Supporting Information for

# Hybrid Perovskite at Full Tilt: Structure and Symmetry Relations of the Incommensurately Modulated Phase of Methylammonium Lead Bromide, MAPbBr<sub>3</sub>

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## 1 Experimental Details

Data were acquired using an "Agilent SuperNova" dual-source diffractometer equipped with a goniometer in  $\kappa$  geometry, an "EosS2" CCD detector, and a mirror-monochromated "Mova" Mo- $K_{\alpha}$  source. The raw data set had originally been collected for a study published elsewhere and was now re-evaluated herein.<sup>1</sup> (The average structure that had been derived using standard methods for periodic crystals is contained in CCDC 2008697.)

Inspection of reciprocal space and indexing confirmed that the sample was twinned by a rotation of ca. 180° around <101>. Furthermore, first-order satellite reflections were discernible along the **c**\* direction at **q**  $\approx$  0.2**c**\*. For the lack of a procedure allowing simultaneous twin and satellite integration, both domains had to be handled separately. Diffraction images were integrated, scaled, and empirically corrected for absorption using the SCALE3 ABSPACK algorithm of CrysAlisPro.<sup>2</sup> In addition, spherical absorption correction using the equivalent radius was performed.

The structure was solved with SUPERFLIP using a charge-flipping algorithm.<sup>3</sup> Initial solutions were of the average space-group types *Immm* an *Imma*. However, only the latter led to physically sensible and refinable models. Satellite extinction rules identified the superspace-group type as *Imma*(00 $\gamma$ )s00. Subsequent refinements were carried out with JANA2006 against  $F_0^2$  data using the full-matrix least-squares algorithm.<sup>4</sup> Initial models of the  $^3_{\infty}$ [PbBr<sub>3</sub>]<sup>-</sup> framework containing the atoms Pb1, Br1, and Br2 refined smoothly with first-order positional-modulation parameters. For the lack of discernible higher-order satellites, the inclusion of higher-order modulation functions was inadvisable. Test refinements showed a better modelling of electron density using continuous vs. discontinuous modulation functions (leaving, however, somewhat larger residual density), as illustrated by de-Wolff sections and "*t* movies" with observed Fourier maps generated in MoleCoolQt.<sup>5</sup> Lead and bromide ions were modelled anisotropically; introduction of displacement modulations led to further significant improvement.

Fourier difference maps showed two unique maxima around the methylammonium position, each generating an ion in a distinct orientation. Each one was initially modelled as a mixed carbon/nitrogen site with a 1:1 occupancy ratio using same-position (nitrogen shifted to an equivalent position for contiguity) and same-displacement constraints. Using a development version of JANA2020, hydrogen atoms were then added at positions inferred from neighboring sites to yield tetrahedral geometry and an ideally staggered conformation with one hydrogen atoms per CH<sub>3</sub>/NH<sub>3</sub><sup>+</sup> group directly on the crystallographic mirror. The atomic methylammonium model was converted to a "breathing", rigid molecular model with  $d_0$ (C–N) = 1.495 Å,  $d_0$ (C–H) = 0.96 Å,  $d_0$ (N–H) = 0.87 Å, same-displacement constraints for the carbon/nitrogen atoms, and constrained isotropic displacement for the hydrogen atoms [ $U_{iso}$ (H) = 1.2 $U_{eq}$ (C) or  $U_{iso}$ (H) = 1.5 $U_{eq}$ (N)]. The two orientations were modelled as two instances of this molecule with rotational angles fixed as required by site symmetry and tightly restrained breathing [d(C–N) ≈ 1.50(1) Å]. The occupations were constrained to a sum of unity; their final ratio refined to a: b = 0.67(3):0.33(3). The overall diffuse density distribution led to the refinement of first-order harmonic translational and rotational parameters only; more complex discontinuous models are unwarranted. The modulation of

the rotation of second molecular instance around its C–N axis had to be fixed at zero because of the low distinguishing power of the hydrogen atoms hindering convergence. Carbon and nitrogen atoms were modelled anisotropically; a TLS model did not refine to physically meaningful parameter values.

Because tests showed serious model deterioration upon inclusion of data from the minor domain (initially estimated ratio ca. 3:2), refinement was carried out on data from the integration of the major domain including overlapping reflections. The latter were handled by introducing a twin law corresponding to the matrix representation

/-0.0272	0	1.0272\
0	-1.0000	0
0.9728	0	0.0272/

and regarding angular differences below 0.2° as fully and up to 0.3° as partially overlapped. The actual criteria had little influence on model quality within an ample range and finally led to an exclusion of 126 reflections while the volume fraction of the minor domain refined to 0.220(6). Data were weighted using the instability factor from merging and Wilson's modification of intensities.<sup>6</sup> Because of problems with concomitant single-domain and satellite integration, 25 mismeasured reflections with  $|F_0 - F_c| > 6\sigma(F_0)$  were excluded from the final refinement.

Structure representations were produced using VESTA v3.5.5.<sup>7</sup> Structural distortion modes were analyzed using ISODISTORT v6.7.2.<sup>8,9</sup> CCDC 2049312 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via <u>https://www.ccdc.cam.ac.uk/structures</u>.

CH <sub>6</sub> Br <sub>3</sub> NPb	
479.00	
orthorhombic, <i>Imma</i> (00γ)s00	
8.4657(9), 11.7303(12), 8.2388(8)	
90, 90, 90	
0.2022(8) <b>c</b> *	
818.16(14)	
4	
824	
3.8885	
Mo- $K_{\alpha}$ ( $\lambda = 0.71073$ Å)	
35.169	
block, intense orange	
$0.219 \times 0.161 \times 0.098$	

#### Table S1. Crystallographic Details

Data Collection				
Measurement method	$\omega$ scans			
Absorption correction	spherical and empirical			
T <sub>min</sub> , T <sub>max</sub>	0.03325, 0.05874			
No. of measd, indep., and obsd <sup>a</sup> reflections	16912, 1582, 934			
main reflections	5632, 564, 457			
first-order satellites	11280, 1018, 477			
R <sub>int</sub>	0.1209			
$(\sin \theta / \lambda)_{\text{max}}$ (Å <sup>-1</sup> )	0.70			
$\theta_{\min}, \theta_{\max}$ (°)	3.45, 29.75			
h, k, l, m	$-11 \rightarrow 11$ , $-14 \rightarrow 15$ , $-10 \rightarrow 11$ , $-1 \rightarrow 1$			
Refinement				
$R_1, wR_2, ^b S \text{ (all)}$	0.0816, 0.1313, 1.4929			
main reflections only	0.0489, 0.0985, —			
first-order satellites only	0.1659, 0.2077, —			
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> , <sup><i>b</i></sup> <i>S</i> (obsd) <sup><i>a</i></sup>	0.0531, 0.1193, 1.7785			
main reflections only	0.0421, 0.0955, —			
first-order satellites only	0.0883, 0.1794, —			
No. of data	1582			
main reflections	564			
first-order satellites	1018			
No. of parameters, constraints, restraints	44, 30, 2			
H-atom treatment	H-atom parameters constrained			
$(\Delta/\sigma)_{\rm max}$	0.0001			
$\Delta \varrho_{ m max}$ , $\Delta \varrho_{ m min}$ (Å <sup>-3</sup> )	3.56, -2.22			
	= 2) /2			

 ${}^{a}I > 3\sigma(I). \ {}^{b}w = 1/[\sigma^{2}(F_{\rm o}{}^{2}) + (0.015696P)^{2}] \ {\rm where} \ P = (F_{\rm o}{}^{2} + 2F_{\rm c}{}^{2})/3.$ 

# 2 Geometrical Details

Table S2. Bond Lengths in Å

	Average	Minimal	Maximal
Pb1-Br1	2.9728(14)	2.961(2)	2.983(2)
Pb1-Br2	2.9724(5)	2.9621(6)	2.9826(6)
C1a-N1a	1.51(5)	1.50(5)	1.52(5)
C1b-N1b	1.4955(4)	1.4955(4)	1.4955(4)

Table S3. Hydrogen Bonds (Distances in Å, Angles in °)

	t	<i>d</i> ( <i>D</i> -H)	<i>d</i> (H…A)	<b>d(</b> <i>D···A</i> <b>)</b>	<b>∢(D-H</b> …A)
N2a-H2aa…Br2	average	0.87(3)	3.00(2)	3.72(3)	140.3(7)
	0.0	0.88(5)	2.98(4)	3.72(3)	143(4)
	0.1	0.89(5)	2.84(4)	3.63(3)	149(4)
	0.2	0.88(5)	2.80(4)	3.59(3)	152(4)
	0.3	0.87(5)	2.86(4)	3.64(3)	150(4)
	0.4	0.87(5)	2.97(4)	3.72(3)	145(4)
	0.5	0.88(5)	3.08(4)	3.78(3)	138(4)
	0.6	0.89(5)	3.17(4)	3.82(3)	132(4)
	0.7	0.88(5)	3.22(4)	3.84(3)	130(4)
	0.8	0.87(5)	3.22(4)	3.85(3)	131(4)
	0.9	0.87(5)	3.13(4)	3.81(3)	136(4)
N2a-H2ba…Br1	average	0.870(17)	2.841(16)	3.700(15)	170(2)
	0.0	0.87(3)	2.62(3)	3.44(2)	158(4)
	0.1	0.88(3)	2.68(3)	3.51(2)	159(4)
	0.2	0.87(3)	2.80(3)	3.65(2)	165(4)
	0.3	0.87(3)	2.95(3)	3.82(2)	173(3)
	0.4	0.87(3)	3.08(3)	3.95(2)	172(4)
	0.5	0.87(3)	3.13(3)	3.99(2)	167(4)
	0.6	0.88(3)	3.06(3)	3.91(2)	166(3)
	0.7	0.87(3)	2.91(3)	3.76(2)	167(3)
	0.8	0.87(3)	2.74(3)	3.59(2)	166(3)
	0.9	0.87(3)	2.64(3)	3.47(3)	162(4)

	t	<i>d(D-</i> H)	<i>d</i> (H…A)	d( <i>D</i> …A)	<b>∢(D-H</b> …A)
N2b-H2ab…Br2	average	0.87(8)	2.90(5)	3.61(6)	139.6(15)
	0.0	0.87(8)	2.91(5)	3.62(6)	139.5(16)
	0.1	0.87(8)	2.90(5)	3.61(6)	139.6(16)
	0.2	0.87(8)	2.91(5)	3.61(6)	139.6(16)
	0.3	0.87(8)	2.91(5)	3.62(6)	139.4(17)
	0.4	0.87(8)	2.91(5)	3.62(6)	139.4(17)
	0.5	0.87(8)	2.91(5)	3.62(6)	139.5(16)
	0.6	0.87(8)	2.90(5)	3.61(6)	139.6(16)
	0.7	0.87(8)	2.91(5)	3.61(6)	139.6(16)
	0.8	0.87(8)	2.91(5)	3.62(6)	139.4(17)
	0.9	0.87(8)	2.91(5)	3.62(6)	139.4(17)
N2a-H2bb…Br1	average	0.87(4)	2.84(4)	3.64(4)	154(3)
	0.0	0.87(8)	3.03(4)	3.81(5)	151(4)
	0.1	0.87(8)	3.06(5)	3.86(5)	154(4)
	0.2	0.87(8)	3.02(5)	3.84(5)	158(5)
	0.3	0.87(8)	2.92(5)	3.75(5)	161(5)
	0.4	0.87(8)	2.79(5)	3.62(5)	161(5)
	0.5	0.87(8)	2.68(5)	3.50(5)	158(5)
	0.6	0.87(8)	2.63(5)	3.43(5)	154(5)
	0.7	0.87(8)	2.68(5)	3.46(5)	150(5)
	0.8	0.87(8)	2.80(4)	3.57(5)	148(4)
	0.9	0.87(8)	2.94(4)	3.70(5)	148(4)

*t*: modulation phase, *D*: donor atom, *A*: acceptor atom.

# 3 De-Wolff Sections

De-Wolff sections are contour plots of the summary observed, calculated, or difference electron density vs. a fractional spatial coordinate vs. *x*<sub>4</sub>. The sum is calculated over an interval in the remaining two spatial dimensions.



**Figure S1.** Observed de-Wolff sections for Pb1 (gray line). Plot of uniform contours with  $\Delta \rho = 10 \text{ Å}^{-3}$ ;  $x_1 = x$ ,  $x_2 = y$ ,  $x_3 = z$ .



**Figure S2.** Observed de-Wolff sections for Br1 (brown line). Plot of uniform contours with  $\Delta \rho = 3 \text{ Å}^{-3}$ ;  $x_1 = x$ ,  $x_2 = y$ ,  $x_3 = z$ .



**Figure S3.** Observed de-Wolff sections for Br2 (brown line). Plot of uniform contours with  $\Delta \rho = 3 \text{ Å}^{-3}$ ;  $x_1 = x$ ,  $x_2 = y$ ,  $x_3 = z$ .



**Figure S4.** Difference de-Wolff sections for Pb1 (gray line). Plot of uniform contours with  $\Delta \rho = 0.15 \text{ Å}^{-3}$ ;  $x_1 = x$ ,  $x_2 = y$ ,  $x_3 = z$ .



**Figure S5.** Difference de-Wolff sections for Br1 (brown line). Plot of uniform contours with  $\Delta \rho = 0.15 \text{ Å}^{-3}$ ;  $x_1 = x$ ,  $x_2 = y$ ,  $x_3 = z$ .



**Figure S6.** Difference de-Wolff sections for Br2 (brown line). Plot of uniform contours with  $\Delta \rho = 0.15 \text{ Å}^{-3}$ ;  $x_1 = x$ ,  $x_2 = y$ ,  $x_3 = z$ .

# 4 Symmetry Relationships

**Table S4.** Decomposition of Isotropy Subgroups into Distortion Modes of Parent Groups (Displacive Modes Only)

SG IR	OPD	As/Å	Atom	PG IR	PbBr <sub>6</sub> Distortion
$\alpha^{10} \rightarrow 1$	IC (avera	ge)	Pm <u>3</u> m → In	nma	
<b>R</b> 4 <sup>+</sup>	( <i>a a</i> 0)	-0.75235	Br1 (3 <i>d</i> )	$E_{\mathrm{u}}$	octahedron tilt ( <i>a</i> - <i>b</i> <sup>0</sup> <i>a</i> -)
<b>R</b> 5 <sup>+</sup>	( <i>a</i> – <i>a</i> 0)	0.09691	Br1 (3 <i>d</i> )	$E_{\mathrm{u}}$	axis tilt with base counter-tilt
		0.00000	MA1 (1 <i>b</i> )	$T_{1u}$	
IC (ave	erage) $\rightarrow$	$\gamma^{11}$	Imma → Pn	ma	
$\Gamma_1^+$	( <i>a</i> )	-0.23789	Br1 (8g)	Α	base tilt around <b>a</b>
		0.62137	Br2 (4 <i>e</i> )	$A_1$	axis tilt around <b>a</b>
		0.00000	MA1 (4e)	$A_1$	
$X_4^+$	( <i>a</i> )	1.02244	Br1 (8g)	В	base shear along <b>a</b>
		-0.92512	Br1 (8g)	В	base shear along <b>c</b>
		-0.51810	Br2 (4 <i>e</i> )	$B_1$	axis tilt around <b>c</b>
		0.00000	MA1 (4e)	$B_1$	
IC (average) $\rightarrow$ IC Imma $\rightarrow$ Imma(00 $\gamma$ )s00					
$\Gamma_{1}^{+}$	( <i>a</i> )	0.00000	Br1 (8g)	Α	base tilt around <b>a</b>
		0.00000	Br2 (4 <i>e</i> )	$A_1$	axis tilt around <b>a</b>
		0.00000	MA1 (4e)	$A_1$	
Λ4	(a 0)	0.11370	Pb1 (4a)	$A_{\mathrm{u}}$	center shift along <b>a</b>
		0.48042	Br1 (8g)	Α	base tilt/twist around <b>c</b>
		0.25021	Br1 (8g)	В	base shear/shift along <b>a</b>
		-0.09437	Br1 (8g)	В	base shear/keystone-distortion along ${f c}$
		-0.15143	Br2 (4 <i>e</i> )	$B_1$	axis bending along <b>a</b>
		-0.36179	Br2 (4 <i>e</i> )	$B_1$	axis tilt around <b>c</b>
		0.00000	MA1 (4 <i>e</i> )	$B_1$	
		0.00000	MA1 (4e)	$B_1$	

SG IR: irreducible representation of the space-group symmetry of the parent structure (for primary order parameters in bold), OPD: order-parameter direction,  $A_s$ : standard supercell-normalized mode amplitude (zero for MA modes because of modelling as centroid in idealized position), Atom: affected (pseudo-)atom (Wyckoff position in parentheses), PG IR: irreducible representation of the point-group symmetry of the local Wyckoff position, PbBr<sub>6</sub> Distortion: distortion of the lead coordination polyhedron (axis: Br2–Pb–Br2 along **b**, base: Pb(Br1)<sub>4</sub> in **ac** plane).

### 5 References

(1) Guo, Y.; Yaffe, O.; Paley, D. W.; Beecher, A. N.; Hull, T. D.; Szpak, G.; Owen, J. S.; Brus, L. E.; Pimenta, M. A. Interplay between Organic Cations and Inorganic Framework and Incommensurability in Hybrid Lead-Halide Perovskite CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub>. *Phys. Rev. Mater.* **2017**, *1*, 042401.

(2) Rigaku Oxford Diffraction *CrysAlisPro Software System*, 1.171.40.84a; Rigaku Corporation: Oxford, U.K., 2020.

(3) Palatinus, L.; Chapuis, G. *SUPERFLIP* – A Computer Program for the Solution of Crystal Structures by Charge Flipping in Arbitrary Dimensions. *J. Appl. Crystallogr.* **2007**, *40*, 786–790.

(4) Petříček, V.; Dušek, M.; Palatinus, L. Crystallographic Computing System JANA2006: General Features. *Z. Kristallogr. – Cryst. Mater.* **2014**, *229*, 345–352.

(5) Hübschle, C. B.; Dittrich, B. *MoleCoolQt* – A Molecule Viewer for Charge-Density Research. *J. Appl. Crystallogr.* **2011**, *44*, 238–240.

(6) Wilson, A. J. C. Statistical Bias in Least-Squares Refinement. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1976**, *32*, 994–996.

(7) Momma, K.; Izumi, F. *VESTA 3* for Three-Dimensional Visualization of Crystal, Volumetric and Morphology Data. *J. Appl. Crystallogr.* **2011**, *44*, 1272–1276.

(8) Campbell, B. J.; Stokes, H. T.; Tanner, D. E.; Hatch, D. M. ISODISPLACE: A Web-Based Tool for Exploring Structural Distortions. *J. Appl. Crystallogr.* **2006**, *39*, 607–614.

(9) Stokes, H. T.; Hatch, D. M.; Campbell, B. J. *ISODISTORT, Isotropy Software Suite*, Brigham Young University: Provo, UT, 2020; <u>https://iso.byu.edu</u>.

(10) Jaffe, A.; Lin, Y.; Beavers, C. M.; Voss, J.; Mao, W. L.; Karunadasa, H. I. High-Pressure Single-Crystal Structures of 3D Lead-Halide Hybrid Perovskites and Pressure Effects on Their Electronic and Optical Properties. *ACS Cent. Sci.* **2016**, *2*, 201–209.

(11) López, C. A.; Martínez-Huerta, M. V.; Alvarez-Galván, M. C.; Kayser, P.; Gant, P.; Castellanos-Gomez, A.; Fernández-Díaz, M. T.; Fauth, F.; Alonso, J. A. Elucidating the Methylammonium (MA) Conformation in MAPbBr<sub>3</sub> Perovskite with Application in Solar Cells. *Inorg. Chem.* **2017**, *56*, 14214–14219.