (from cubic II to orthorhombic). This 2 GPa transition is accompanied by a coupling of the MA cation with the PbBr<sub>6</sub> lattice, which is reflected in the Raman spectra. In particular, the lattice modes at  $70 \text{ cm}^{-1}$  and  $325 \text{ cm}^{-1}$  and the vibrations associated with the MA cation (C–H stretch at 2830 cm<sup>-1</sup> and N–H stretch at 2970 cm<sup>-1</sup>) show anomalous behavior in their peak positions at 2 GPa. Concomitant changes in the PL at 2 GPa further reflect the coupling of the electronic states to the vibrations of the PbBr<sub>6</sub> framework and the MA cation. The narrowing of the band gap with pressure observed in the DFT calculations is consistent with the experimental pressure-dependent PL energies in the cubic I  $(Pm\bar{3}m)$  phase. Such comparisons provide a critical test for improved first-principles approaches of the electronic structure of OIHPs under pressure in the future, where electron-phonon interactions along with the dynamical motion of the cation need to be incorporated. Our study provides direct evidence that the suppression of structural and orientational disorder of the organic cation initiates the structural phase transition at 3 GPa in MAPbBr<sub>3</sub>.

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