
Supplementary information

Atomically resolved edges and defects in lead halide perovskites

In the format provided by the
authors and unedited

Supplementary Information for Atomically Resolved Edges and Defects in Lead Halide Perovskites

Biao Yuan^{1,2,3†}, Zeyu Wang^{4†}, Shuchen Zhang^{5†},
Christoph Hofer¹, Chuang Gao¹, Tamazouzt Chennit¹,
Hongsheng Shi⁴, Xiaoyan Wu⁴, Yu Han^{2,3,6}, Letian Dou^{7,8*},
Yi Yu^{4*}, Timothy J. Pennycook^{1*}

¹Electron Microscopy for Materials Science, University of Antwerp,
Antwerp, Belgium.

²Center for Electron Microscopy, South China University of Technology,
Guangzhou, China.

³School of Emergent Soft Matter, South China University of Technology,
Guangzhou, China.

⁴State Key Laboratory of Quantum Functional Materials & Shanghai Key
Laboratory of High-Resolution Electron Microscopy, School of Physical
Science and Technology, ShanghaiTech University, Shanghai, China.

⁵State Key Laboratory of Precision and Intelligent Chemistry, Department
of Materials Science and Engineering, School of Chemistry and Materials
Science, University of Science and Technology of China, Hefei, China.

⁶State Key Laboratory of Pulp and Paper Engineering, South China
University of Technology, Guangzhou, China.

⁷Davidson School of Chemical Engineering, Purdue University, West
Lafayette, IN, United States.

⁸Department of Chemistry, Emory University, Atlanta, GA, United States.

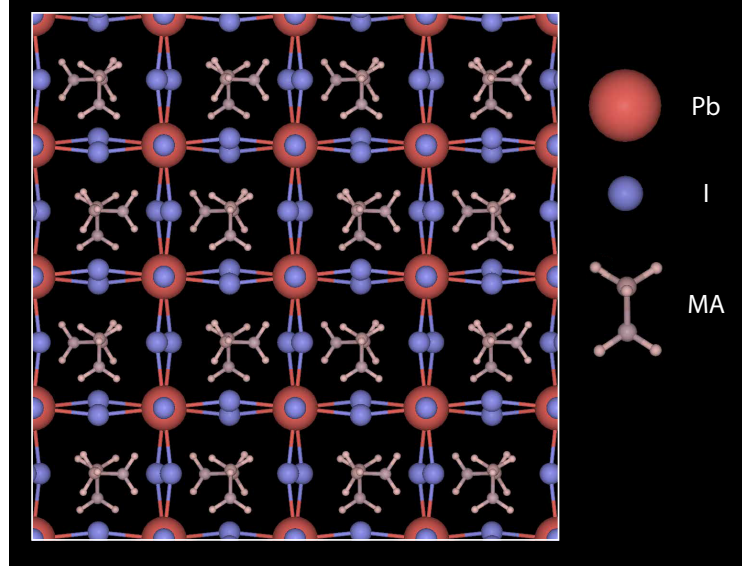
*Corresponding author(s). E-mail(s): dou10@purdue.edu;
yuyi1@shanghaitech.edu.cn; tpennycook@gmail.com;

[†]These authors contributed equally to this work.

Crystal structure of MAPbI₃

MAPbI₃ has a perovskite structure with a 3D network of lead (Pb), iodine (I), and methylammonium (CH₃NH₃ or MA) as shown in SFig. 1. In this structure, Pb²⁺ and I⁻ form an octahedral arrangement centered around Pb²⁺, while MA⁺ resides within

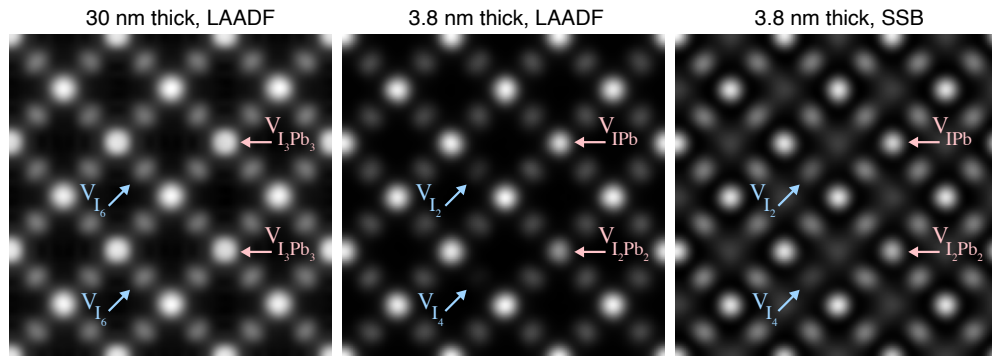
cages formed by eight PbI_6^{4-} units. Due to its small volume, MA^+ has the possibility of rotation, and the octahedra also exhibit tilting under certain conditions.¹



SFig. 1 Model of the perovskite structure MAPbI_3 .

The need for ultrathin MAPbI_3 nanosheets and ptychography

The contrast in annular dark field (ADF) imaging, including low angle ADF (LAADF), is dominated by the atomic number and thickness of the atomic or molecular columns it is used to image. This means that the brightness of a column will tend to increase overall as the thickness is increased from a single atom to the 30 nm used by Rothmann et al.² with the highly related halide perovskite FAPbI_3 in which the FA (formamidinium) takes the place of the MA in MAPbI_3 . 30 nm is a typical thickness for atomic resolution electron microscopy. In comparison to a thinner material the location of the columns will be clearer in ADF images, and this facilitated Rothmann et al.'s detection of the relatively light FA columns which scatter much less than the heavier I and especially the even heavier Pb-I columns. Furthermore FA has an average atomic number 1.5 times higher than MA, so it is also easier to detect FA than MA.



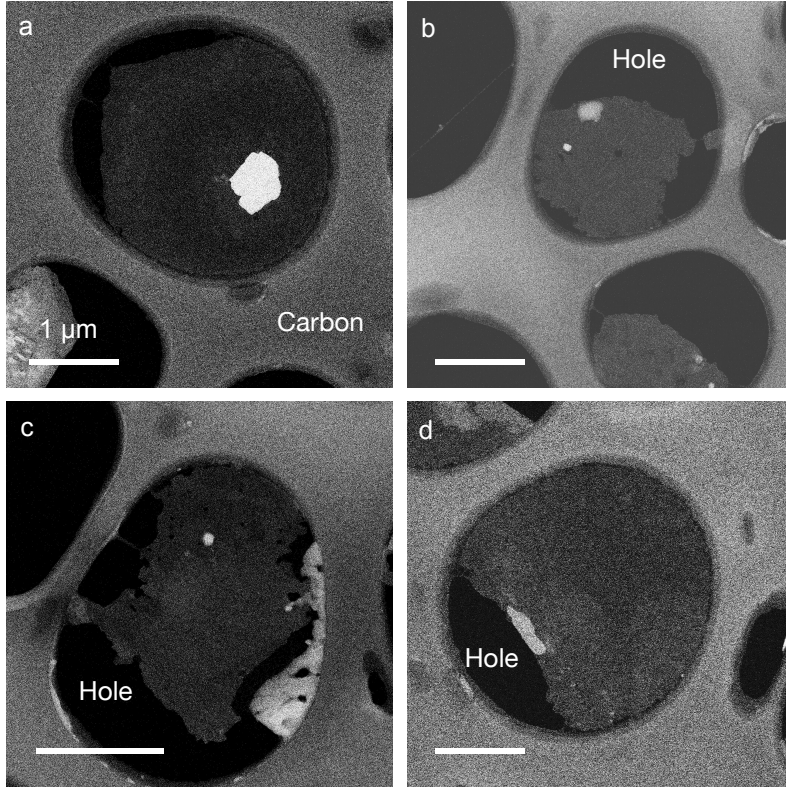
SFig. 2 Comparison of the contrast of vacancies in thick and thin MAPbI_3 using multislice simulations at 200 kV. V_{I_x} indicates a vacancy of x I atoms, and $V_{P_xI_x}$ a vacancy of x Pb and x I atoms. A 20 mrad convergence angle was used for the 30 nm thick sample, and a 13 mrad convergence angle for the 3.8 nm ultrathin material.

However, detecting a small change in the occupancy of the columns cannot be expected in a sample of similar thickness to the 30 nm thick sample used by Rothmann et al. at

low doses. Defects consisting of only a few atoms or vacancies will form a very small fraction of atomic columns of such thicknesses, and result in a correspondingly small change in signal that will be difficult to detect in general and essentially impossible in the ultralow dose regime. Small changes in the number of atoms due to the formation of vacancies are much easier to detect when the removed atoms represent a larger fraction of the column occupancy.

This is illustrated in SFig. 2 where we compare noise free imaging of 30 nm thick and ultrathin MAPbI₃ containing vacancies. The multislice simulations used parameters that matched those of Rothmann et al. for the 30 nm thick sample, and those of our experiments for the ultrathin material. The simulations were performed using *abTEM* with up to 100 phonon configurations.

The 30 nm thick simulation contains two columns with six I vacancies (V_{I_6}), and two columns with three Pb vacancies and three I vacancies each ($V_{P_3I_3}$). The columns containing $V_{P_3I_3}$ are slightly less bright than some of the other Pb-I columns, but the change in the brightness of the I columns containing six I vacancies is imperceptible by eye, despite the lack of noise. With the ultrathin material we used fewer vacancies per column, one I column with four I vacancies (V_{I_4}), one I column with two I vacancies (V_{I_2}), one Pb-I column with two I vacancies and two Pb vacancies ($V_{P_2I_2}$) and one Pb-I column with just one I vacancy and one Pb vacancy (V_{PI}). All of the vacancy sites are discernible in both the LAADF and SSB images of the ultrathin material. As the pristine layers are only several atoms thick, the change in contrast is relatively high. This is why we require ultrathin MAPbI₃ nanosheets that are only several atoms thick. Synthesising ultrathin MAPbI₃ nanosheets is challenging, and has only recently been made possible by our synthesis method,³ but it enables us to see the fine structural details that can be important to damage.



SFig. 3 Low-magnification HAADF showing the morphology of MAPbI₃ nanosheets.

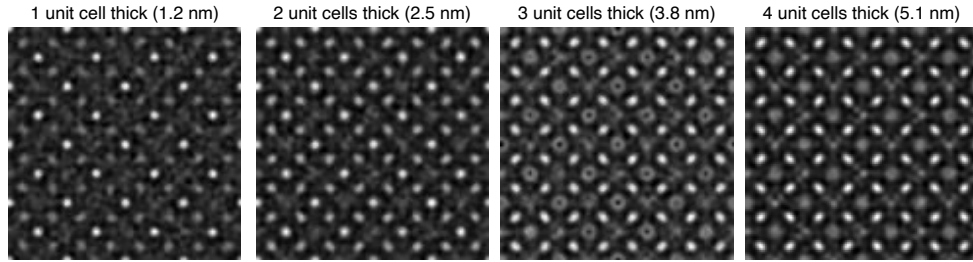
However, being thin decreases the overall signal, which is why we also desire a more efficient form of imaging than LAADF to make up for the reduction in the overall

signal, especially for low dose work. Note that the images in SFig. 2 are shown with the contrast adjusted for each image rather than on an absolute scale and therefore do not illustrate the drop in signal in the LAADF with thickness. Additional simulations at a wide range of doses are discussed shown in section Simulated imaging of the edge structure of MAPbI₃.

SFig. 2 also shows the lack of visibility of the MA columns in the LAADF images. This is the well known problem of detecting light columns next to heavier columns in ADF imaging in general. Fortunately, ptychography also addresses the issue of imaging lighter columns.^{4,5} Overall, phase imaging provides greater efficiency and visibility of structure, while Z-contrast ADF provides images which are more reliably interpreted in terms of elemental identity.

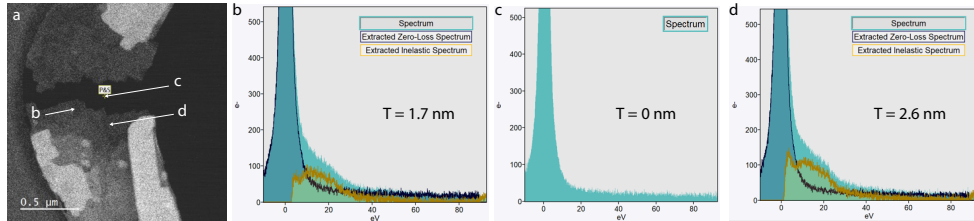
Morphology and estimation of sample thickness

The morphology of our MAPbI₃ nanosheets displays minimal thickness variation over wide micron-scale distances as shown in SFig. 3 using high angle ADF (HAADF). Note that there are small bright flakes of much greater thickness in the area, but the areas used for high resolution imaging are of relatively uniform thickness. AFM was used⁶ to determine the thickness of the thinnest layers of the ultrathin MAPbI₃, showing that the mean thickness is about 4 nm, and that the thinnest regions can be just slightly less than 4.0 nm corresponding to around three unit cells.



SFig. 4 Thickness series of SSB image simulations of MAPbI₃, increasing one unit cell at a time.

This assessment of the thickness of the thinnest regions, those that we used for high resolution imaging, being around 3 unit cells matches the results of simulating SSB images of MAPbI₃ with increasing thickness, which show contrast that matches that of the experiment at three unit cells thick or 3.8 nm thick as shown in SFig. 4. The contrast reversals, the dips that appear on the Pb-I columns in the experimental data of the thinnest regions, only appear at three unit cells thick in the simulations. Therefore this is the most likely thickness of the MAPbI₃ in our experimental STEM images. See SFig. 20 for an example of an experimental image showing contrast reversals and the surrounding discussion for further details including on how they are removed for most of the images we show.



SFig. 5 Thickness (T) measurements using electron energy loss spectroscopy (EELS). **a**, A Low magnification HAADF image. **b–d**, EELS spectra corresponding to the positions at the locations indicated in **a**.

The sample thickness was also calculated from electron energy loss spectroscopy (EELS) indicating thicknesses of approximately 1–3 nm as displayed in SFig. 5. However, we view this as less reliable due to the uncertainties in the calculation and also the likelihood that the material has thinned during the EELS measurement making these likely underestimates of the true thickness. For the EELS thickness calculations we used the theoretically estimated plasmon mean free path (MFP) and the experimentally derived relative thickness according to Egerton.⁷ The MFP for MAPbI₃ was calculated to be 88 nm using Equation 5.2 of Egerton in Digital Micrograph with our experimental convergence semi-angle of 20 mrad, collection semi-angle of 28 mrad, and 300 kV accelerating voltage. The absolute thickness of the sample was then calculated using the log-ratio method as in equation 5.1 of Egerton.

Probe current for ultra low dose work

Normally the probe current is measured on Thermo Fisher microscopes using the so-called screen current. However, the probe currents we employed for the ultra low dose work are too low to be reliably measured with this method. Therefore, we use the method of Jannis et al.⁸ for using the Timepix3 camera itself to determine the probe current. These are displayed in Table 1, alongside the probe position step size and the resulting doses for each individual scan and for the total dose used in the images for each figure.

step size (Å)	probe current (pA)	Total electron dose (e ⁻ /Å ²)	Single scan dose (e ⁻ /Å ²)	Figures
0.30	0.312	10.8	10.8	Fig. 1c–e
0.30	0.306	31.8	10.6	Fig. 2, SFigs. 10, 20, 45,
0.30	0.306	10.6, 31.8	10.6	SFigs. 22, 23, 33, 34
0.30	0.306	53.1	10.6	SFig. 38a
0.30	0.311	32.6	10.8	Fig. 3a,d,e, SFigs. 41–44, 24
0.30	0.311	97.8 [†]	10.8	Fig. 3b
0.30	sim.	100	100	Fig. 3c
0.30	0.311	32.6, 65.2	10.8	SFig. 36, 38e
0.30	0.308	32.1	10.7	Fig. 4a–c, SFigs. 47, 55a–c
0.30	0.365	100.8	12.6	Fig. 4d,e, SFigs. 55f–h, 49d
0.21	0.310	41.8	20.9	SFig. 35
0.21	0.310	104.5	20.9	Fig. 4g,h, SFigs. 53, 52
0.30	0.312	10.8, 32.5	10.8	SFig. 46
0.11	0.301	77.6	77.6	SFig. 27
0.30	0.359	24.9	12.4	SFig. 25
0.21	0.310	62.7	20.9	SFig. 49a
0.30	0.359	62.5	12.4	SFig. 26
0.30	0.304	10.6, 21.2, 31.8	10.6	SFig. 8, 48a–c
0.30	0.317	32.9	11.0	SFig. 39
0.30	0.315	32.6	10.9	SFig. 40a
0.30	0.310	32.3	10.8	SFig. 40e
0.30	0.365	12.6, 37.8	12.6	SFig. 48f–h

Table 1 probe currents, probe step sizes and the resulting electron doses for the figures in this paper. Doses with a † are equivalent doses determined by multiplying the number of unit cells over which the images are averaged by the dose of the original image.

The electrons in each probe position are calculated by dividing the number of detected events by the cluster size and then multiplying by the ratio between the electron current at the camera energy threshold of 7 keV and the actual threshold value.⁸ The energy threshold determines the energy above which hits will be counted by the detector. Hits under the threshold will be rejected by the Timepix3, and higher threshold values result in more events remaining undetected.

As we used extremely low current, which is far below the maximum current capacity of the camera, we set the threshold value to either 7 keV or 15 keV. For example, when 1×10^6 events per second are detected with a threshold of 15 keV at a 200 kV accelerating voltage, the incoming electron current is calculated by multiplying this

value by $1/3.25$, the inverse of the average cluster size, and 0.98 , the ratio between the detector electron current at 7 and 30 keV thresholds. The corresponding electron current is expressed in pA, and electron dose for the image is expressed in $\text{e}^-/\text{\AA}^2$. See Jannis et al.⁸ for further details of the methodology.

We cannot precisely determine how many electron hits occurred outside the Timepix3 detector because the HAADF detector was not calibrated, and the extrapolated line shown in Fig. 1e is for illustrative purposes only. However, we calculate that the amount of hits on the Timepix3 drops by approximately 4% when scanning on the ultrathin MAPbI₃ compared to scanning in vacuum. Since the dose calculations are effectively based on the transmitted beam detected by the Timepix3, rather than the total incident beam, this suggests the actual incident dose could be up to 1.04 times the indicated values, due to the omission of electrons scattered into the high-angle detectors in our counting.

Collection angles

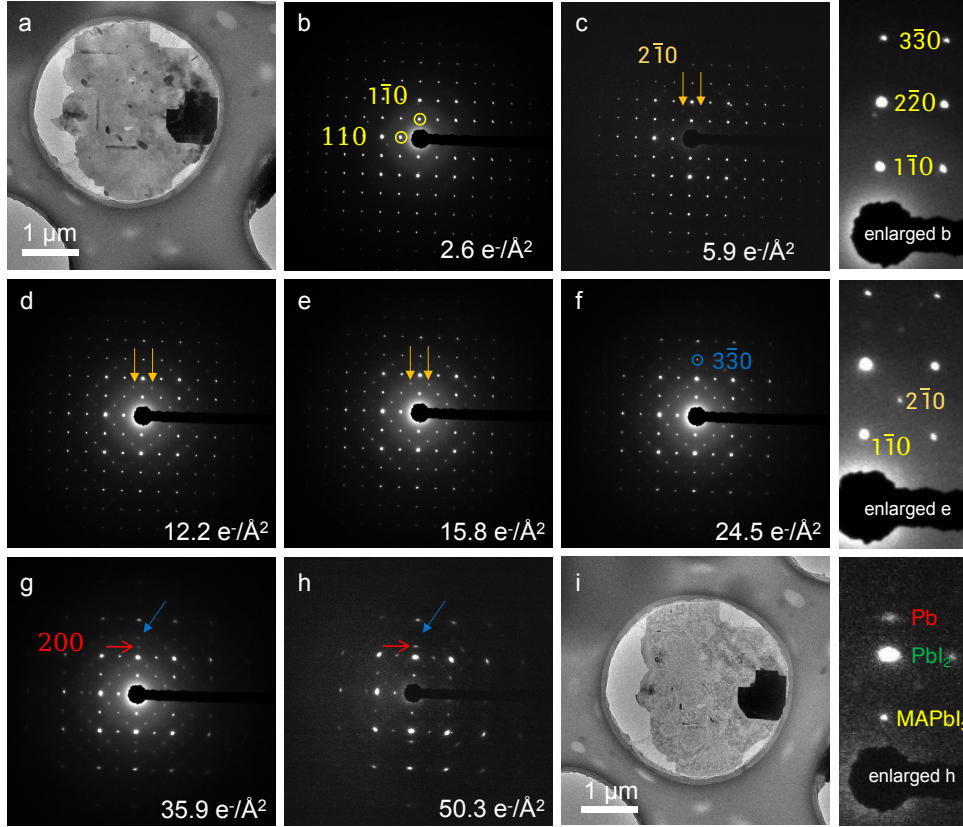
The collection angles used for each method are listed in Table S2 alongside whether or not they can be used with a focused and defocused probe configuration in which significant defocus is used to create a large illumination spot on the sample in combination with a significantly larger probe step size. Note that SSB and WDD can actually be used with defocus, but require a higher real space sampling than iterative methods such as ePIE. Note also that achieving perfect focus is very difficult at low doses, although it is easier to achieve sufficiently good focus when the depth of field is larger, as with the relatively small convergence angle used in the present work.

Method	Collection angle	Focused probe configuration	Defocused probe configuration
HAADF	44–180 mrad	✓	×
LAADF	13–44 mrad	✓	×
ePIE	0–44 mrad	✓	✓
iCOM	0–13 mrad	✓	×
WDD	0–13 mrad	✓	×
SSB	0–13 mrad	✓	×

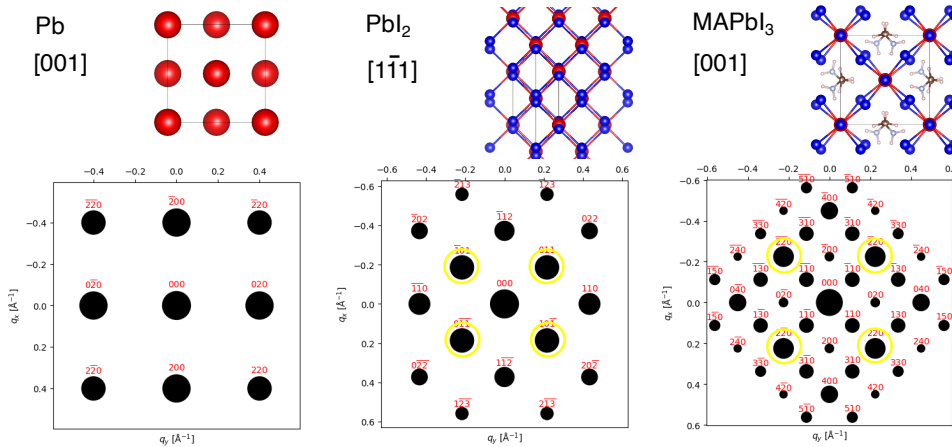
Table 2 Overview of the collection angles used for each method and the applicability of focused and defocused probe configurations.

Damage rate under conventional plane wave TEM illumination

Diffraction patterns, including those displayed in SFig. 6, were acquired at 200 kV with an electron dose rate of $0.035 \text{ e}^-/\text{\AA}^2/\text{s}$, as determined by the screen current. SFig. 7 shows models and simulated diffraction patterns for MAPbI₃, PbI₂ and Pb metal. A simulated diffraction pattern for the orthorhombic phase is shown in SFig. 8e alongside a structural model of the phase. The yellow-circled lattice planes in SFig. 6b are characteristic of the MAPbI₃ perovskite structure, specifically the Pb-I-Pb planes. Orange arrows point to locations corresponding to the (210) and $(2\bar{1}0)$ planes in the orthorhombic perovskite phase. Initially there are no such orthorhombic spots but as the irradiation surpasses $5.9 \text{ e}^-/\text{\AA}^2$, two distinct diffraction spots emerge and become clearer with increasing dose. At $24.5 \text{ e}^-/\text{\AA}^2$ however, the high-frequency diffraction spots, such as the $(3\bar{3}0)$ plane, begin to fade and by $50.3 \text{ e}^-/\text{\AA}^2$, the $(3\bar{3}0)$ spot disappears (SFig. 6h), indicating degradation of the perovskite structure. At this point, the intensity of the $(1\bar{1}0)$ plane associated with the perovskite has significantly decreased compared to the initial SAED pattern (SFig. 6b). Meanwhile, the diffraction spot originally assigned to the $(2\bar{2}0)$ plane of the perovskite reaches its maximum intensity. This is attributed to the fact that most of the perovskite has transformed into PbI₂, and the (011) plane of PbI₂ has a similar d-spacing to that of the perovskite $(2\bar{2}0)$ plane, suggesting that the observed diffraction intensity at this position is predominantly due to PbI₂.



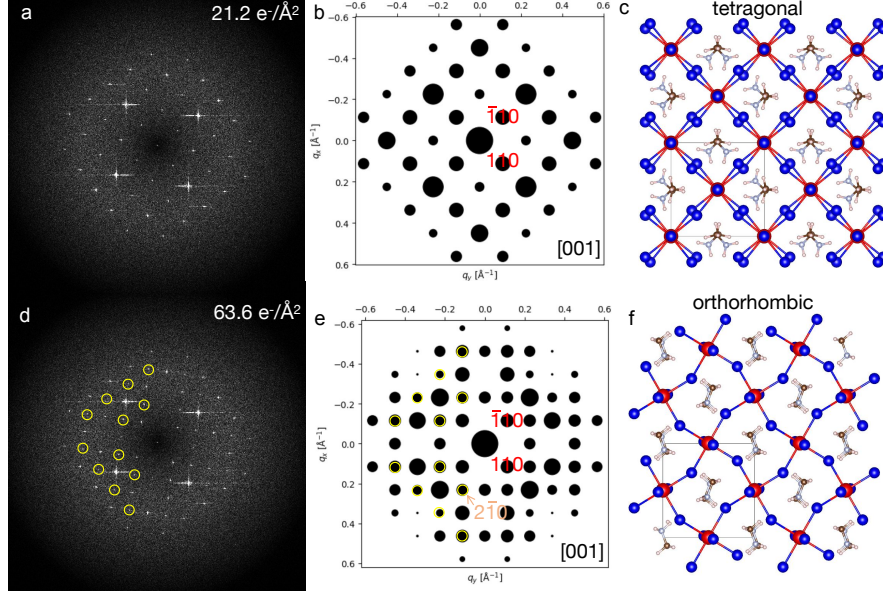
SFig. 6 Electron diffraction pattern evolution of MAPbI₃ using a parallel electron beam. **a**, Low-magnification morphology before damage, displaying relatively uniform contrast. **b–h**, The MAPbI₃ spots first display a transition to the orthorhombic phase and then gradually fade with increasing electron dose as PbI₂ and Pb metal spots become increasingly prevalent. The orange arrows highlight the (210) and (2 $\bar{1}$ 0) planes in the orthorhombic perovskite phase. Blue arrows denote the (330) planes in both tetragonal and orthorhombic perovskite phases. Red arrows denote the (200) planes in cubic phase of Pb metal. **i**, Low-magnification morphology after damage, showing uneven thickness and fragmentation into smaller particles.



SFig. 7 Simulated diffraction patterns for [001] Pb metal, [1 $\bar{1}$ 1] PbI₂, and [001] MAPbI₃. Note that the PbI₂ and MAPbI₃ share many of the same spacings, and we highlight some of these in yellow.

Notably, at a dose of $35.9 \text{ e}^-/\text{\AA}^2$, an additional diffraction spot appears (indicated by a red arrow), which corresponds to the (200) planes of Pb metal based on d-spacing comparisons (experimental value: $2.5 \text{ \AA}$, standard value: $2.495 \text{ \AA}$ for cubic Pb, Fm-3m, 225). By the time the dose reaches $50 \text{ e}^-/\text{\AA}^2$, the intensity of this new diffraction spot

has increased, indicating a progressive formation of Pb crystals as structural damage worsens. However, its intensity remains significantly lower than that of the PbI_2 (011) planes, which have a larger d-spacing. This suggests that PbI_2 is the dominant product of degradation, with the formation of a small amount of metallic Pb as a secondary phase.

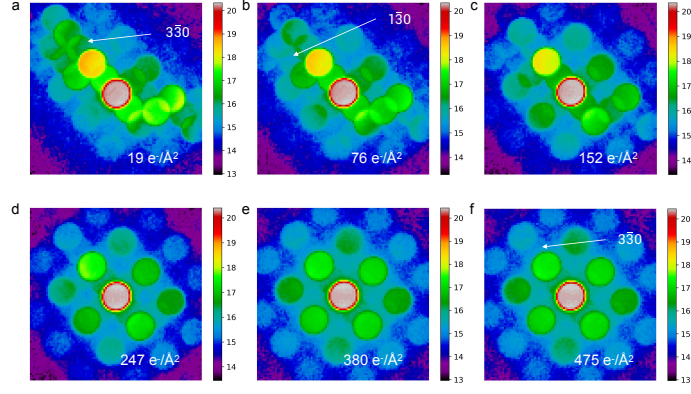


SFig. 8 Phase transition from tetragonal to orthorhombic. **a**, The power spectrum of an experimental SSB image before phase transition (accumulated dose: $21.2 \text{ e}^-/\text{\AA}^2$). **b**, Simulated diffraction in the $[001]$ zone axis of the tetragonal phase. **c**, Tetragonal structure model in the $[001]$ zone axis. **d**, The power spectrum of an experimental SSB image after the phase transition using data collected from 42.4 to $63.6 \text{ e}^-/\text{\AA}^2$. The yellow circles highlight newly emerging spots that do not belong to the tetragonal phase but rather to the orthorhombic phase. These spots are fully consistent with the simulated diffraction pattern of the orthorhombic phase along the $[001]$ zone axis. **e**, **f**, Orthorhombic structure model in the $[001]$ zone axis.

Damage rate with a convergent scanned probe

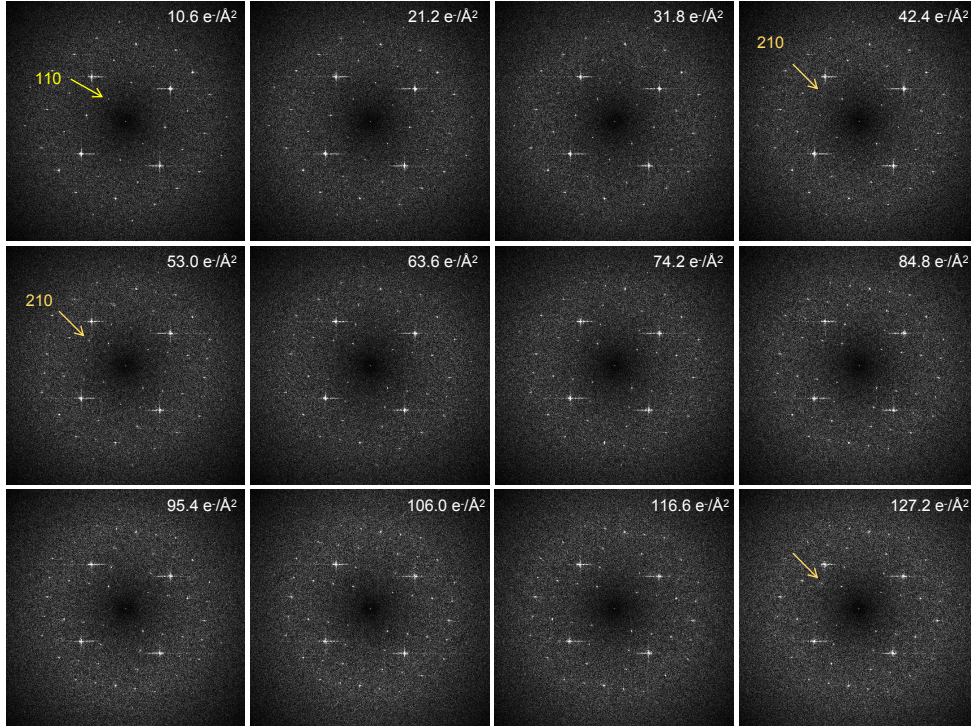
Position averaged convergent beam electron diffraction (PACBED) data of our MAPbI_3 is shown in SFig. 9 as a function of dose, using a small one mrad convergence angle and a short dwell time of $1 \mu\text{s}$. Significant damage to the $(3\bar{3}0)$ plane becomes evident after $475 \text{ e}^-/\text{\AA}^2$, whereas the same planes disappeared after less than $50 \text{ e}^-/\text{\AA}^2$ with plane wave illumination, almost 10 times faster than in STEM. Similarly, the $(1\bar{3}0)$ plane disappears after approximately $152 \text{ e}^-/\text{\AA}^2$ in the PACBED, but only withstood $35.9 \text{ e}^-/\text{\AA}^2$ using plane wave illumination. This shows the material can survive a remarkably higher amount of electron irradiation when using a scanned convergent beam than with plane wave illumination.

SFig. 10 displays power spectra from SSB ptychography data of the MAPbI_3 recorded with a 13 mrad convergence angle. The much larger, but still moderate, convergence angle does not appear to significantly affect the rate of damage, with the $(1\bar{3}0)$ plane disappearing after $144.9 \text{ e}^-/\text{\AA}^2$, consistent with the PACBED results. The first evidence of the presence of the orthorhombic phase appearing in the STEM data is the appearance of spots corresponding to the (210) planes of this phase. Note that the (210) spots are relatively weak and are not visible in the 1 mrad PACBED data over the stronger disks surrounding their location. However in the power spectra shown in SFig. 10 these spots appear between 42.4 and $53.0 \text{ e}^-/\text{\AA}^2$ with them clearly visible in the $53.0 \text{ e}^-/\text{\AA}^2$ power spectrum as highlighted in the figure. The orthorhombic



SFig. 9 Scanning electron diffraction pattern evolution of MAPbI₃ using a convergent beam (1 mrad). The PACBED were acquired under the following conditions: voltage: 200 kV; convergence angle: 1 mrad; probe current: 1.6 pA; dwell time: 1 μ s; step size: 0.42 $\text{\AA}$ by 0.42 $\text{\AA}$. The electron dose was measured by the direct detection Timepix3 camera.

spots are highlighted and related to the differences in structure and diffraction patterns in the two phases in SFig. 8. Generally the orthorhombic spots strengthen with additional dose, however no orthorhombic spots are visible in the 31.8 $\text{e}^-/\text{\AA}^2$ power spectrum, indicating that no significant transition from the tetragonal to orthorhombic phase has occurred within the first 31.8 $\text{e}^-/\text{\AA}^2$. Again we see that using a fast scanned probe, the sample can withstand a much higher dose compared to using a parallel electron beam.



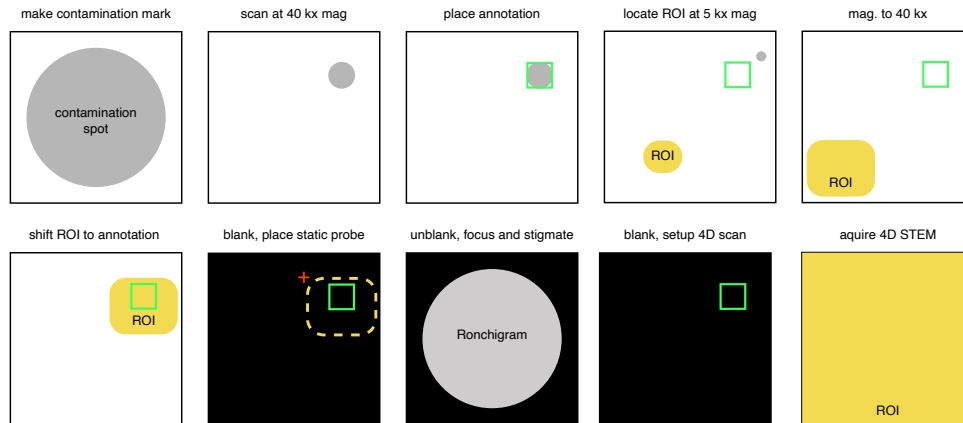
SFig. 10 Power spectra evolution of SSB phase images of MAPbI₃ as a function of dose in the dose fractionated data used for Fig. 2 of the main paper. Note the appearance of the (210) spots of the orthorhombic phase between 42 and 53 $\text{e}^-/\text{\AA}^2$. The (110) spot shared by both the tetragonal and orthorhombic structures is also highlighted to distinguish it from the (210) spots. The 4D-STEM data was acquired using the following conditions: voltage: 200 kV; convergence angle: 13 mrad; probe current: 0.306 pA; dwell time: 0.5 μ s; step size: 0.3 $\text{\AA}$ by 0.3 $\text{\AA}$. The electron dose was measured by the Timepix3 camera. The power spectra are cropped to show the relevant regions.

Data acquisition protocol for dose minimisation

To locate regions of interest in the specimen and focus the beam, we used low magnifications as much as possible with a low probe current. The specific experimental protocol is illustrated in schematic form in SFig. 11 and proceeds as follows:

1. Marker creation: We began by selecting a sacrificial area outside the region of interest (ROI) at low magnification. The probe is placed in the sacrificial area and left stationary to intentionally deposit carbon contamination, thereby forming a visible mark. The magnification is then set to 40 kx, and the location of the contaminated area in the 40 kx field of view recorded as an on-screen annotation.
2. Locating the ROI: At low magnification, typically about 5 kx, we scan rapidly to find areas of interest. Once a specific ROI is located, the magnification is increased back to 40 kx, and the region is shifted under the annotation. We then blank the beam to prevent this region of interest from being exposed before data acquisition.
3. Focus and astigmatism: The scan is stopped and the static probe is moved out of the region of interest. The beam is unblanked and the focus and astigmatism are adjusted according to the Ronchigram. After these adjustments, the electron beam is again blanked in preparation for 4D data acquisition.
4. 4D data acquisition: 4D-STEM parameters are set, and data acquisition begins immediately after the beam is unblanked in the region of interest.
5. Post-imaging adjustments: Degraded areas are used to refine focus and astigmatism briefly for additional imaging of other regions.
6. Imaging of subsequent regions: Adjacent areas are imaged with minimal adjustments, avoiding low magnification scanning.

This protocol minimizes electron exposure during alignment, keeping pre-imaging exposure to about $0.1 \text{ e}^-/\text{\AA}^2$.



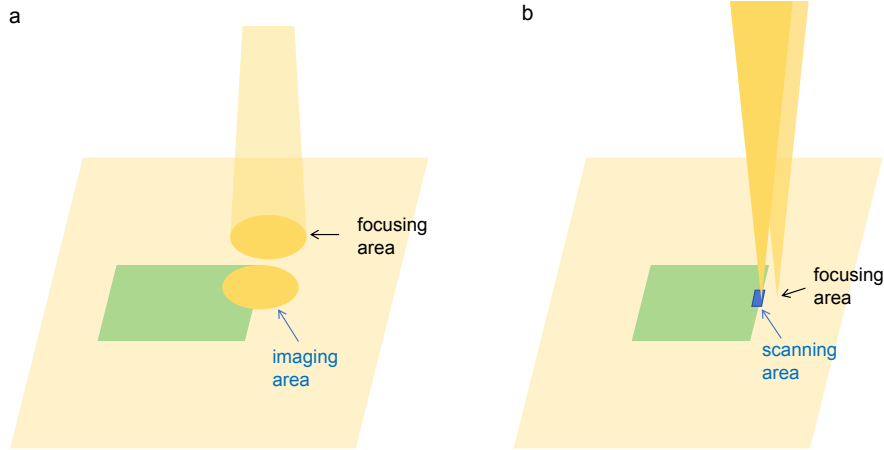
SFig. 11 Schematic of the pre-imaging protocol used for the present work that allows accurate zooming into the region of interest (ROI) by accounting for inaccurate magnification centring of the scan system. Final focusing is performed using the Ronchigram with a static probe close to the region of interest to be as near as possible to the ROI height while avoiding irradiation of the ROI before imaging. Beam blanking is used to avoid ROI exposure pre-imaging whenever possible.

Discussion of MAPbI₃ dose tolerance in STEM and TEM

As we showed using the data above, our MAPbI₃ remains stable up to $32 \text{ e}^-/\text{\AA}^2$ in STEM, with the first sign of the transition to orthorhombic appearing above that dose, whereas the transition occurs at $6 \text{ e}^-/\text{\AA}^2$ in plane wave TEM. Our room temperature TEM result matches those of Song et al.⁹ who also showed MAPbI₃ degrading by $6 \text{ e}^-/\text{\AA}^2$. Even under cryogenic conditions ($-175 \text{ }^\circ\text{C}$), Li et al.¹⁰ report a critical dose of only $12 \text{ e}^-/\text{\AA}^2$. No other reports have however seen such an improvement, even if minor, in critical dose with the use of cryogenic cooling, with cooling even reportedly accelerating damage.^{11,12}

Therefore, using a rapidly scanned focused STEM probe presents a substantial advantage in terms of the additional dose that can be applied before damage occurs in MAPbI₃. It appears the material can withstand five times the dose in STEM than TEM in room temperature experiments before damaging. Even if we take the most optimistic cryogenic TEM critical dose, room temperature STEM still allows a factor of three higher dose.

Practically the pre-imaging procedure we apply in STEM is also easier to avoid exposing the sample to the beam before imaging than in TEM due to the smaller area exposed with the STEM probe compared to plane wave TEM as illustrated in SFig. 12. To address the issue of determining the correct focus for the sample in TEM, the pre-imaging protocol involves determining the focus at positions sufficiently far from the sample that the broad TEM beam does not impinge on the area of interest. This is more prone to focus error due to changes in the sample height than tuning closer to the region of interest as is possible with the fine STEM probe.



SFig. 12 Pre-imaging protocols in HRTEM **a** and STEM **b** illustrating the greater distance required from the area of interest in TEM compared to STEM to avoid irradiating the imaging area before imaging begins.

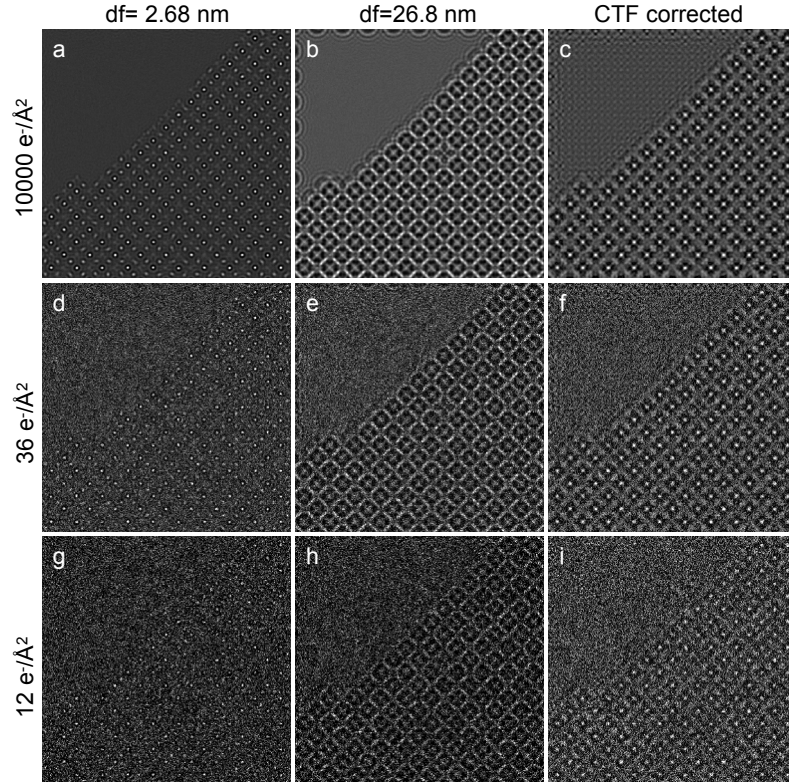
However, the most significant improvement in dose tolerance gained from working in STEM compared to plane wave TEM seems most likely related to the way in which the electron dose is imparted to each point in the sample over a very short time during each scan, and allowed significant time before being irradiated again in subsequent scans.

Velazco et al.¹³ and Jannis et al.¹⁴ have studied the effect of scan speed and non-standard scans in STEM, and formulated a damage model based on a generalised diffusion constant and a threshold for damage. The model includes the concept of both damage which only occurs during the scan and that which can occur after the scan. Their model predicts significantly reduced damage using multiple faster scans with shorter dwell times, interlaced scans or both when the diffusion constant is high enough with a sufficiently high threshold, assuming that the damage occurs primarily

during the scan rather than afterwards. If damage continues long after the scan then a single slower scan with a more continuous build up of signal from each probe position would instead cause less damage because of the damage that would continue between the subsequent scans of the probe positions. Also, if the diffusion constant is not high enough then using multiple faster scans could actually increase the damage compared to a single slower scan.

For the beam sensitive zeolite sample Velazco et al.¹³ and Jannis et al.¹⁴ used in their experiments, the model matched the observed damage behaviour with a high diffusion constant and a relatively high threshold. Diffusion has been identified as a major cause of degradation in perovskites such MAPbI₃.^{15,16} It would therefore make sense that a high diffusion constant can also be applied in the model of Jannis et al. for MAPbI₃.

If we assume a similarly high threshold for MAPbI₃ as the zeolite in Jannis et al., and also that the damage occurs primarily during the scan as with the zeolite, then the model predicts that multiple faster scans help reduce the damage rate. This could then explain the fact that the MAPbI₃ is more resilient under rapid scanned STEM than plane wave TEM illumination. Plane wave TEM continuously irradiates the sample and therefore can be considered the opposite of rapid scanned STEM in which a given point in the sample is only illuminated for a short time followed by a much longer period without significant irradiation. The benefit of multiple scans also increases if damage can heal after exposure as suggested by Velazco et al.¹⁴ and Mkhoyan et al.¹⁷ The observation of significantly greater dose resilience in STEM than TEM for MAPbI₃ suggests ptychography can potentially has significant potential for improving low-dose imaging of other beam sensitive materials, especially the types for which rapid scanning can help as predicted in the damage model of Jannis et al.



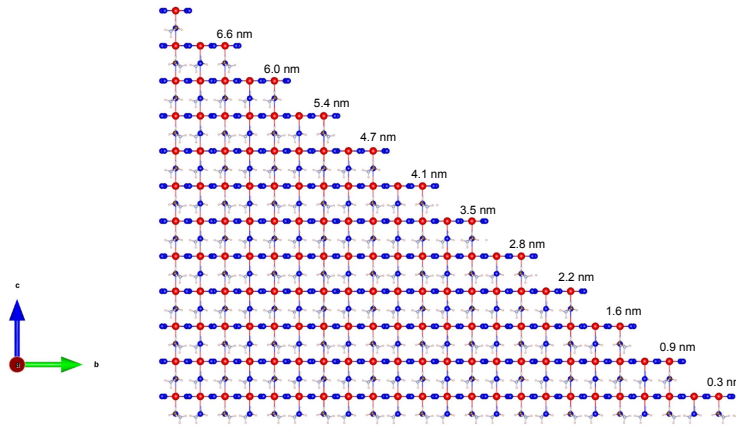
SFig. 13 HRTEM simulations of the edge. **a, d, g**, HRTEM images simulated at different electron doses with a spherical aberration coefficient (Cs) of 2 μm and at Scherzer defocus; **b, e, h**, HRTEM images simulated at ten times the Scherzer defocus under the same Cs and dose conditions; **c, f, i**, CTF-corrected (phase-flipped) images corresponding to **b, e, h**, respectively. Simulation parameters: voltage = 200 kV; focal spread = 1 nm; Cs = 2 μm .

Discussion of MAPbI₃ contrast in TEM

In addition to TEM having a higher damage rate for halide perovskites, the complex contrast transfer of high resolution TEM imaging imposes significant challenges for interpretation. SFig. 13 displays TEM images simulated using Scherzer defocus and a defocus ten times larger at several doses using the model of an edge of MAPbI₃ shown in SFig. 28.

Under Scherzer defocus (2.68 nm in these simulations) and with sufficiently thin samples, the image contrast is approximately proportional to the projected potential, making interpretation possible. However, at low doses the relatively weak contrast using Scherzer conditions makes it difficult to see the structure clearly as seen in the 36 and 12 e⁻/Å² images in SFig. 13. At 36 e⁻/Å² the heavy Pb-I sites are generally readily visible, but the other sites are more difficult to discern. Decreasing the dose to 12 e⁻/Å² makes discerning the lattice considerably more difficult, with the MA and I sites particularly difficult to detect. Increasing the defocus can improve image contrast substantially, but at the expense of interpretability due to contrast delocalization. Indeed, as seen in the figure, increasing the defocus by a factor of ten to 26.8 nm greatly improves the amount of contrast, but the image no longer shows the lattice correctly in terms of bright spots being able to be interpreted as the location of atomic or molecular columns.

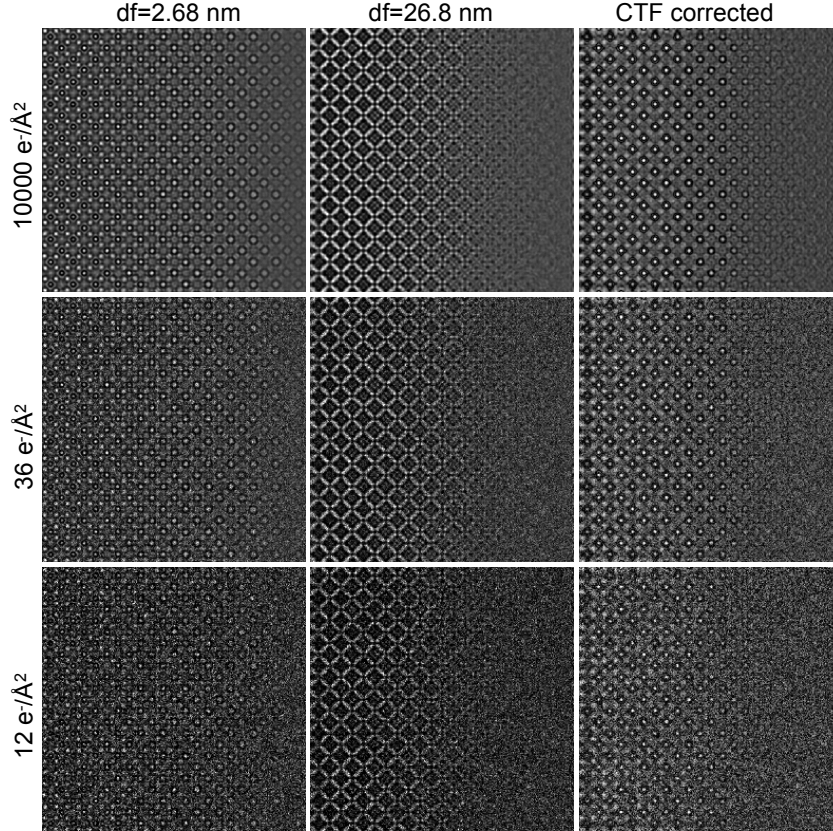
In low dose TEM, focusing is usually performed a significant distance away from the region of interest to avoid irradiating it during focusing with the broad beam. This is often hundreds of nanometers away. As a result, it can be difficult to accurately determine the actual defocus value used during acquisition, and deviations of tens to hundreds of nanometers from the intended defocus are common. The probability of acquiring images exactly at Scherzer defocus is extremely low. This can be problematic because TEM contrast is highly sensitive to defocus, again frustrating interpretation. Although post-acquisition contrast transfer function (CTF) correction can partially compensate for oscillations in the CTF created by defocus, and low-order aberrations such as astigmatism, it depends on accurate defocus estimation, which is notoriously difficult to achieve in practice. Even with precise defocus values, the presence of zero-crossings in the CTF causes irreversible information loss. At large defocus values, contrast delocalization makes defect identification in the material particularly challenging as can be seen in SFig. 13. For instance, the terminating I vacancies that are visible under Scherzer defocus (SFig. 13a) become indistinguishable in the CTF corrected image in SFig. 13c. Furthermore, changes in thickness can also introduce complex contrast changes in TEM images, as illustrated with the simulations in SFig. 15 using the wedge shaped model shown in SFig. 14.



SFig. 14 Projection of the wedge-shape model along the side b-axis direction, revealing the thickness of each atomic column layer within the wedge.

High-resolution phase information can also be obtained from TEM using advanced exit wave reconstruction techniques.^{18,19} For example, by acquiring a focal series of TEM images at sufficiently low electron doses to avoid damaging the sample,²⁰ this method can achieve resolutions down to 1 Å at 50 e⁻/Å²,^{21,22} even without the need for precise control of the focus.²¹ However, the method assumes the structure does not change during the course of the focal series. This makes it unsuitable for imaging rapidly changing regions such as the unstable edges and defects we study here where the critical dose for TEM is an order of magnitude lower. Furthermore, the need for a focal series rules out capturing structural evolution that occurs during the acquisition of the series.

In contrast, fast 4D-STEM ptychography enables phase reconstruction from individual ultra-low-dose scans without the need for a focal series and is therefore more capable of revealing dose-dependent dynamic structural changes. In addition, ptychography offers a much flatter transfer function than individual TEM images. Although contrast reversals can occur, these can be corrected using methods such as the phase offset method we discuss elsewhere or avoided with multislice ptychography.

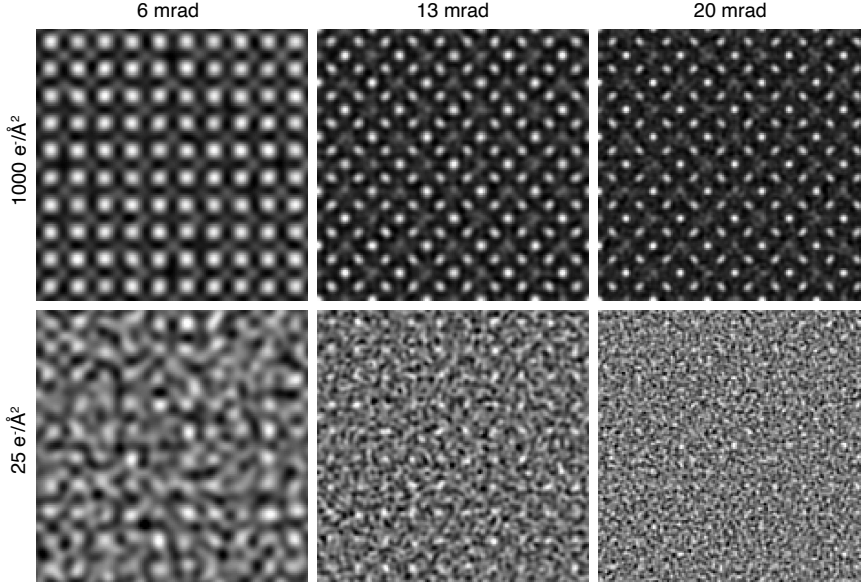


SFig. 15 HRTEM simulations of the wedge-shaped model shown in SFig. 14 with a voltage of 200 kV, a focal spread of 1 nm and a spherical aberration coefficient (C_s) of $C_s = 2 \mu\text{m}$. The Scherzer defocus is 2.68 nm.

Selection of probe convergence angle

The probe convergence angle determines the strength at which spatial frequencies are transferred in STEM imaging. Generally speaking, increasing the convergence angle will pass more higher spatial frequency information. However, in STEM phase methods such as ptychography, the strength of transfer drops off at lower spatial frequencies beginning at a frequency slightly lower than that corresponding to the convergence angle.²³ Thus, for ptychography the transfer of low spatial frequencies

decreases as the convergence angle increases, and a balance must be struck between passing high frequencies and retaining sufficiently strong pass of lower frequencies. In other words, particularly for low dose work where efficient transfer is most important, one desires to choose a convergence angle that optimally balances the weighting of the frequencies of interest in the material being studied. Note that although the use of superresolution can extend the transfer to higher frequencies, its ability to do so is limited by the amount of scattering outside the direct beam formed by the convergence angle. At very low doses relatively few electrons fall outside the direct beam, restricting superresolution, although using all available electron hits likely still helps the overall signal.



SFig. 16 Comparison of SSB images using different convergence angles illustrating the tradeoff between transfer of higher spatial frequencies and the overall strength of the lattice signal.

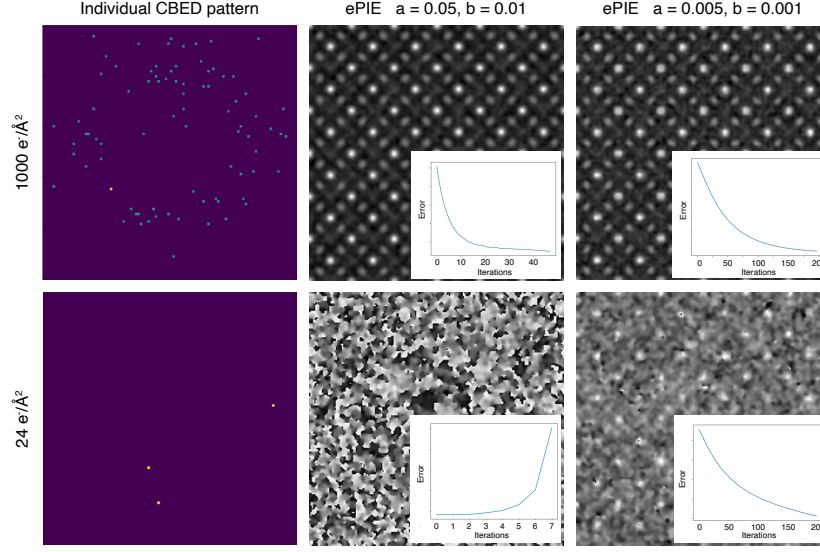
SFig. 16 shows a comparison of imaging different convergence angles used with simulated SSB ptychography of MAPbI₃ at doses from 25 e⁻/Å² to 1000 e⁻/Å². While at higher doses the higher convergence angle reveals finer structural details, at low doses the figure shows how using a smaller convergence angle can be beneficial at low doses for revealing the structure above the noise. We choose 13 mrad as it provides a good compromise between low dose sensitivity and resolution, maximizing the weighting of the frequencies of interest in the material.

Convergence of iterative ptychography at ultra low doses

In iterative ptychography it can be critical to choose appropriate convergence step size parameters. Such is the case with low dose work, and especially when the number of hits per diffraction pattern is very low. Choosing parameters that converge data with such sparse diffraction patterns can be very difficult. While using relatively large convergence step sizes can converge iterative ptychography faster when the signal is strong enough, using too large a convergence step size for lower dose data can cause it to either diverge or converge to an incorrect image. There is no guarantee of correct convergence in iterative ptychography. As the dose becomes lower one must generally reduce the step size and use more iterations.

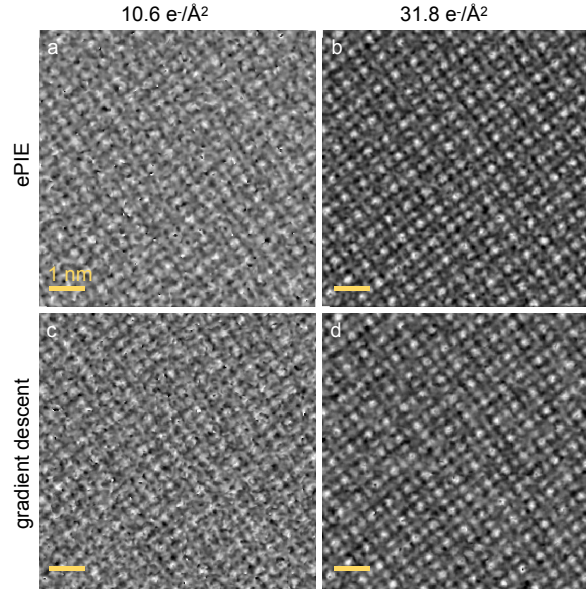
We illustrate this in SFig. 17 where we compare ePIE convergence with relatively sparse and very sparse CBED patterns using aberration free simulated data with 4 nm thick MAPbI₃ and microscope parameters matching our experiments. Here we refer

to the ePIE object update step size parameter as a and the probe update parameter as b .



SFig. 17 Comparison of ePIE convergence with relatively sparse and very sparse CBED patterns using aberration free simulated data of 3 unit cell thick MAPbI₃ and microscope parameters matching our experiments. Note that one pixel in the 1000 e⁻/Å² CBED pattern displayed contains two hits, making it appear orange, with the single hits as blue. In the Lower dose CBED pattern displayed, all hits are single hits.

With the higher hits per diffraction pattern in the 1000 e⁻/Å² dataset ePIE converges well with less than 50 iterations using the larger $a = 0.05$ and $b = 0.01$ parameters, producing a slightly better converged result than after 200 iterations using a factor of ten smaller a and b parameters. However in the 24 e⁻/Å² scan there are far fewer hits per diffraction pattern, and ePIE diverges with the larger step size parameters, requiring the smaller $a = 0.005$ and $b = 0.001$ to produce a meaningful image.

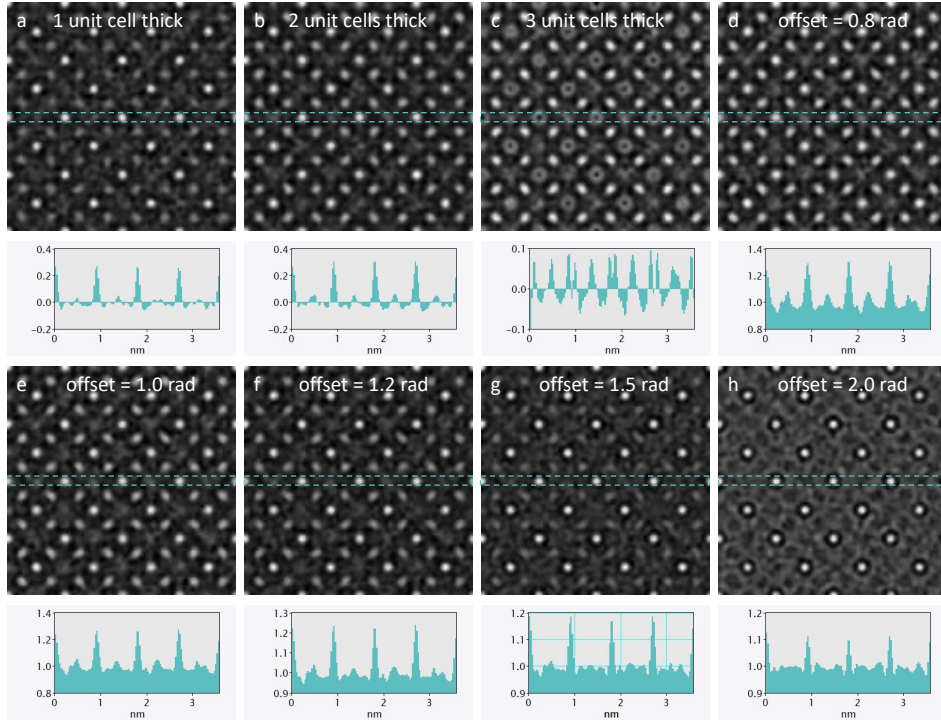


SFig. 18 Comparison of phase reconstructions obtained via ePIE and gradient-descent algorithms. **a, b**, The phase images retrieved using ePIE at doses of 10.6 e⁻/Å² and 31.8 e⁻/Å², respectively. **c, d**, The phase images reconstructed using the gradient-descent algorithm in py4DSTEM.

SFig. 18 compares the results of ePIE to those of the stochastic gradient descent (GD) method implemented in py4DSTEM²⁴ at $10.6 \text{ e}^-/\text{\AA}^2$ and $31.8 \text{ e}^-/\text{\AA}^2$. The py4DSTEM GD method is essentially a batch version of rPIE,²⁵ and bears significant resemblance to the least-squares approach²⁶ of Odstrcil et al. Although initial testing of py4DSTEM's GD implementation did not converge at the lowest doses, we later found, potentially after an update of the package, that we could achieve convergence at these doses using a gradient-descent step-size of 0.5. The ePIE images in the figure use the same $a = 0.005$ and $b = 0.001$ parameters mentioned previously and used elsewhere. As can be seen the two methods produce very similar results.

Contrast reversals and their counteraction

Contrast reversals in atomic resolution electron ptychography were first reported by Yang et al.²⁷ on the heavier Ga sites of GaN. The noise-free simulations accompanying their experiments showed that the image phase could reverse sign at the centre of the heavier Ga sites as they increased the thickness, forming donut shaped columns. Such contrast reversals have subsequently been observed in other materials in both experiments and simulations and have been the subject of multiple publications. Gao et al.⁵ explored the effect of defocus, both applied to the probe physically before the data were collected and post-collection using the ability of ptychography to introduce aberrations after taking the data. Post-collection defocus could remove the reversals, but it was found that central focusing in thicker materials was generally best. The effectiveness of central focusing for thicker samples was confirmed by Clark et al.,²⁸ who also pointed out that these reversals also occur in iCoM and iterative ptychography as well as direct methods of ptychography.



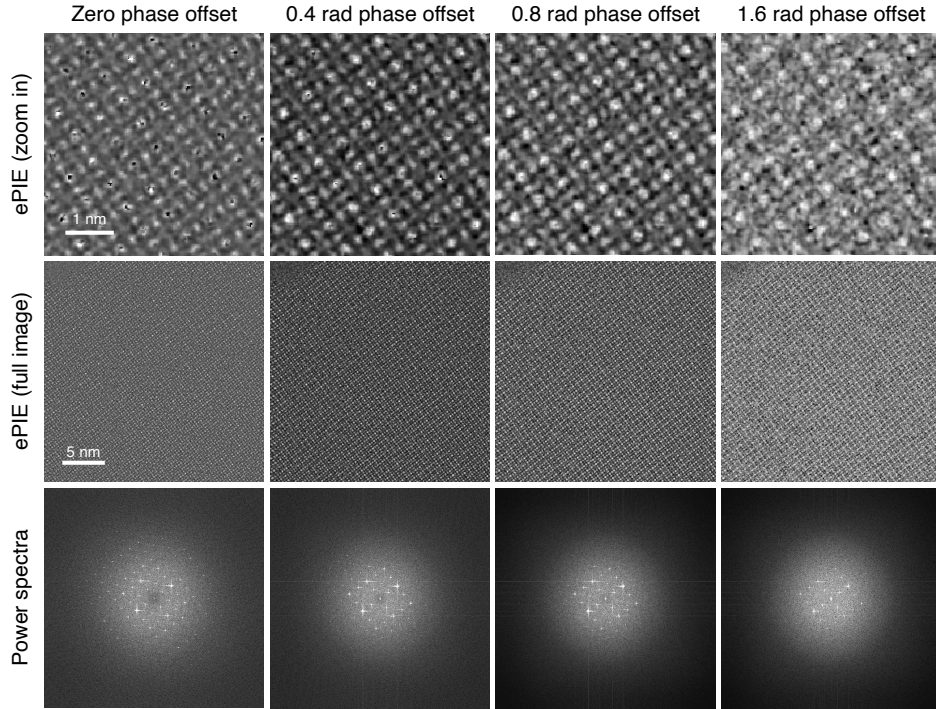
SFig. 19 Phase offset selection for counteracting contrast reversals. **a–c**, SSB images simulated with MAPbI₃ that is 1 unit cell (1.26 nm), 2 unit cells (2.52 nm), and 3 unit cells (3.78 nm) thick. **d–h**, Phase images obtained by setting different offsets for the 3 unit cell thick data. Line profiles are displayed taken from the region within the dashed lines on each image. Note the range of the phase is much lower than 2π radians.

Clark et al. found that the donut like contrast reversals can also appear in extremely thin materials, in both direct and iterative ptychography. Similar effects were reported

by Hofer et al.²⁹ for ultrathin MAPbI₃. For such materials central focusing cannot help with the entire sample essentially in focus at the same time, and the optical sectioning effect also means that focusing away from a material reduces the contrast in direct ptychography. Hofer et al. showed that such reversals also occur with a defocused probe configuration in iterative ptychography of ultrathin MAPbI₃, suggesting this is an issue for single slice ptychography generally.

We developed the phase offset method of contrast reversal correction²⁹ to address circumstances in which central focusing is either undesirable or will not help, as with ultrathin materials. The method works by adjusting the offset between the zero frequency phase and the phase of all the other frequencies by a uniform phase offset. This has been found to work reliably for both thick and thin materials using both iterative and direct methods of ptychography.²⁹

SFig. 19 shows the application of various phase offsets to simulated SSB imaging of 3 unit cell (3.78 nm) thick MAPbI₃. Note that the range of phase values remains much smaller than 2π and therefore conventional phase unwrapping will not help. While a poor choice of offset can produce images that are much harder to interpret, an appropriate value produces images that provide probe shaped atoms, as one is used to expecting from atomic resolution STEM. We selected an offset of 0.8 rad for the ptychography images displayed in this paper as it eliminates the contrast reversals in the noise-free simulations while retaining strong contrast on all sites.



SFig. 20 Application of various phase offsets to experimental ePIE images. The power spectra are taken from the full images rather than the cropped versions displayed in the first row images.

SFig. 20 shows that an 0.8 rad offset also provides a good compromise between removal of the dips due to the contrast reversals and retention of contrast for our experimental low dose imaging using ePIE. Larger offsets begin to reduce the contrast of both MA and I sites. Note that the power spectra of the 0.8 rad phase offset ePIE image shows spots out to 1.1 Å, consistent with the LAADF showing spots out to 1.2 Å.

As the contrast reversals here only occur on the heavy Pb-I columns, which are also easily identified in the LAADF images, the dips on the Pb-I columns do not significantly affect our ability to identify the structures in our images. However, we have

nonetheless applied our phase offset method to the images as we believe this makes them easier to understand.

Event driven 4D-STEM with Timepix3

With fast scans at low probe currents, very few hits occur on a 4D-STEM camera at each probe position, forming very sparse diffraction patterns. Most cameras are framing cameras, which read out the entire pixel array for each image regardless of if they contain a hit. For sparse diffraction patterns, this transfers a large amount of data describing pixels with zero hits, consuming valuable bandwidth for zero gain in information. An event driven camera substantially reduces the bandwidth required to read out sparse diffraction patterns by only recording the hits, allowing one to greatly accelerate the readout speed and therefore the scan speed.

Here we used the Timepix3 as described in detail in our previous work, Jannis et al.⁸ As shown there, we can collect data at 100 ns dwell times, with the camera recording events timed in ns with a practical time resolution of around 20 ns. We choose 500 ns dwell time scans for our present work as they are already sufficiently fast, and faster scans would be more likely to incur issues with the scan coils.

4D-STEM cameras such as the Medipix3 and EMPAD, offer standard frame rates of only a few thousand Hz translating into dwell times of hundreds of μ s. This is put in perspective by considering that to achieve a 500 ns dwell time scan with a framing camera would require two million frames per second. O’Leary et al. were able to reach a dwell time of 80 μ s using the extremely limited dynamic range of the 1 bit mode of a Medipix3,³⁰ but this is 160 times slower than our 500 ns dwell time. Fortunately, framing cameras have been increasing in speed with Dectris recently releasing their Arina³¹ camera which can reach 120 kHz or 8.3 μ s dwell times. This is indeed very welcome, especially with its larger current capacity compared to the Timepix3. However, this is still about 17 times slower than our 500 ns dwell times. It is also worth noting that for 2D scan the scan time goes as the square of the dwell time, with doubling the dwell time resulting in a scan taking four times as long. In the future, Timepix4 should simplify the use of event driven data at higher probe currents.

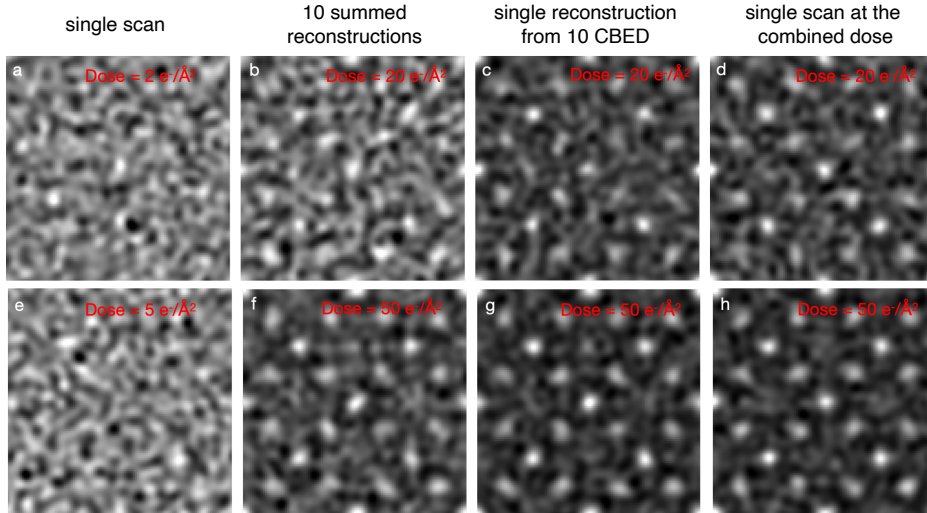
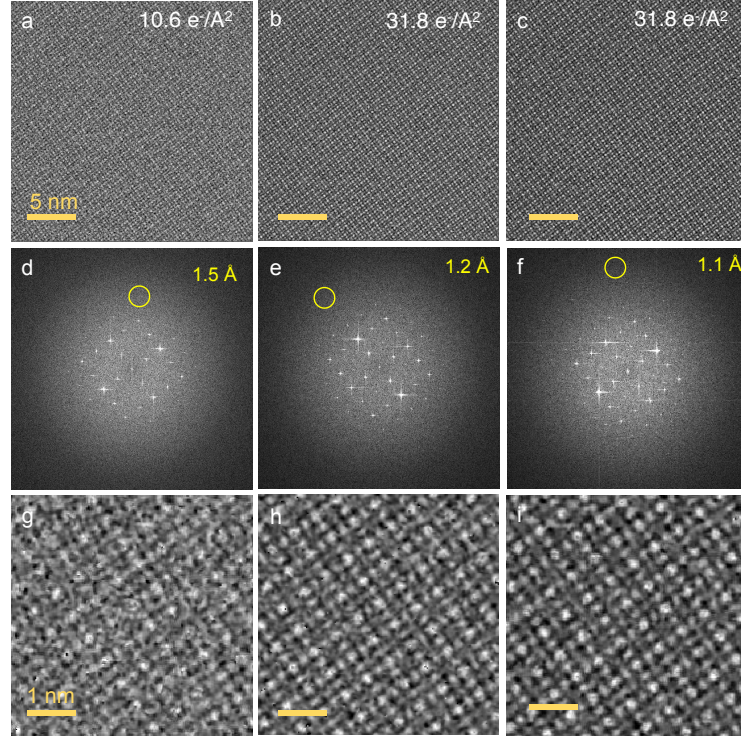


Fig. 21 Comparison of summing individual SSB reconstructions and performing a single SSB reconstruction from the aligned CBED using data simulated at $2 \text{ e}^-/\text{\AA}^2$ and $5 \text{ e}^-/\text{\AA}^2$. **a, e**, Individual SSB reconstructions. **b, f**, Summing 10 aligned SSB images, one for each simulated scan. **c, g**, Summing instead the CBED of the 10 simulated scans and performing a single SSB reconstruction for each dose fractionated dataset. **d, h**, SSB reconstructions using a single scan at the same dose as the accumulated dose of the dose fractionated scans. The simulated scans are drift free, simply using different Poisson statistical distributions of hits matching the required doses.

Dose fractionated imaging and drift correction

In addition to slowing damage in perovskites, the speed of our scans also enables us to utilise dose fractionation in a similar manner to TEM.³² Acquiring a series of very rapidly scanned images allows one to observe the dynamics of the sample with finer temporal resolution than is possible with slower scans. This allows us to build up the signal over multiple scans and align them after applying drift correction. Because we can see when damage occurs, we can build up signal up until the point at which damage sets in, maximizing the signal in images of the undamaged material and also of the material in its subsequent transformed states.

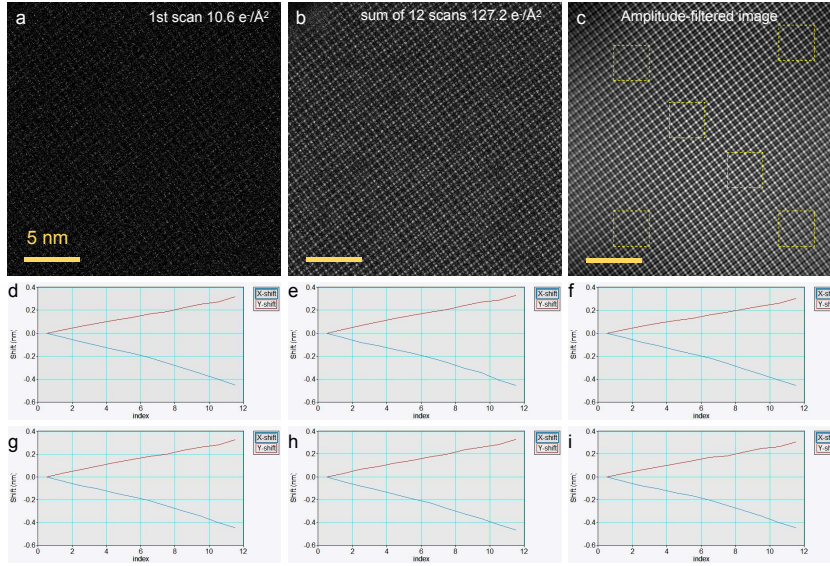
Drift correction of rapidly scanned images is a commonly performed operation in conventional STEM imaging, however for 4D-STEM based reconstructions such as ptychography one can choose to either sum the individual images from each scan or instead sum the drift corrected CBED and then perform the ptychographic reconstructions from this combined higher signal 4D-STEM dataset. We compared these two routes and found that performing the ptychographic reconstructions on the combined drift corrected CBED produces better results.



SFig. 22 Comparison between two different alignment approaches for ePIE. **a**, Single phase image retrieved from a single experimental scan. **b**, Sum of three reconstructed and well-aligned phase images. **c**, The retrieved phase image from instead summing the 4D dataset from these same three scans and then performing a single reconstruction. **d–f**, The corresponding power spectra, cropped to clearly display the Bragg spots. **g–i**, Enlarged view of images shown in **a–c**.

In SFig. 21 we examine this for SSB with two sets of 10 scans simulated with doses of 2 and 5 $\text{e}^-/\text{\AA}^2$ per scan by introducing different noise into a single noise free scan. There is therefore no drift to correct in these datasets but they allow us to see difference due to choosing to add ptychographic images or perform the ptychography on the summed CBED. The latter route provides higher quality images with the differences more apparent in the lower dose data. This does not seem particularly surprising given that we do not simply add counts in ptychographic images.

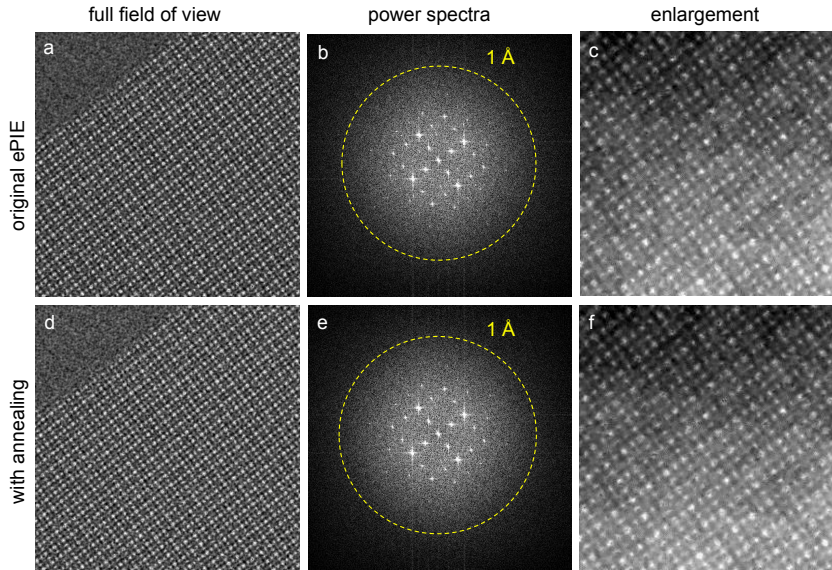
The two routes are compared for experimental data using ePIE in SFig. 22. Given that iterative ptychography is more difficult to correctly converge when there are few



SFig. 23 Calculating drift for drift correction. **a**, Single-scan LAADF image generated from a 4D-STEM dataset. **b**, 12-scan summed LAADF image after drift correction. **c**, Amplitude-filtered image generated from the 12-scan LAADF images, with yellow boxes marking six regions selected for drift calculation. **d–i**, Measured drift profiles for each of the six cropped regions from the image.

hits per diffraction pattern, it is no surprise that it benefits from using the summed CBED, and indeed the ePIE images in SFig. 22 show this route produces a slightly better result than summing individual ePIE images.

As the Pb-I columns provide particularly strong contrast in the LAADF images, we used the LAADF images to determine the drift between scans. An amplitude filter was first applied following Zhang et al.³² to the low-dose LAADF, before phase correlation³³ was used to determine the shift between the images. To achieve sub-pixel alignment, we increase the probe position sampling by a factor of two. SFig. 23 illustrates how regions of interest were selected and compared between scans to determine the drift and displays the calculated drift for these across 12 scans. The x and y axis drift is seen to be linear and rule out significant rotations.

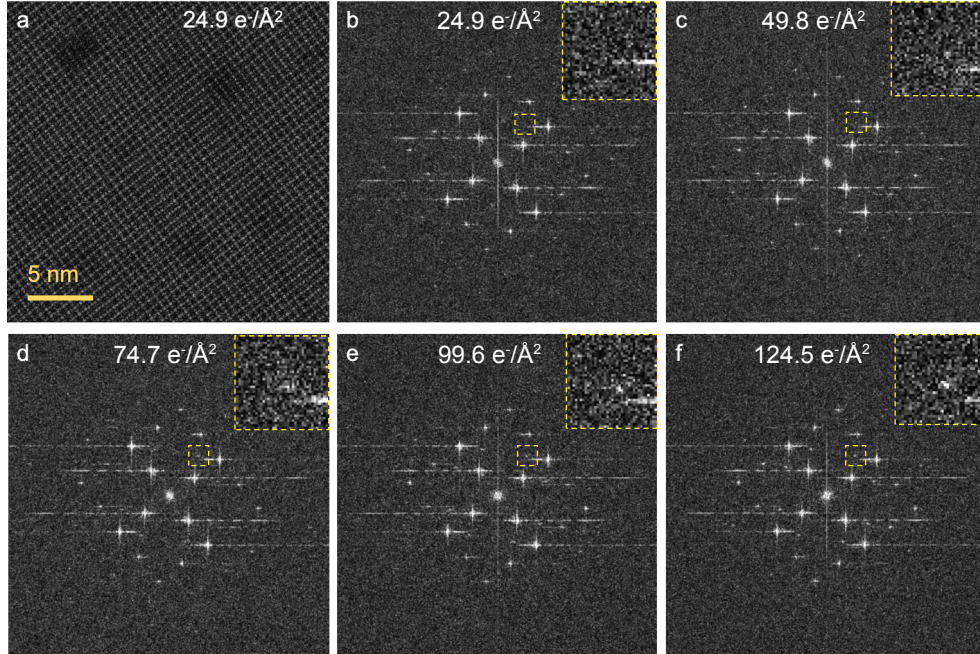


SFig. 24 Comparison of experimental ePIE images of MAPbI₃ with and without probe position annealing for probe position correction. As can be seen, there is essentially no difference in the results because the standard STEM drift correction methods which have already been applied to the dose fractionated data work well for high scan speed datasets using dense probe position grids.

While probe position annealing³⁴ is common in iterative ptychography as a means of correcting errors in probe positions, it is generally applied to data using far fewer and much larger probe position step sizes than used here. Per probe position it is relatively computationally expensive and thus for datasets with very large numbers of probe position very expensive. We tested if probe position annealing benefits for our rapidly scanned data but did not find it improved the data which we drift corrected using the usual methods for rapid scan STEM as shown in SFig. 24.

Evolution of pristine MAPbI₃ under electron irradiation

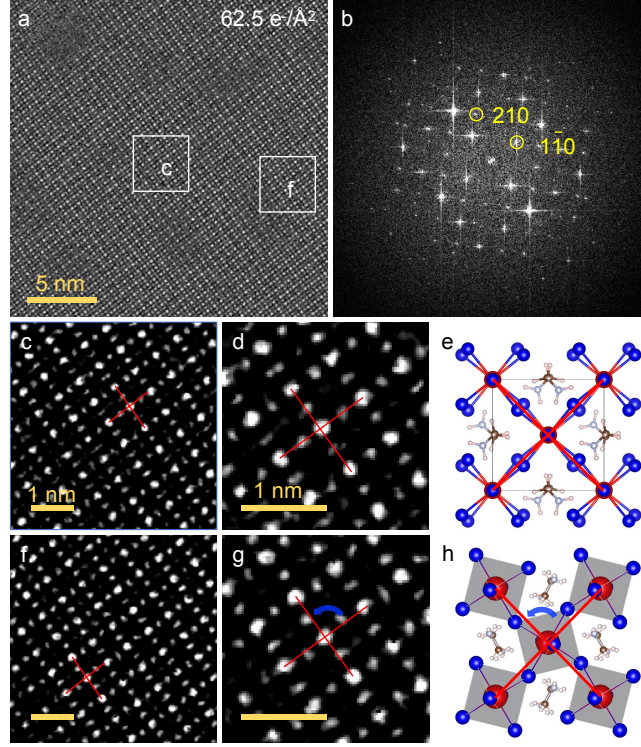
As discussed earlier using SSB power spectra, from the dynamics we record with our dose fractionated data we find that the first transformation that occurs inside the crystal is from tetragonal to orthorhombic. The phase transformation begins to appear after the 32 e⁻/Å² of the first three scans in our imaging. SFig. 25 shows the evolution of the LAADF power spectra as the dose increases. The different spots of the tetragonal and orthorhombic phases are illustrated in SFig. 8. The LAADF power spectra, like the SSB power spectra in SFig. 10, show the gradual increase in the strength of the orthorhombic spots.



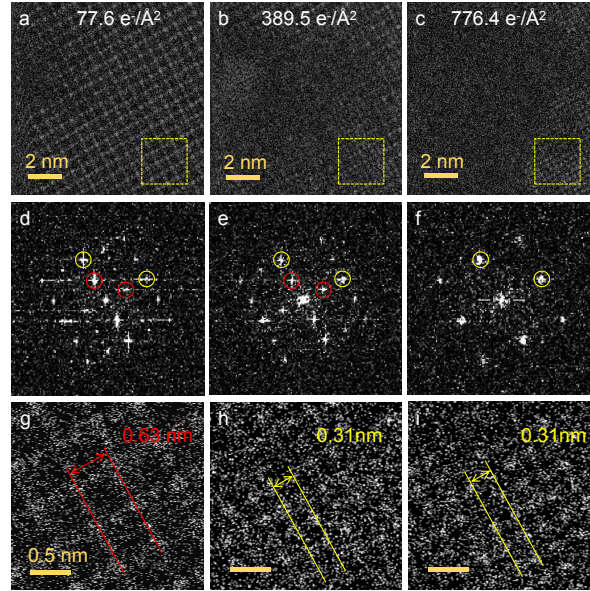
SFig. 25 Evolution of the LAADF power spectra under electron irradiation. **a**, LAADF image generated from the first two scans. **b–f**, LAADF power spectra from every two consecutive scans across 10 scans. The insets highlight the emergence and gradual intensity increase of the (210) plane of the orthorhombic phase as the dose builds up.

In addition to analysing the spots in reciprocal space, differences in the structures of the tetragonal and orthorhombic phases can be discerned directly in the real space images. For example, the rotations of the I octahedra can be identified directly in the experimental images, as illustrated in SFig. 26.

Irradiation of the pristine material tends to form vacancies. Regions containing sufficiently large amounts of I vacancies can form Pb crystallite similar to that shown in SFig. 44 and 45. However, when less I is lost PbI₂ can form instead. The development of regions of PbI₂ is illustrated in SFig. 27. The transformation is visible in the real space LAADF images in the figure, with the alternating pattern of darker and brighter I and Pb-I columns changed to all bright Pb containing columns in the PbI₂ region. The 0.31 nm spacing of the PbI₂ planes is almost the same as the (220) plane spacing in MAPbI₃ distinguishing it from the (200) spacing of pure Pb crystal.



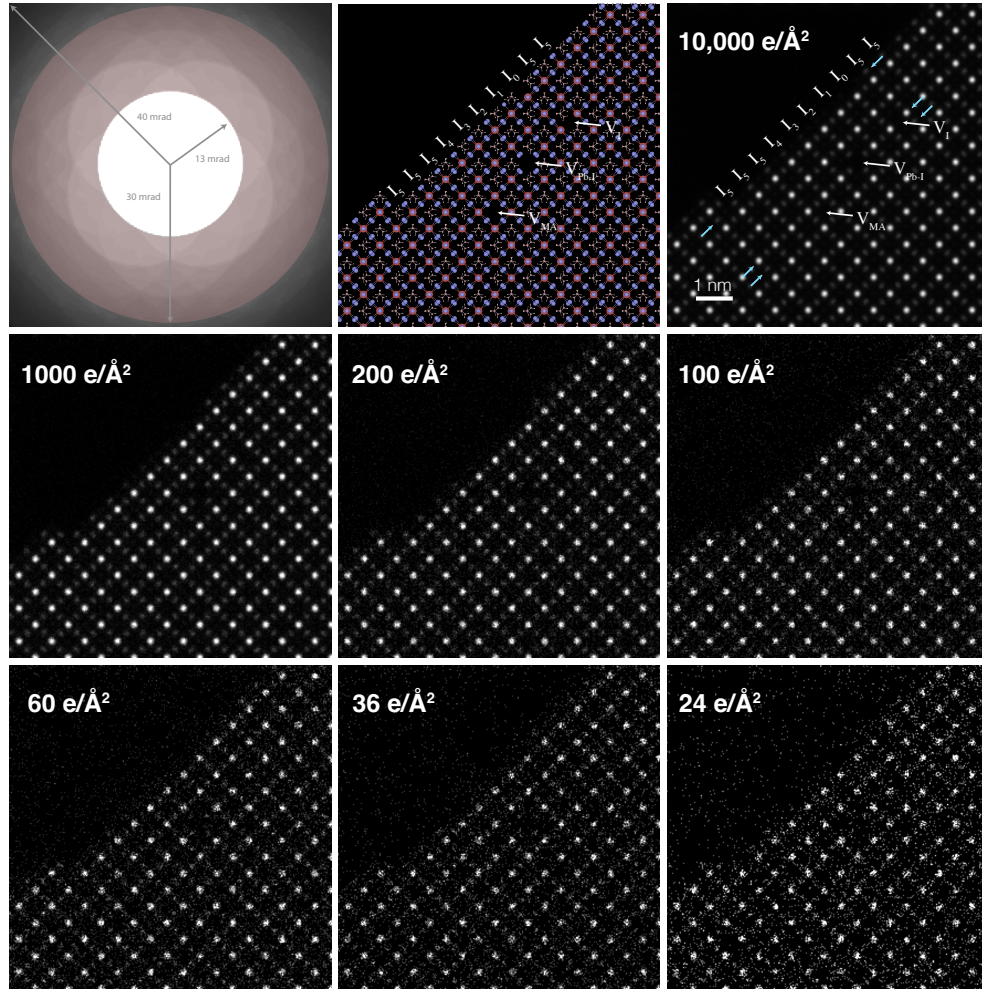
SFig. 26 Phase transition of MAPbI₃ from tetragonal to orthorhombic. **a**, ePIE image retrieved from five scans. **b**, The power spectrum of **a**. The (210) plane belongs to the orthorhombic phase, while the (110) plane is present in both phases. **c**, Cropped phase image corresponding to the tetragonal region in **a**. The red cross indicates the perpendicular (110) and (1 $\bar{1}$ 0) planes in the tetragonal phase. **d**, Enlarged view. **e**, Structural model of tetragonal MAPbI₃. **f**, Cropped phase image corresponding to the orthorhombic region in **a**. The red cross indicates the perpendicular (110) and (1 $\bar{1}$ 0) planes in the orthorhombic phase. **g**, Enlarged view, with a blue arrow indicating the tilt of PbI₆⁴⁻ octahedron. **h**, Structural model of orthorhombic MAPbI₃.



SFig. 27 High-resolution LAADF imaging of the transition from MAPbI₃ to PbI₂. **a-c**, LAADF images from the first, fifth, and tenth scans, with a total dose of 78 e⁻/Å² per scan. By the time **b** and **c** were captured, the sample region had already been exposed to a total dose of 390 e⁻/Å² and 780 e⁻/Å², respectively. **d-f**, Power spectra of **a-c**. The red circles indicate the 0.63 nm spacing of the Pb containing planes in MAPbI₃, while the yellow circles mark the smaller 0.31 nm spacing of the Pb containing planes in PbI₂, which contains Pb in every row of columns. **g-i**, Magnified views of the regions marked by yellow boxes in **a-c** showing the 0.63 nm spacing of the bright Pb containing planes transitioning to the 0.31 nm spacing as Pb fills into every plane.

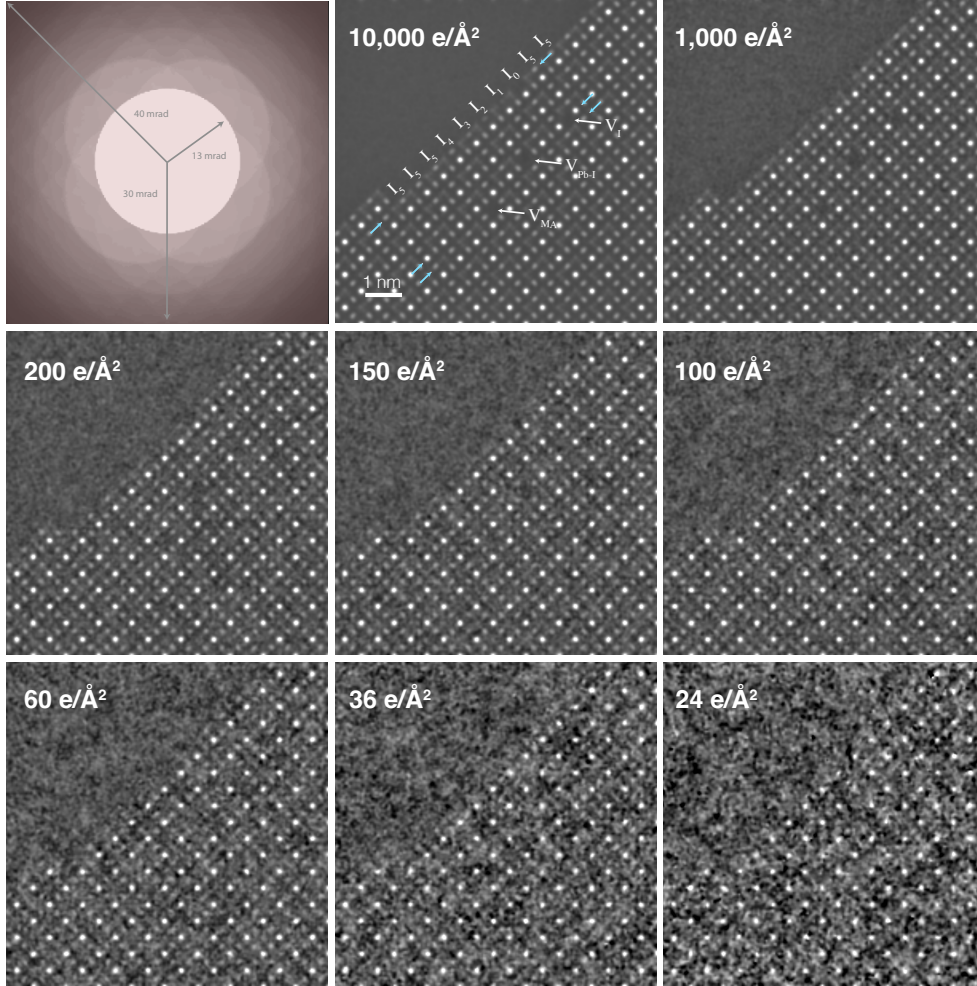
Simulated imaging of the edge structure of MAPbI₃

Image simulations were carried out using the three unit cell thick model of a (110) edge of MAPbI₃ displayed in SFig. 28 with a range of doses for LAADF (SFig. 28), ePIE (SFig. 29) and SSB (SFig. 30). The simulations were performed using the same 13 mrad convergence angle and 200 kV accelerating voltage as the experiments, but did not include phonons. The model contains a varying number of I vacancies in the I columns along its I-MA terminating edge. Between one and five vacancies were included in an increasing amount moving along the edge from left to right, as indicated with annotations showing the number of I atoms in the edge region containing the vacancies. Note that in this model a full I column in the I-MA layers contains five I atoms, one less than used in the model for the simulations displayed in Fig. 3. Further inside the material the model also contains fully vacant MA, Pb-I and I sites (one of each). SFig. 32 displays line profiles comparing the visibility of the different sites in the images taken along the lines indicated by the pairs of blue arrows shown on the highest dose image in each figure.



SFig. 28 LAADF images simulated at different doses using the displayed three unit cell thick model of MAPbI₃ terminated with the (110) plane. 1–5 I vacancies were introduced in the I columns along the edge. The I column occupancy in this region is indicated by I_x where *x* is the number of atoms in the column. The model also contains fully vacant MA (V_{MA}), Pb-I (V_{Pb-I}) and I (V_I) sites further inside the material. The blue arrows overlaid on the 10,000 e⁻/Å² image indicate the locations used for the line profiles in SFig. 32. The PACBED from the simulation (top left) illustrates the area used for the LAADF with the coloured overlay.

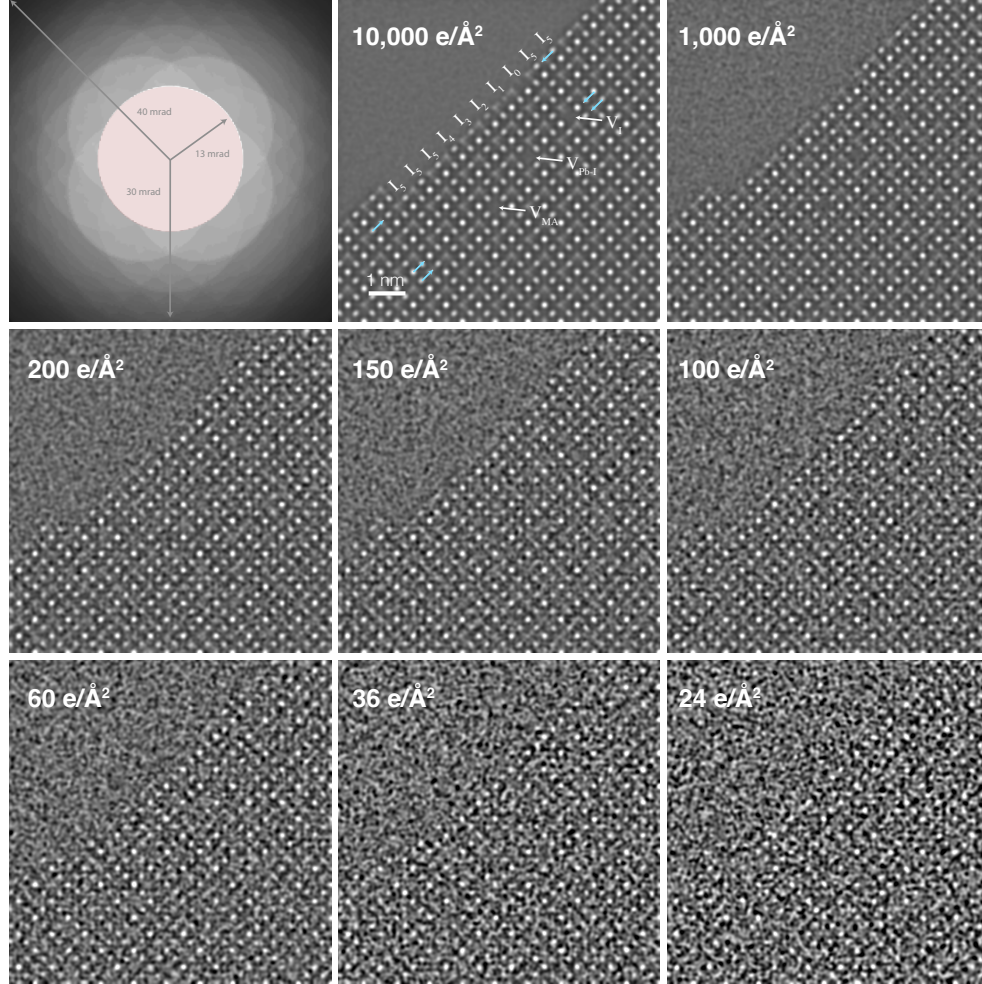
LAADF provides Z-contrast images and therefore the heavier Pb-I columns are much brighter than the lighter I columns. The MA molecules are lighter still and are correspondingly darker in the LAADF images. All of these columns are discernible in the $10,000 \text{ e}^-/\text{\AA}^2$ image, although the difference in the intensity of the columns means that to make the MA visible the brightness must be increased to the point that the Pb and I atoms are saturated, which we have not done in the displayed images. Without saturating the Pb-I columns the I columns are also relatively dark. This strong contrast, with the Pb being so much brighter than the other sites, allows the Pb-I columns to be clearly visible at very low doses indeed. This can be very useful, for instance when aligning images. However, the other sites become less clear as the dose is reduced. The MA columns become less clear at $1,000 \text{ e}^-/\text{\AA}^2$, and although MA columns are generally visible, with the image brightness enhanced, some MA sites appear similar to that with a missing MA column. By $200 \text{ e}^-/\text{\AA}^2$ it is difficult to discern the MA columns at all.



SFig. 29 ePIE images simulated at the indicated doses using the MAPbI_3 edge model shown in SFig. 28. ePIE uses the full range of angles available in the CBED as illustrated with the PACBED (top left). The I occupations (I_x) are indicated in the area of edge containing I vacancies on the $10,000 \text{ e}^-/\text{\AA}^2$ image as well as the location of the vacant MA (V_{MA}), Pb-I ($V_{\text{Pb-I}}$) and I (V_{I}) columns. The blue arrows indicate the locations used for the line profiles in SFig. 32.

The completely vacant inner I column can be discerned in the LAADF images down to about $60 \text{ e}^-/\text{\AA}^2$. Partial vacancies are naturally more difficult to detect and therefore require higher doses to discern. At $1000 \text{ e}^-/\text{\AA}^2$ the I_1 cannot be distinguished from the I_0 column at the edge, although otherwise the linear decrease in occupancy along

the edge I columns is reflected in the LAADF intensity. At $200 \text{ e}^-/\text{\AA}^2$ only the I_4 and possibly the I_3 sites can be distinguished from the completely vacant I_0 edge site. The other vacancy containing edge I columns do not appear significantly different to the vacant edge site at this dose in the LAADF image. Decreasing the dose further makes discerning vacancy levels more difficult.

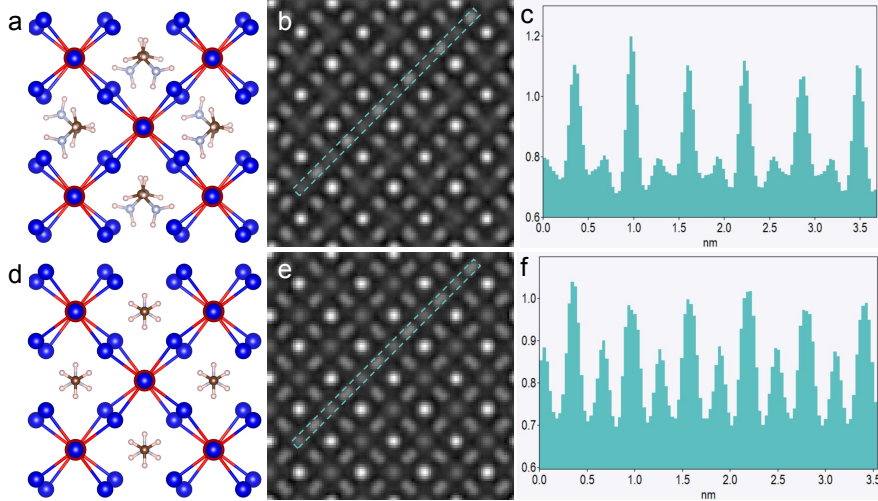


SFig. 30 SSB images simulated at the indicated doses using the MAPbI₃ edge model shown in SFig. 28. SSB uses the range of angles within the convergence angle as illustrated in the PACBED (top left) with the pink overlay. The I occupations (I_x) are indicated in the area of edge containing I vacancies on the $10,000 \text{ e}^-/\text{\AA}^2$ image as well as the location of the vacant MA (V_{MA}), Pb-I (V_{Pb-I}) and I (V_I) columns. The blue arrows indicate the locations used for the line profiles in SFig. 32.

The ptychography reveals all the atomic sites very clearly at the higher doses, including the light MA molecules. Note that these images have been treated with our standard 0.8 rad offset with our phase offset method. As the dose is reduced, noise in the images increases but they remain more clear overall than the LAADF images, although we again note that the particularly strong contrast of the heavy Pb-I columns allows them to be clearly discerned in the Z-contrast LAADF images at the lowest doses. At times the reduced visibility of lighter elements can actually cause LAADF and other ADF imaging modes to display heavy sublattices more prominently than the ptychography images. In the present case, the lower intensity of the I and MA columns in the LAADF in effect makes the Pb-I columns stand out particularly well even at $24 \text{ e}^-/\text{\AA}^2$. In the ePIE images at $24 \text{ e}^-/\text{\AA}^2$ the Pb-I column centres are actually smoother but stand out slightly less compared to the LAADF. Similarly in the $24 \text{ e}^-/\text{\AA}^2$ SSB image, the

Pb-I columns also appear smooth, but are less prominent than in the ePIE image due to the other features, both atomic columns and noise, being weighted more equally.

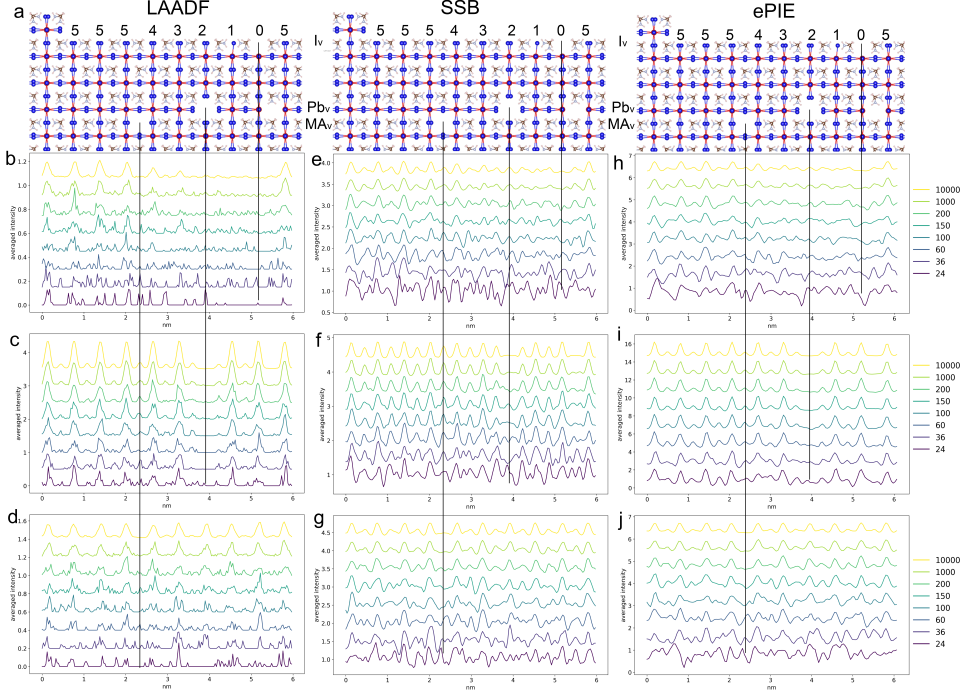
This behaviour is something we see generally when comparing SSB to ePIE results. The same noise features are often visible in ePIE and SSB images from the same data, but the SSB makes these features appear brighter. This can make the SSB appear less clear. However this behaviour can also make I columns, with their lower potential, brighter in the SSB images as well, more similar to the Pb-I columns. This can mean that the I columns are actually more visible in the SSB images, especially when these are partially filled. Such is the case in simulation shown in Fig. 3c of the main text where the partially occupied I columns are brighter in the SSB image than the ePIE image. It is also the case with the simulations presented here in SFig. 29 and 30. It appears that less strong features are less bright in ePIE compared to SSB whether they are noise or lighter columns. This makes the ePIE images appear less noisy, but if we wish to see the lighter columns such as the partially occupied I columns, the noise level is not necessarily better. This suggests an alternative weighting of the SSB transfer³⁵ could potentially make images from the two methods appear more similar. However, when displayed together, the extra brightness in the SSB image can help make the lighter atomic columns more visible, while the ePIE image appears more clear overall.



SFig. 31 ePIE simulations illustrating the substantial MA column contrast difference resulting from different MA orientations. **a**, A structural model with a cross-aligned distribution of MA. **b**, ePIE image simulated from the model in **a**. **c**, Line profile showing that the contrast of MA is significantly lower than that of I. **d**, A structural model with all MA molecules aligned along the electron beam direction. **e**, ePIE image simulated from the model in **d**. **f**, Line profile showing higher MA contrast compared to **c**.

It is important to note that the contrast of the MA columns strongly depends on the orientation of the MA molecules. This is illustrated in SFig. 31, where we compared two structural models, one with a cross-aligned MA distribution and another with all the MA molecules aligned along the beam direction. The ptychographic simulations based on these models show that the MA columns appear with much higher contrast when they are aligned along the beam direction with the projected potential more concentrated in the centre of the columns. Unless otherwise noted, our simulations used the cross-aligned MA distribution that produces a lower MA column contrast. Therefore the dose threshold for detecting MA columns will be higher than predicted by our simulations if the MA columns are not cross-aligned. We believe this likely explains the discrepancy we see between the visibility of the MA columns in our experiments and simulations.

In the simulated ptychography images in SFig. 29 and 30 the I sublattice remains visible down to $24 \text{ e}^-/\text{\AA}^2$, although it can be difficult to discern the sites from the noise. Increasing the dose to $36 \text{ e}^-/\text{\AA}^2$ helps significantly with this. The fully vacant columns also appear darker than all the partially vacant I columns along the edge at $200 \text{ e}^-/\text{\AA}^2$. As the dose is lowered it becomes more difficult to detect the I columns with lower occupancies, however the I_4 and I_3 sites remain visible at $60 \text{ e}^-/\text{\AA}^2$. At $36 \text{ e}^-/\text{\AA}^2$ these columns are much less clear, although peaks still appear at the sites.



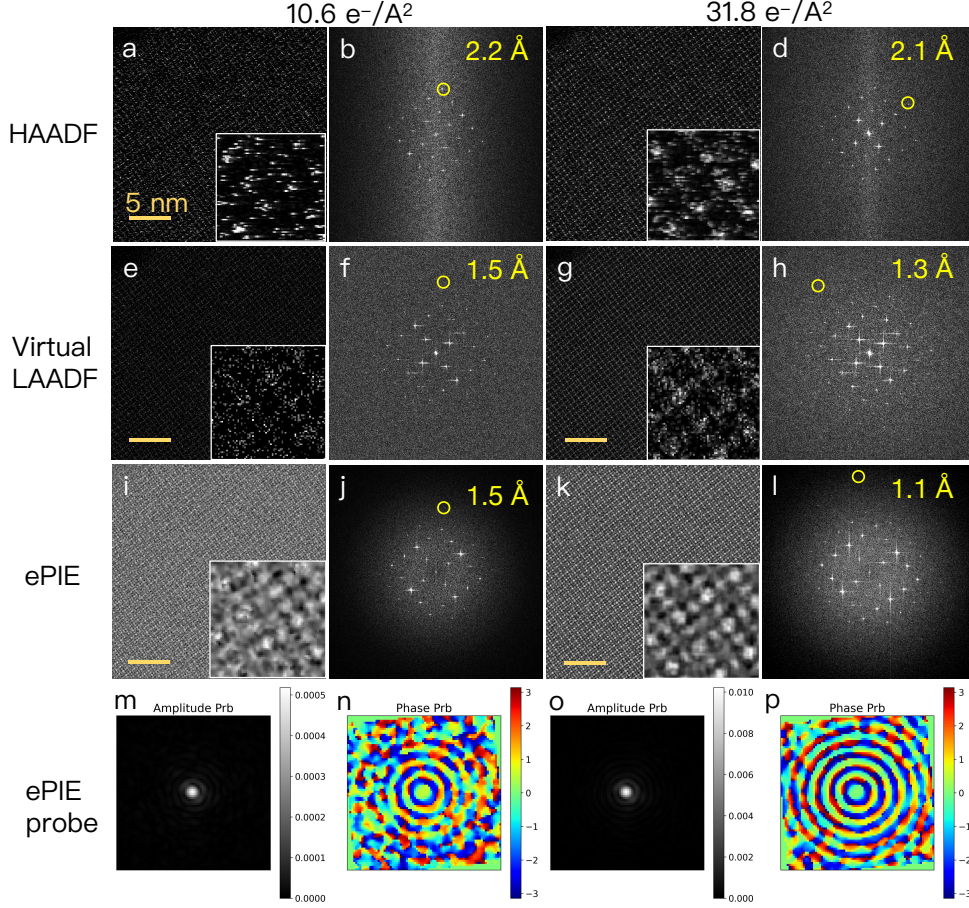
SFig. 32 Line profiles of the images in SFig. 28, 29, and 30. **a**, Models terminated with the (110) plane containing I vacancies at the edge, and MA, I, and Pb vacancies in the inner region. The numbers 5, 4, 3, 2, and 1 represent the number of I atoms at the edge. **b–d**, LAADF profiles for the edge (Iv), Pb vacancy containing layer (Pbv) and MA vacancy containing layer. **e–g** SSB and **h–j** profiles in the same order. Vertical dashed lines are used to guide the eye to the locations of the Pb and MA vacancies.

Experimental comparison of different imaging modalities

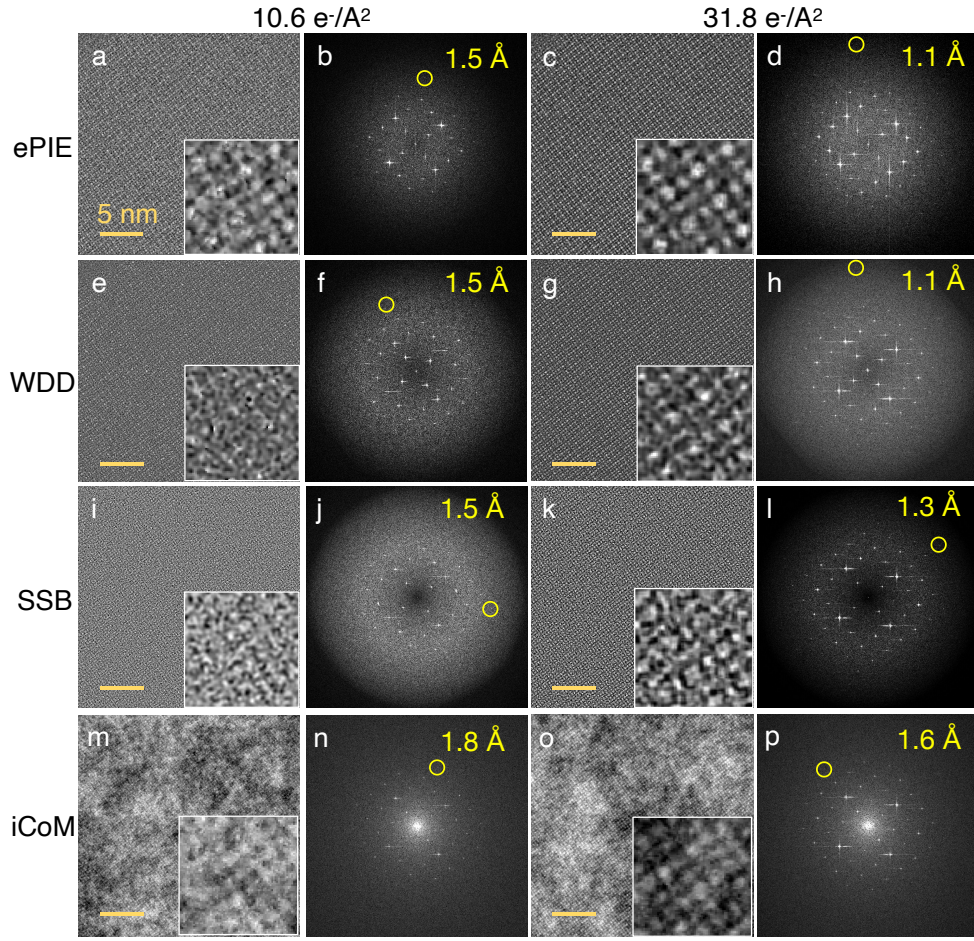
SFig. 33 compares experimental HAADF, LAADF and ePIE images of MAPbI_3 using $10.6 \text{ e}^-/\text{\AA}^2$ and $31.8 \text{ e}^-/\text{\AA}^2$ of dose fractionated data. The HAADF uses the physical HAADF detector, with an inner angle of 44 mrad , just beyond the outer angle of the Timepix3 camera. The LAADF and ePIE images make use of the 4D data collected on the Timepix3. The figure also displays the reconstructed probes for both ePIE reconstructions. Although the power spectra of all the images contain spots of sufficiently high resolution to resolve the relatively large spacings of the MA, Pb-I and I columns in MAPbI_3 , the ePIE ptychography provides substantially clearer images at these doses as expected.

SFig. 34 compares the same ePIE results to images produced from the same data using the Wigner distribution deconvolution (WDD), SSB and iCoM methods. Although the atomic columns are visible, the iCoM shows its characteristic low frequency noise, due to the way it amplifies low frequencies.^{36,23} Interestingly, at least at the higher dose, the WDD produces an image that looks closer to the ePIE image than the SSB does, with the intermediate strength features in the WDD appearing less bright in a similar way to the ePIE. Again this includes both noise and the lighter columns. This might

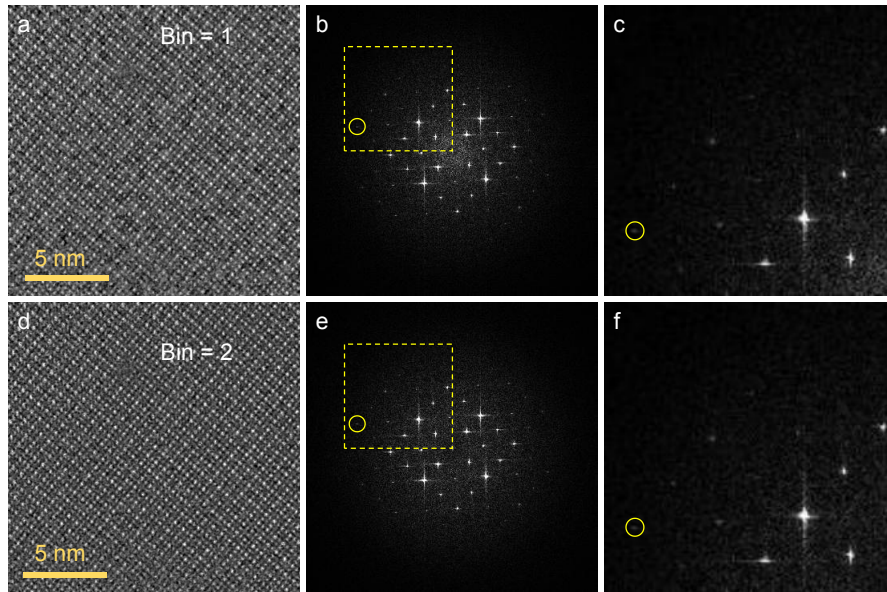
be due to a relatively large ϵ being used in the Wiener filter of the WDD providing additional damping compared to the SSB. The deconvolution step involved in WDD is associated with noise amplification, however as noted by O'Leary et al.³⁵ this can be suppressed using a large value of ϵ in the Wiener filter at the potential cost of also suppressing useful sample information. However, in the lower dose images ePIE seems to have more of an advantage. Possibly additional processing of the direct ptychography images could be beneficial here, but we leave this for future study.



SFig. 33 Experimental HAADF, LAADF, and ePIE images of ultrathin MAPbI₃ and their corresponding power spectra using different amounts of dose fractionated data. The reconstructed probes from ePIE are also shown.

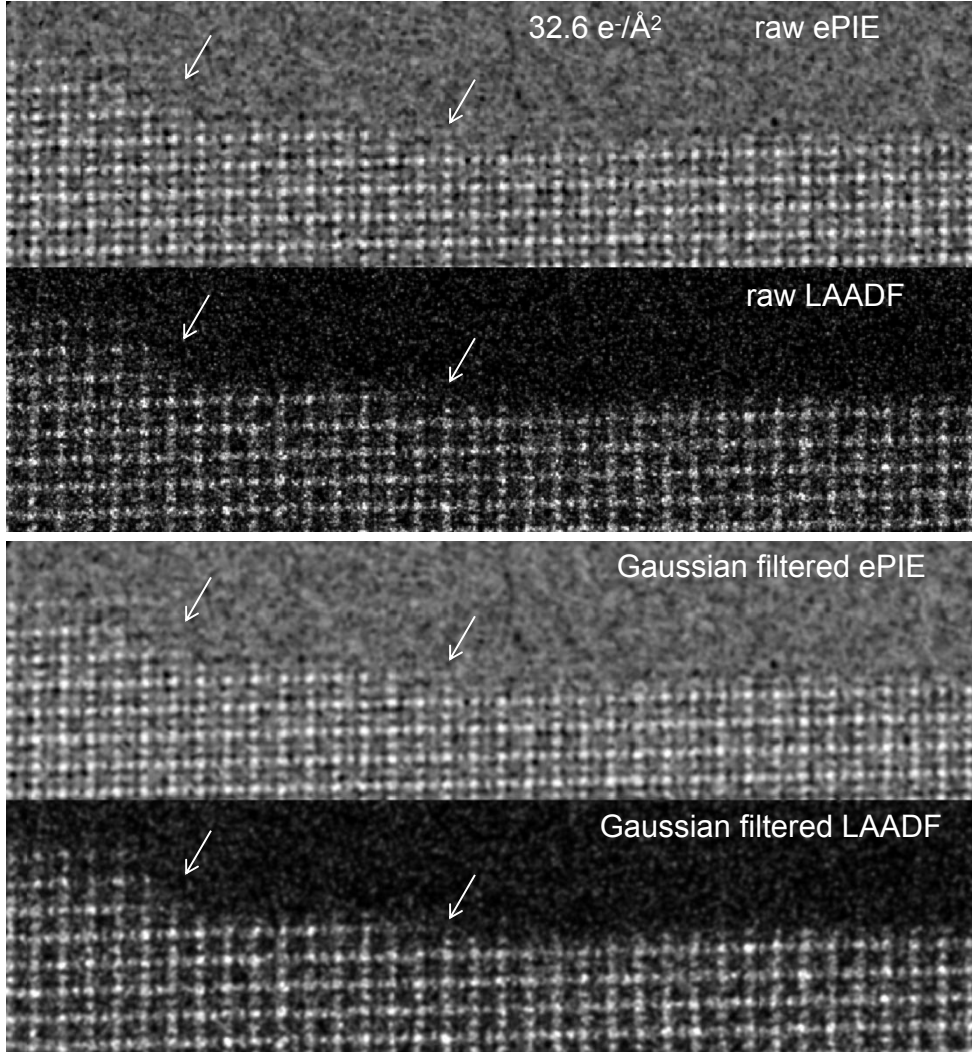


SFig. 34 Experimental ePIE, WDD, SSB, and iCoM images of ultrathin MAPbI₃ and their power spectra. Enlargements are shown overlaid on the wider field of view images to show the atomic structure more clearly.



SFig. 35 The impact of binning on the resolution of the ePIE reconstruction. **a, d**, ePIE images with 4D-STEM datasets using 800×800 probe positions (unbinned data) and 400×400 probe positions (bin=2). **b, e**, The power spectra of **a** and **d**. **c, f**, Two enlarged portions from the top left corner of the power spectra **b** and **e**.

SFig. 35 illustrates that we are significantly oversampling with our probe positions for the imaging process itself. Binning the probe position grid by a factor of two makes no apparent difference to the ePIE images. We used oversampling to keep the probe in motion as much as possible to ameliorate damage, considering the difference we observed regarding a rapidly scanned probe versus plane wave TEM. Because our data are oversampled in real space, we can also apply blurring filters to smooth the noise somewhat without losing the resolution required to resolve the lattice. SFig. 36 compares Gaussian filtering of $32.6 \text{ e}^-/\text{\AA}^2$ dose experimental ePIE and LAADF images of the edge shown in Fig. 3 of the main text to the same images without the filtering. We also tested the use of Savitzky-Golay filtering, but found it attenuated high-frequency components and reduced the resolution more than Gaussian filtering when both are optimised to reveal the structure most clearly.



SFig. 36 Comparison between raw and Gaussian filtered LAADF and ePIE images of the edge of MAPbI_3 .

Although smoothing the signal with the filter can make the LAADF appear less noisy, it does not make up for the stronger overall signal provided by ptychography. The left most arrows in SFig. 36 point to an area of lattice that is visible in the ptychography, but not in the LAADF images. The columns visible in the ePIE images in this region are less bright, and likely contain many vacancies. The filtering does not make this area visible in the LAADF, and we note that this is not dependent on the brightness

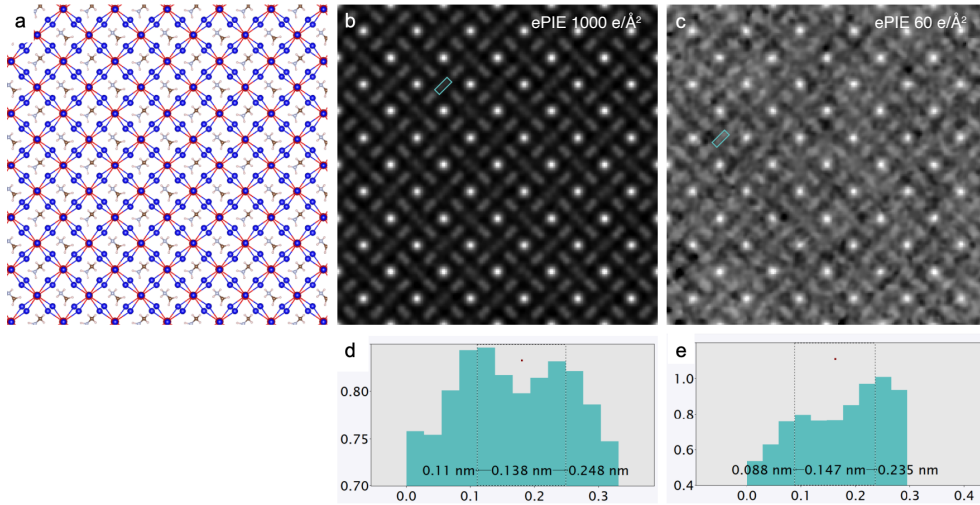
settings of the image as there is no brightness and contrast setting which can be found that reveals this lattice in the LAADF image.

The set of arrows further to the right in the images in SFig. 36 point to a Pb-I column that is likely only partially occupied. The column can only be reliably discerned in the ePIE images, and the Gaussian filter does not significantly help make this column clearer compared to the noise. While there is a small spot in the LAADF images below the position of the column, it appears very similar to the noise seen elsewhere in the image even after filtering, despite Pb-I columns being by far the most visible in the LAADF due to the heavy Pb. Of course it may be that there is much less Pb in the under occupied column, but the lack of visibility in the easiest type of column for LAADF to reveal illustrates the utility of utilising the greater overall dose efficiency of ptychography, especially when we wish to resolve changes in occupancy of the lighter pure I columns.

We do however wish to again note that LAADF actually provides quite clear images of the Pb-I column lattice which are fully occupied due to the strong Z-contrast of these heavy columns, when they are fully occupied, compared to the lighter columns. This, along with the ability to more reliably discern the effective atomic number of the columns makes the LAADF valuable. Our view is that obtaining both LAADF and ptychography imaging is the best option compared to using either one in isolation.

Imaging MA molecules in detail

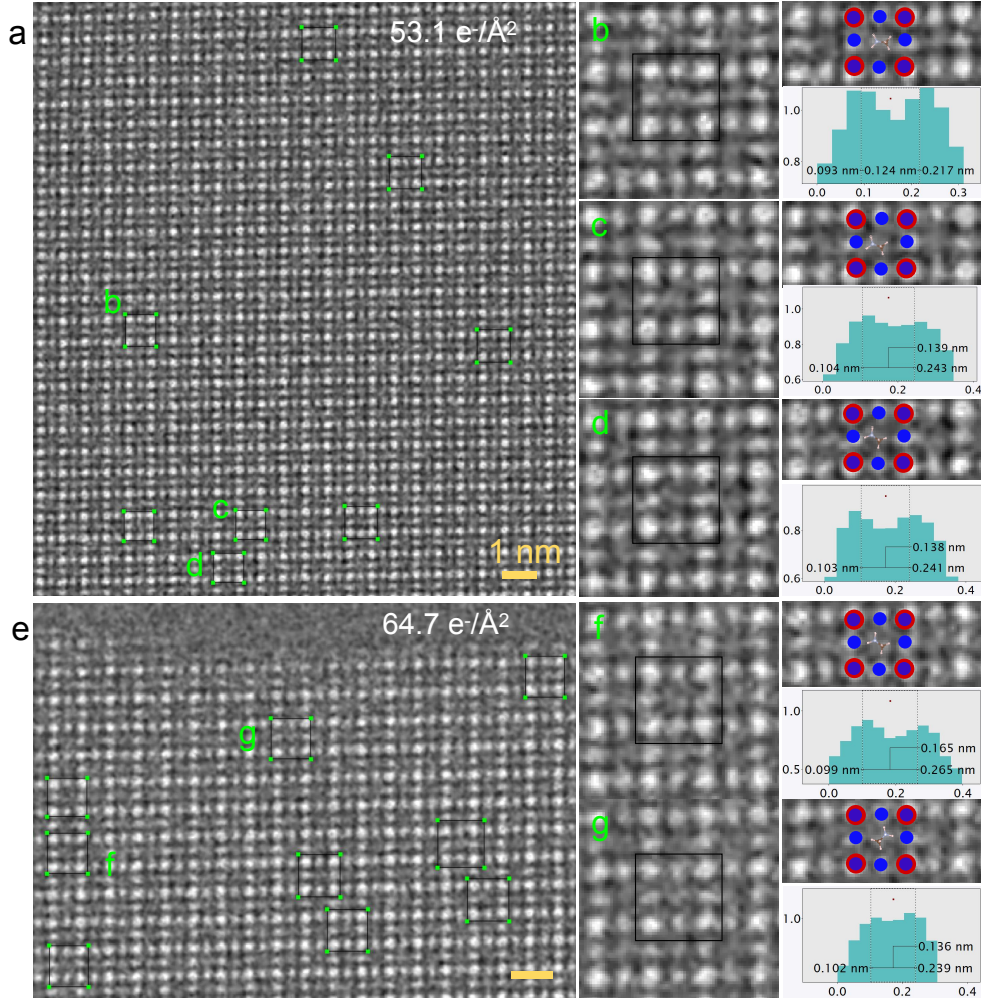
In MAPbI_3 , MA represents the methylammonium ion, with the chemical formula CH_3NH_3^+ . It consists of a methyl group (CH_3) and a protonated amine group (NH_3^+). This cation interacts with the surrounding PbI_6^{4-} octahedral framework through hydrogen bonding and electrostatic interactions, forming the perovskite structure.



SFig. 37 Simulated ePIE imaging with the MA molecules within each individual column aligned. **a**, The three unit cell thick structural model used for the simulations, **b**, ePIE simulations at $1000 \text{ e}^-/\text{\AA}^2$ and **c** $60 \text{ e}^-/\text{\AA}^2$ with line profiles **d** and **e** respectively

The orientation of MA^+ is not fixed due to its ability to form hydrogen bonds with any of the six surrounding I^- ions. It can therefore rotate under thermal fluctuations and electronic excitations, while local electric fields may also affect its orientation. This dynamic disorder makes it difficult to distinguish the methyl and amine groups in most projection images. However, some MA columns do show a significant splitting of the columns that may not simply be due to noise. Examples are shown in SFig. 38 at 54 and $65 \text{ e}^-/\text{\AA}^2$ from two regions of the ultrathin MAPbI_3 , with areas showing significant splitting highlighted.

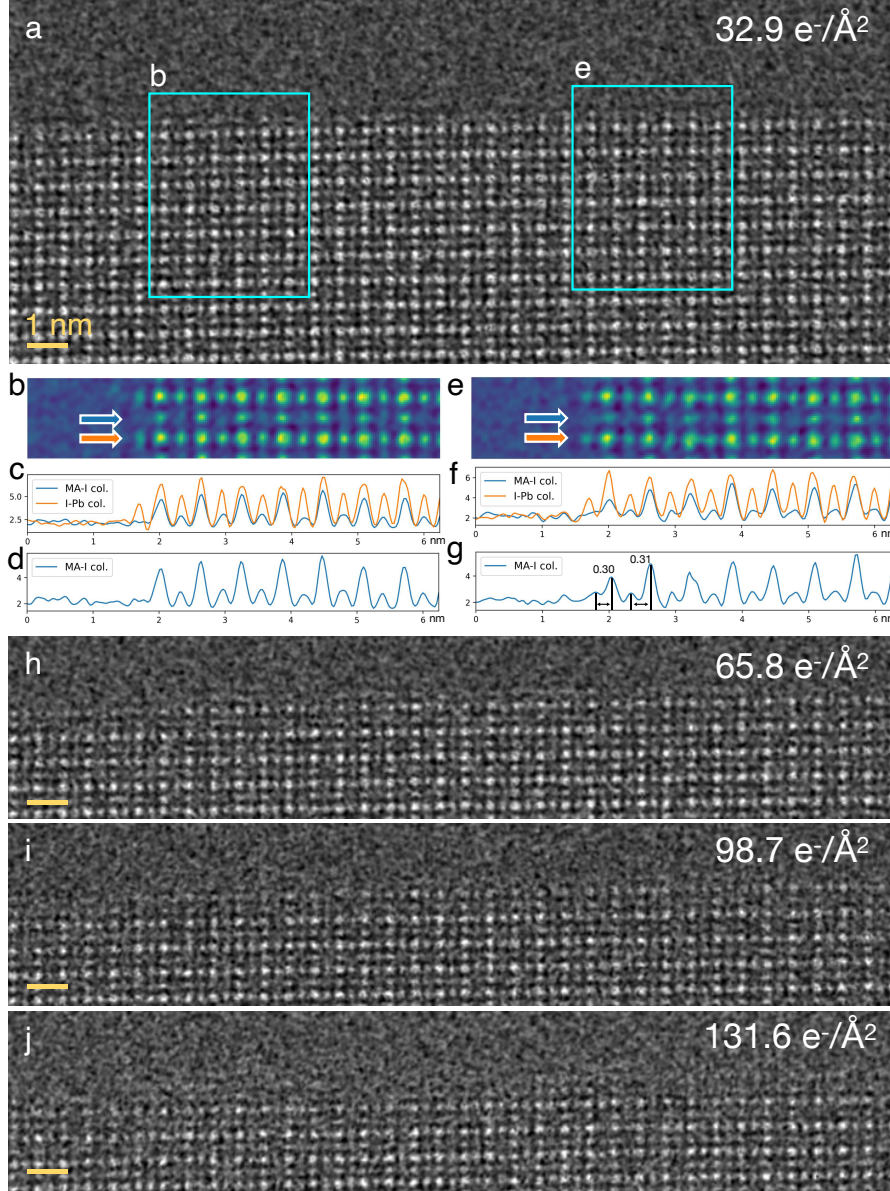
To test if it is possible to detect the orientation of an aligned MA column in ultrathin MAPbI₃ we simulated ePIE images using the three unit cell thick model displayed in SFig. 37a using the same voltage and convergence angle as the experiments, but without including phonons. Unless otherwise noted, in the other models we have used for our simulations the MA orientation alternates back and forth 90 degrees inside each MA column rather than assuming a single orientation. For the simulations in SFig. 37 we instead align the MA molecules in each column. This makes the orientations of the MA molecules easily discernible in the 1000 e⁻/Å² simulation shown in the figure. Detecting the orientation becomes more difficult in the 60 e⁻/Å², but it is still possible to make out at least a proportion of the MA orientations. Examining the experimental line profiles the width of the splitting generally aligns with those seen in the simulations. Therefore it may be possible that we are seeing columns of MA in which the molecules are aligned in the experimental images.



SFig. 38 Experimental ePIE images **a** and **e** of two regions of ultrathin MAPbI₃ displaying significant splitting of the MA columns, potentially revealing their orientation. The overlaid boxes highlight locations where the MA columns appear to be split into two lobes. **b–d** display enlargements of the areas around the regions labelled as such in **a**. **f** and **g** display enlargements of those in **e**. The line profiles are taken along the MA sites in the direction of the splitting. The models illustrate plausible orientations of the molecules.

Termination of the edge of MAPbI₃ and its evolution under electron irradiation

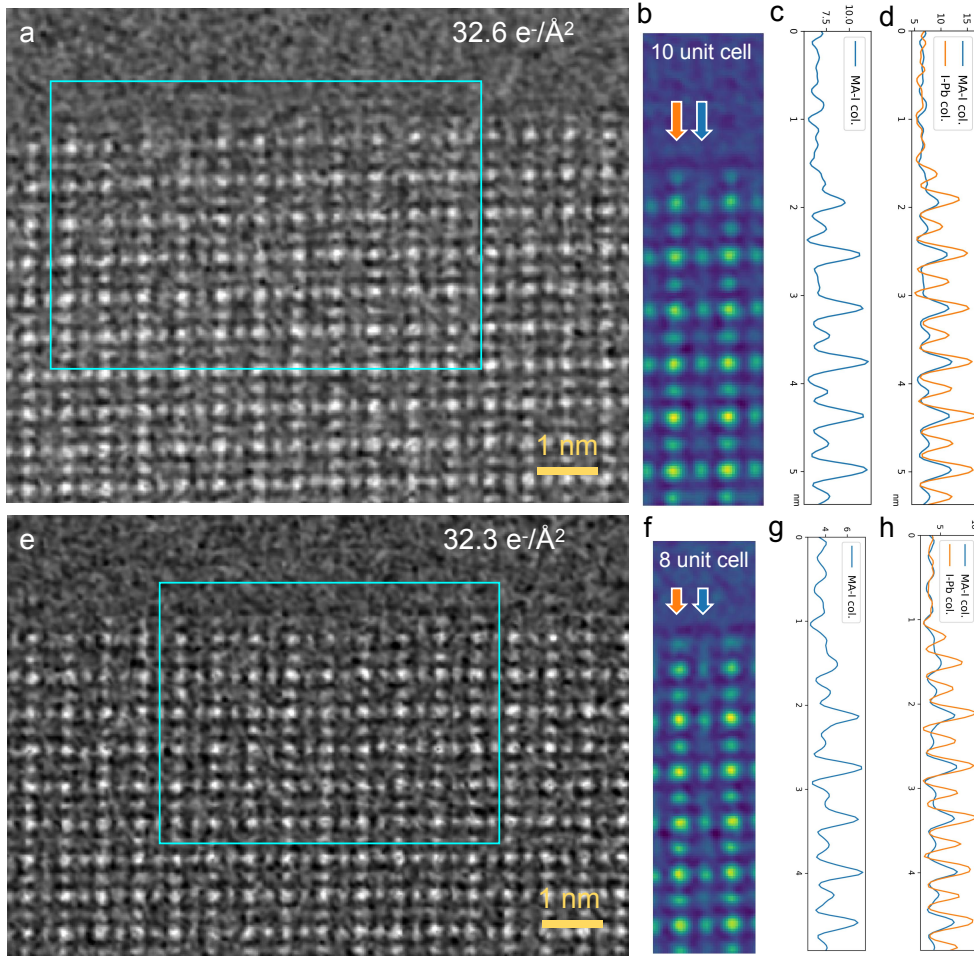
Imaging of additional edge regions of the ultrathin MAPbI₃ not shown in the main text are shown in the ePIE images in SFigs. 39 and 40. Additional imaging and analysis of the region containing the edge shown in Fig. 3 of the main text is presented in SFigs. 41 (ePIE), 42 (LAADF), and 43 (SSB). These edges are all terminated by the (110) plane, which we find to be the predominant plane terminating the material. These planes can either be terminated by the MA-I or Pb-I layers. Our observations indicate that the (110) edges are almost entirely terminated by MA-I layers.



SFig. 39 Another region of I-MA terminated (110) edge imaged with ePIE using dose fractionated data at the accumulated doses indicated. **b** and **e** display unit cell averaged images (rotated) of the edge regions labelled in part **a**. Line profiles are displayed below the averaged images taken along lines running along the MA-I (blue) and Pb-I planes (orange) indicated by the arrows. The first MA column in **e** can be seen to be slightly closer to the next layer inside the material in the image, and also in the MA-I line profile in **g**, with the first pair of columns being 3.0 Å apart and the next pair being 3.1 Å as indicated on the profile with black lines. **h–j** display the evolution of the edge as additional dose is accumulated (as indicated) with each image showing an average of three scans or 33 e⁻/Å² of data.

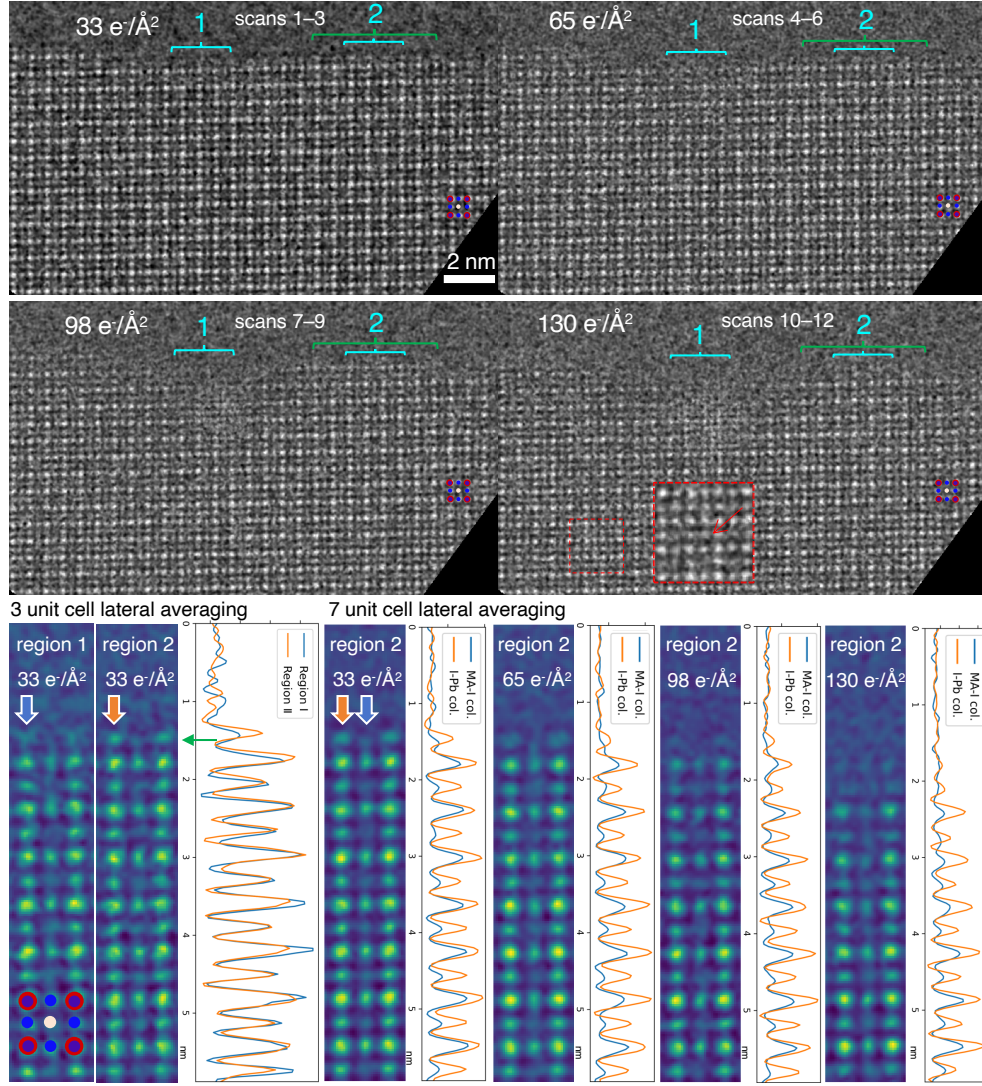
If we examine the lateral unit cell averaged ePIE images of the edge regions in SFig. 39, 40, and 41, the MA columns at the edge (0.30 nm) appear to be slightly closer to the I columns in the next layer (0.31 nm) inside the material (SFig. 39g). This makes sense given the absence of negatively charged I ions beyond the edge which would cause the positive terminating MA to be attracted to the negative I ions in the next layer inside the material, reducing the spacing. This proximity makes the terminating MA column appear less pronounced compared to the MA columns further inside the material in the line profiles, but they overall appear with a similar brightness.

An exception is in region b of SFig. 39, where the line profile shows no perceptible significant peak at the location of the edge MA sites. This seems most likely due to the presence of edge MA vacancies in this area. Despite this, the two highlighted regions in SFig. 39 appear to damage at a similar rate under additional electron exposure, with greater damage occurring instead between these two regions, suggesting the MA vacancies are of lesser importance to the damage rate.



SFig. 40 Additional regions of I-MA terminated (110) edge imaged with ePIE using dose fractionated data at the accumulated doses indicated. **b** and **f** display unit cell averaged images of the edge regions inside the blue boxes on the full field of view images in **a** (10 unit cells) and **e** (8 unit cells). Line profiles are displayed next to the averaged images taken along lines running along the MA-I (blue) and Pb-I planes (orange) indicated by the arrows.

SFigs. 41–43 display wider area images of the edge shown in Fig. 3 of the main text using ePIE, LAADF, and SSB imaging. Lateral unit cell averaging of regions 1 and 2 using the same three unit cell lateral extent as the main text with each of these signals is also displayed. In addition SFigs. 41–43 display lateral averaging of region



SFig. 41 Additional ePIE imaging and analysis of the edge shown in Fig. 3 of the main text. The top images show a wider field of view of the region as the cumulative dose increases with three scans used for each image. A region of PbI_2 that forms in the interior is highlighted in the red box. An enlarged view of the red boxed region is shown with a red arrow pointing to a former MA site that appears to have been filled with Pb. The three unit cell averaging is extended further into the material compared to the main text, with the left column of columns being used for their line profiles as indicated by the blue and orange arrows. The green arrow points to the terminating layer. The seven unit cell averaging of region 2 as a function of accumulated dose is obtained from the top images using the unit cells indicated by the green brackets. The line profiles are taken down the left Pb-I columns and the central MA-I columns.

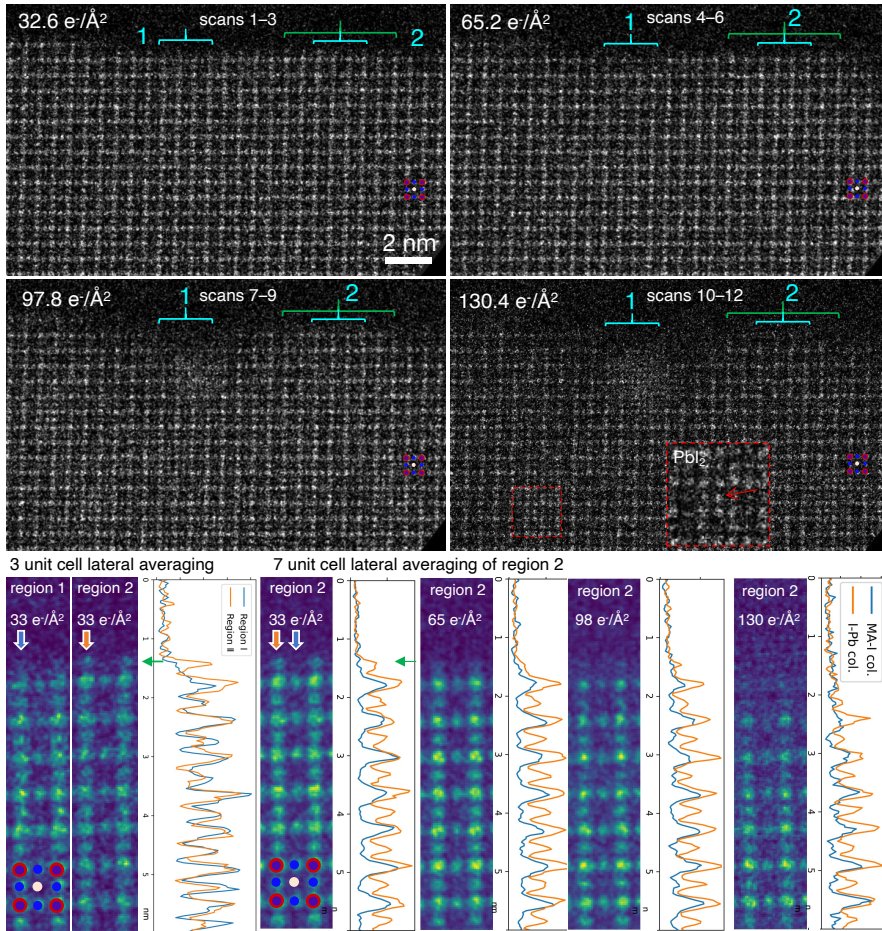
2 using seven unit cells as a function of accumulated dose to show the evolution of the region in greater detail. Note that the doses indicated on the images indicate the total accumulated dose while each image uses data from just three successive scans.

As can be seen from these figures, region 1 decays more rapidly with increasing dose than the surrounding areas, including region 2. The columns in the terminating MA-I layer of region 1 appear darker than those elsewhere, including region 2, as seen most clearly in the three unit cell averaged images in SFigs. 41–43. This indicates region 1 initially contains a higher proportion of vacancies at the edge, and seems the likely cause of its significantly more rapid damage rate.

Aside from a darkening of region 1 due to the apparent loss of material, a region develops as the damage extends further within the material with a different contrast to MAPbI_3 . Instead of the alternating pattern of bright and dark columns of the

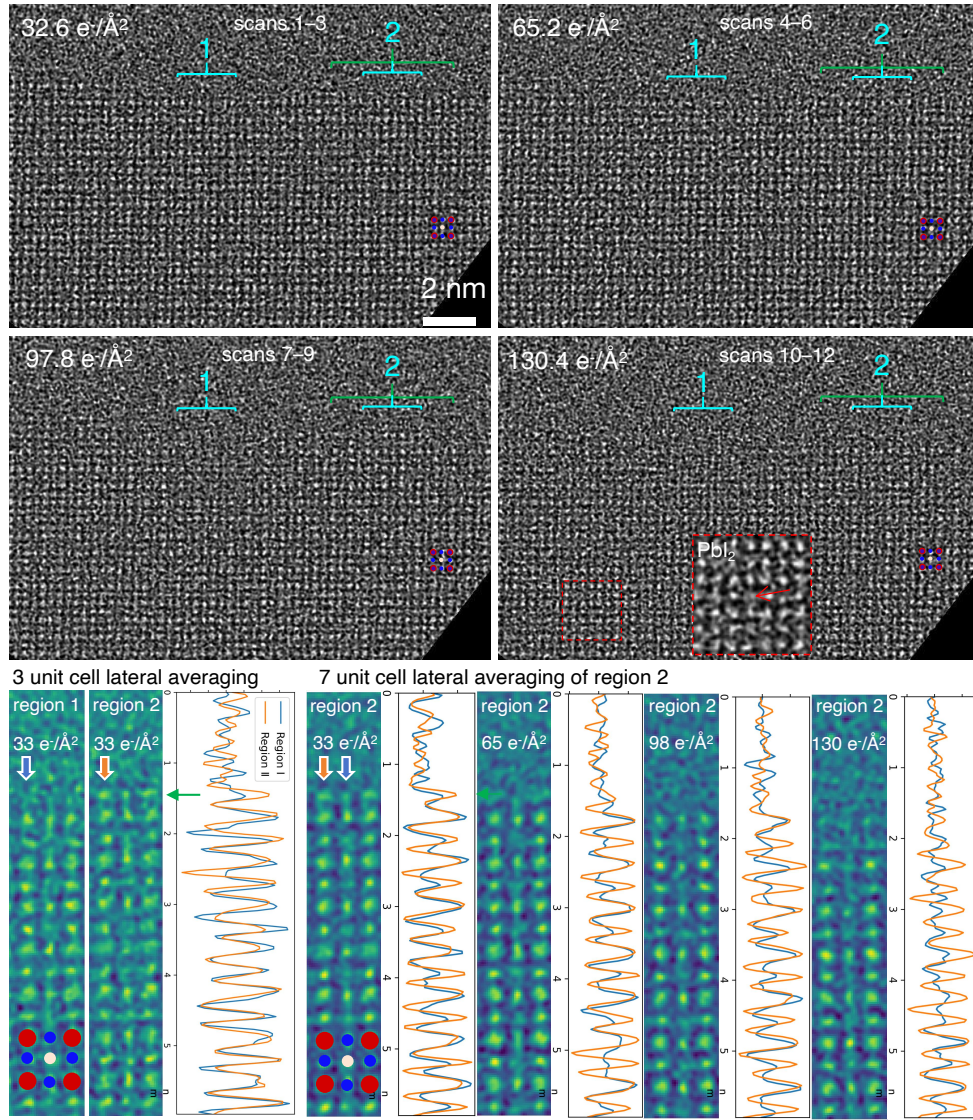
perovskite, the columns in this area all display a similar brightness in the images. This suggests that the columns have all become Pb containing. The lattice also appears to shrink a little.

This change is analysed in further detail in SFig. 44. As shown in the power spectrum in Fig. 44b, the initial perovskite structure of MAPbI₃ is characterized by the presence of Pb-I-Pb (110) planes with a unit cell spacing of 6.3 Å and a plane-to-plane spacing of 3.1 Å. After damage, the new phase exhibits a lattice spacing of 2.5 Å between its now apparently identical planes, which corresponds to the (200) planes of Pb metal. PbI₂ does not have a crystal plane with a 2.5 Å spacing. The closest spacings are the (003) planes at 2.41 Å and the (102) and ($\bar{1}$ 12) planes at 2.68 Å. However, these planes are not mutually perpendicular, so the presence of the PbI₂ phase can be ruled out here. Therefore, we conclude that Pb crystallite forms in this region. This seems reasonable, as the iodine content here is low due to the damage, and therefore there is likely insufficient iodine available to form PbI₂ particles.



SFig. 42 LAADF imaging and analysis of the edge shown in Fig. 3 of the main text. The top images show a wider field of view of the region as the cumulative dose increases with three scans used for each image. A region of PbI₂ that forms in the interior is highlighted in the red box. An enlarged view of the red boxed region is shown with a red arrow pointing to a former MA site that appears to have been filled with Pb. The three unit cell averaging is extended further into the material compared to the main text, with the left column of columns being used for their line profiles as indicated by the blue and orange arrows. The green arrow points to the terminating layer. The seven unit cell averaging of region 2 as a function of accumulated dose is obtained from the top images using the unit cells indicated by the green brackets. The line profiles are taken down the left Pb-I columns and the central MA-I columns.

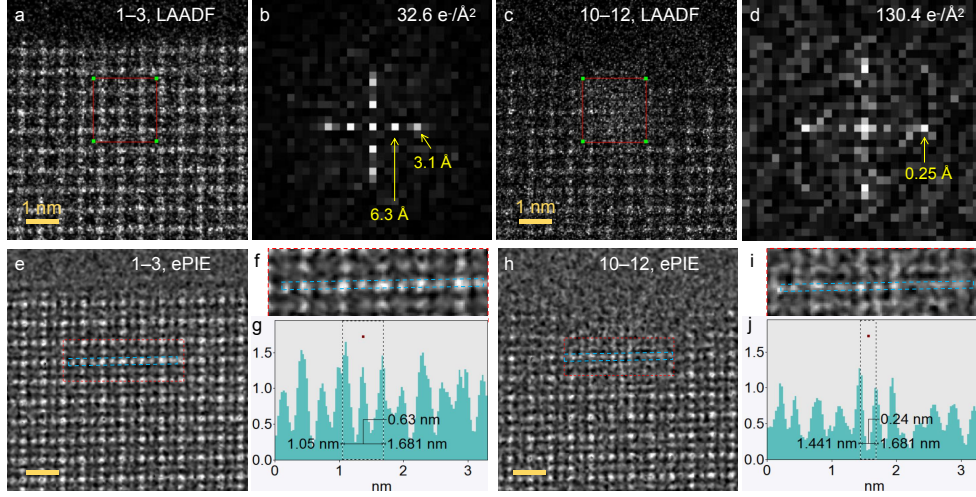
Similar cases of Pb metal formation during the damage of the MAPbI₃ were also observed at other edges such as the one displayed in SFig. 45. This phenomenon



SFig. 43 SFB imaging and analysis of the edge shown in Fig. 3 of the main text. The top images show a wider field of view of the region as the cumulative dose increases with three scans used for each image. A region of PbI_2 that forms in the interior is highlighted in the red box. An enlarged view of the red boxed region is shown with a red arrow pointing to a former MA site that appears to have been filled with Pb. The three unit cell averaging is extended further into the material compared to the main text, with the left column of columns being used for their line profiles as indicated by the blue and orange arrows. The green arrow points to the terminating layer. The seven unit cell averaging of region 2 as a function of accumulated dose is obtained from the top images using the unit cells indicated by the green brackets. The line profiles are taken down the left Pb-I columns and the central MA-I columns.

is consistent with the structural damage observed in the large-area SAED patterns: Pb nanocrystallites form only in localized regions of the MAPbI_3 nanosheets where iodine deficiency is present, while the majority of the area transforms into PbI_2 as we observed elsewhere such as in SFig. 49 and describe in the next section. This insight suggests that the intensity of the (200) and (220) diffraction spots in the electron beam-induced damage patterns (SFig. 6) can be used to estimate the proportion of iodine-deficient regions.

Region 2 of the edge shown in Fig. 3, with its lower level of edge I vacancies compared to region 1, appears to decay more slowly and steadily. This can best be seen in the dose series of seven unit cell averaging of region 2 displayed in SFigs. 41–43. While the three unit cells were selected for averaging for the comparison with region 1 to contain



SFig. 44 Phase transition from MAPbI₃ to Pb metal. **a**, LAADF image from the summation of scans 1 to 3, with the selected region of interest highlighted by the red box. The highlighted region corresponds to region 1 in Fig. 3. **b**, Power spectrum of the area corresponding to the red box. **c**, The LAADF image from the summation of scans 10 to 12 after sustained electron beam damage, with a clearly damaged region highlighted in the red box. **d**, The corresponding power spectrum shows a lattice spacing of 0.25 nm, which does not belong to MAPbI₃ or PbI₂, and is most likely the (200) plane of Pb. **e**, ePIE image of the same region shown in **a**, with the red rectangular area shown expanded in **f**. **g**, Line profile taken along the Pb-I columns. **h**, ePIE image of the same region shown in **c**, with the red rectangular area shown expanded in **i**. **j**, Line profile of **i** taken along the same columns as the line profile in **g**.

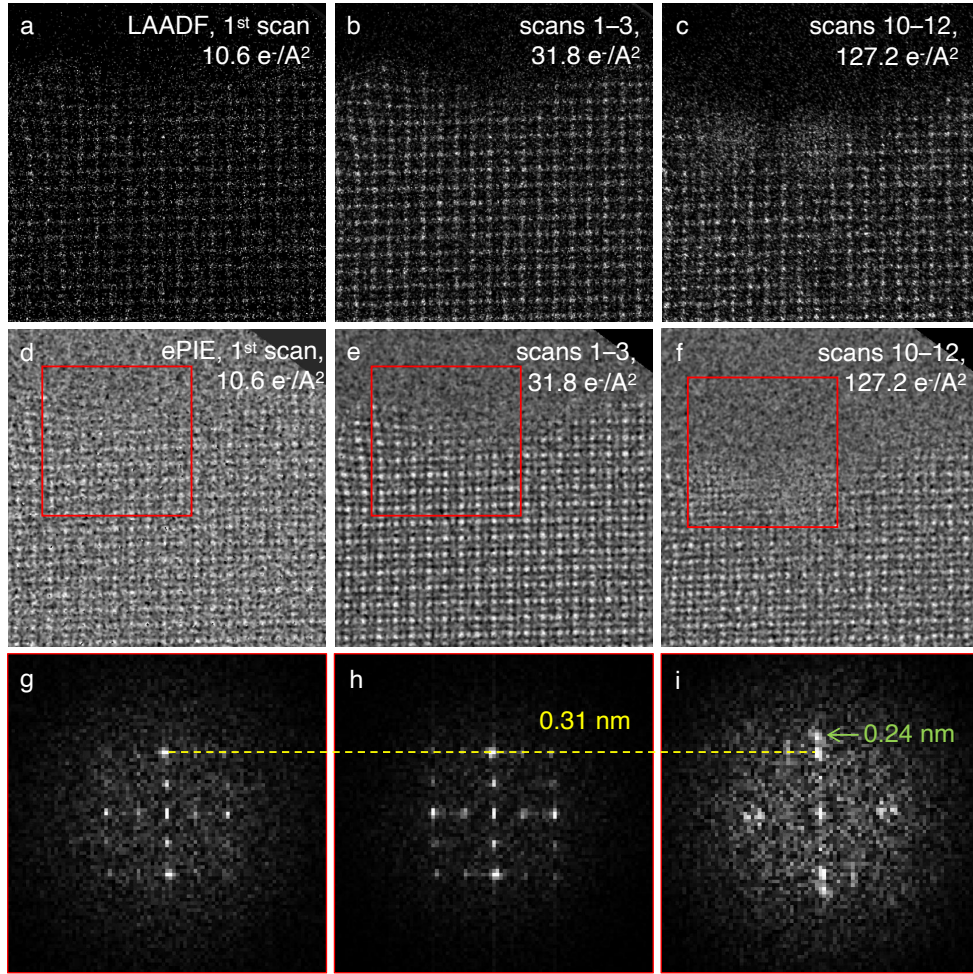
the edge region most clearly initially containing vacancies in region 1, the seven unit cells selected for the wider area around region 2 appear more uniform. Using the wider area for lateral unit cell averaging allows each snapshot in the dose series to have a higher signal. As is seen in the images, the damage causes the material near the edge to become steadily dimmer as the dose increases, indicating a loss of material. The closer to the edge the columns are the more quickly they become dimmer, although it appears material is being lost several unit cells into the material but at a lower rate. Despite the apparent loss of atoms the remaining material retains the perovskite structure, unlike the more rapidly damaged region 1.

SFig. 46 presents another example of sample edge instability caused by iodine vacancies, as observed in the left region of SFig. 46b. A noticeable vacancy containing iodine site is marked by the red arrow on the left, which is clearly evident in the line profile below. Here, the intensity of the outermost iodine layer is significantly lower than that of the inner iodine layer. On the right side, a more unstable defect is observed, which was completely damaged after the first scan and rapidly underwent continuous degradation.

Effect of internal defects on stability

We observe a variety of defects inside our MAPbI₃ and a substantial variation in the damage rate according to the characteristics of these defects. Some defects appear to be more stable than the pristine material, while others damaged far faster, with some even damaging almost instantly, despite the low dose of each scan.

The defect shown in Fig. 4a–c of the main text is an example of an unstable defect. Additional ePIE images of the area containing the defect are shown in SFig. 47. The first scan already shows a defective region, and the damage spreads in the otherwise tetragonal perovskite as the dose increases in each additional scan. Although it is not the most rapid expansion of damage in the first scan, the expansion seen when including scans two and three is still faster than damage would appear in the pristine material, where the relatively subtle transition to the orthorhombic phase occurs only after 32 e[−]/Å². By 64 e[−]/Å² the damage has become much more significant than a

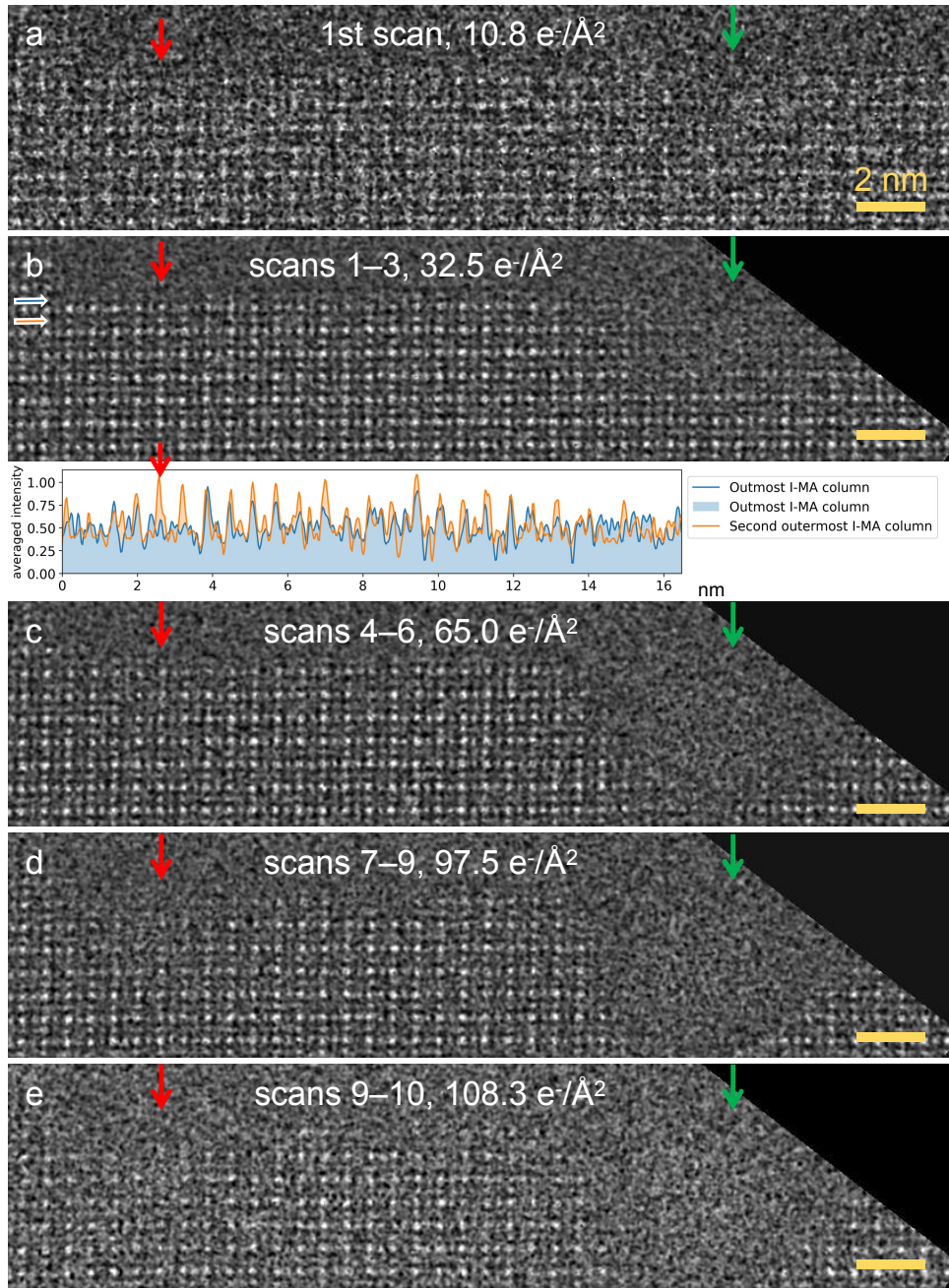


SFig. 45 Phase transition from MAPbI₃ to Pb metal. **a–c**, LAADF images from the first scan, scans 1–3 and 10–12. **d–f**, The corresponding ePIE images, with the red rectangular areas used for the power spectra shown in **g–i**.

transition to orthorhombic as well, with a significantly enlarged darker region likely resulting from material loss, and an area that resembles Pb metal appearing in the bottom left of the damaged region. Power spectra from the higher dose images of this region show spots matching the 2.5 Å lattice spacing of Pb metal.

SFig. 48 shows two more examples of unstable internal defects. These damage especially rapidly. The first defect shown in the top part of the figure damages significantly during the first scan, so it is difficult to determine the initial structure exactly. The power spectrum of the first scan shows spots corresponding to MAPbI₃, suggesting a possible defective MAPbI₃ structure. The second scan shows a darkening of the defect region as the damage expands, which is likely due to material loss already by 21.2 e[−]/Å². Again we wish to compare this to the greater than 32 e[−]/Å² at which the pristine material begins to transition to the orthorhombic phase. By 127 e[−]/Å² the damaged region has expanded and a particle of Pb metal has formed in the top part of the damaged region as can be seen from the contrast in the figure and the power spectra of the area displaying the characteristic spots of Pb metal.

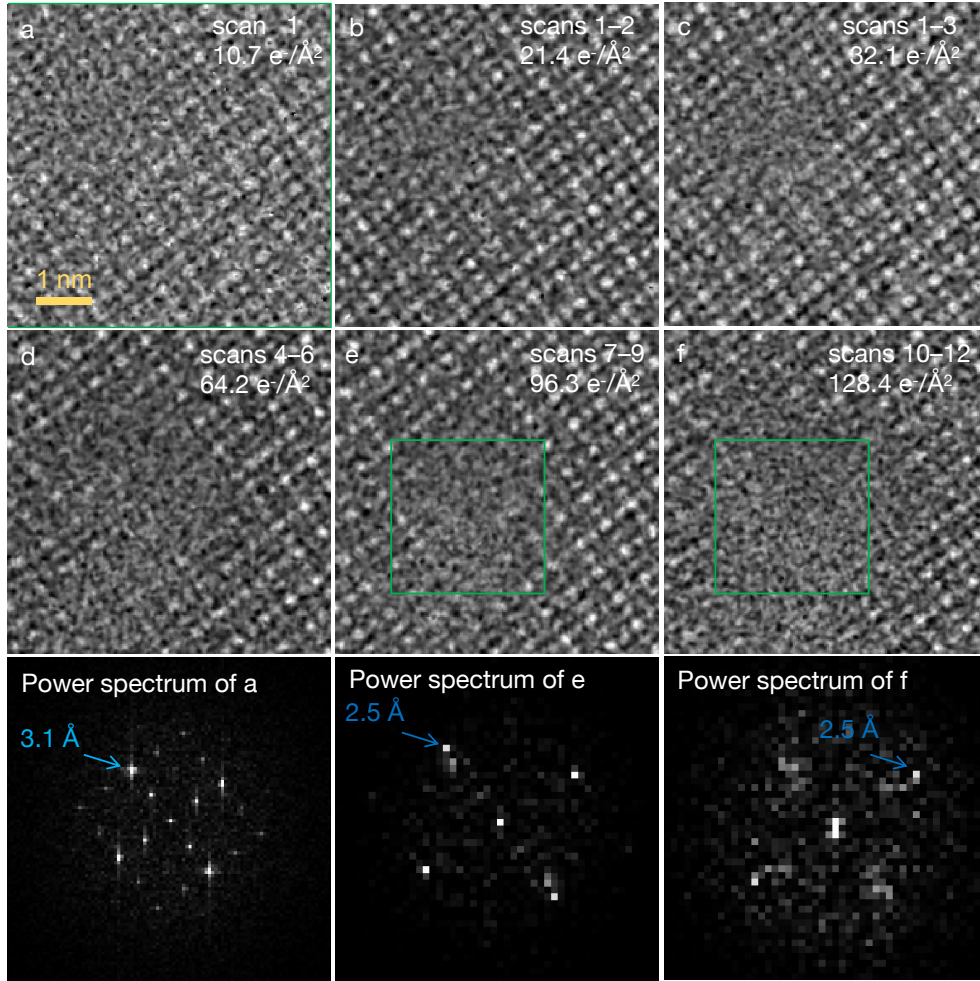
The second defect in SFig. 48 shown in the bottom part of the figure, does not show significant obvious darkening in the first 12.6 e[−]/Å² scan. By 37.8 e[−]/Å², a dose where the pristine material is only beginning to transition to orthorhombic, significant darkening indicative of material loss has occurred. Furthermore, the contrast of the columns at the centre of the defect has become uniform and the lattice appears to have shrunk slightly, consistent with Pb metal already forming. As the scans continue, the



SFig. 46 Significant variations in edge stability caused by different defects. **a**, ePIE image from the 1st scan. Small defects are difficult to image with only $10.8 \text{ e}^-/\text{\AA}^2$; however, the edge does appear to be a flat (110) plane around the red arrow which points to the location of a vacancy containing I site that becomes more clear in the ePIE image from scans 1–3 in **b**. Large-scale structural damage is visible at the site indicated by the green arrow on the right. The intensity profiles are taken along the planes indicated by the blue and orange arrows, comparing the edge I and MA columns (blue) to those in the next layer within the material (orange). The intrinsic defects in the right region led to a rapid collapse of the surrounding structure within 3 scans and $39 \text{ e}^-/\text{\AA}^2$ in the right region.

presence of Pb metal becomes clearer, and by $113 \text{ e}^-/\text{\AA}^2$ only Pb spots are present in the power spectrum of the blue box area from which the Pb metal has begun to expand beyond.

In comparison, the defects shown in Fig. 4d and g are far more stable than these unstable defects and the pristine material, appearing to remain unchanged up to around $100 \text{ e}^-/\text{\AA}^2$, many times the dose that the unstable defects we just discussed exhibit



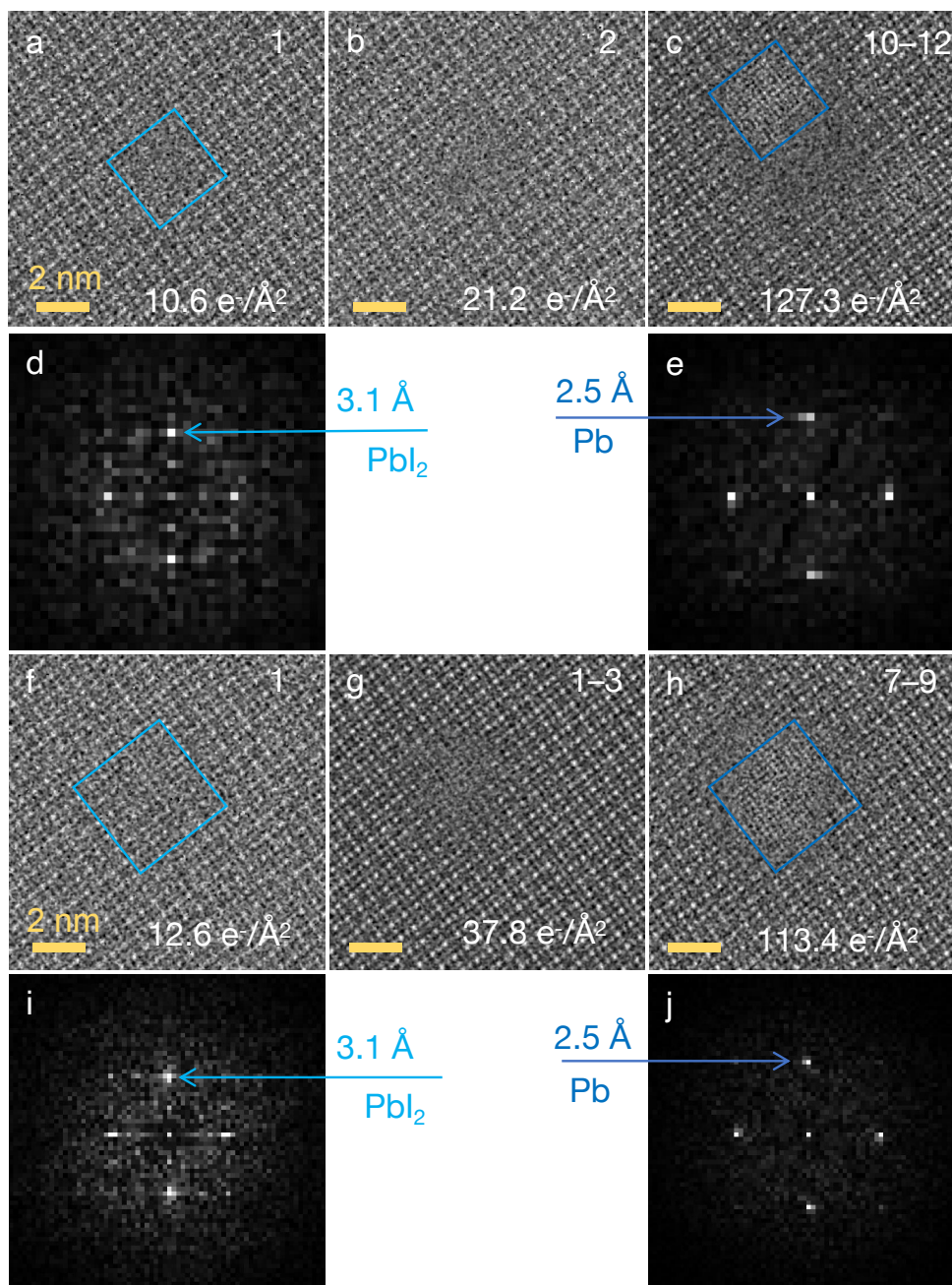
SFig. 47 Additional imaging of the defective region shown in Fig. 4a–c showing its damage evolution. **a–f**, A series of ePIE phase images using the dose fractionated data indicated. The power spectra are collected from the regions enclosed in green boxes.

damage and much more dose than the pristine material withstands before transitioning to the orthorhombic phase. Further LAADF images of the regions containing the defects shown in Fig. 4d and g are shown in SFig. 49, from which it can be seen that they remain relatively small above $100 \text{ e}^-/\text{\AA}^2$, with the defect shown in Fig. 4g only growing a little up to $209 \text{ e}^-/\text{\AA}^2$ (SFig. 49b–c).

SFig. 50 shows $100 \text{ e}^-/\text{\AA}^2$ ePIE and LAADF image simulations based on the identified structures of the Fig. 4d and g defects shown in the models of Fig. 4. The simulations used the same microscope parameters as the experiments. These are a good match with the experimental images, and therefore confirm the model is a good representation of the structure of these defects.

The most obvious differentiating feature in these stable defect structures is the presence of a significant amount of Pb vacancies, around which these defects are centred. While there are I vacancies present, the proportion of Pb vacancies is higher in the stable defects. This is in contrast to areas forming Pb metal in which I vacancies are dominant and fewer Pb vacancies are present. Keeping in mind that we do not observe a significant variation in the damage rate with the amount of MA vacancies, this suggests that I vacancies are the dominant driver of damage in MAPbI_3 .

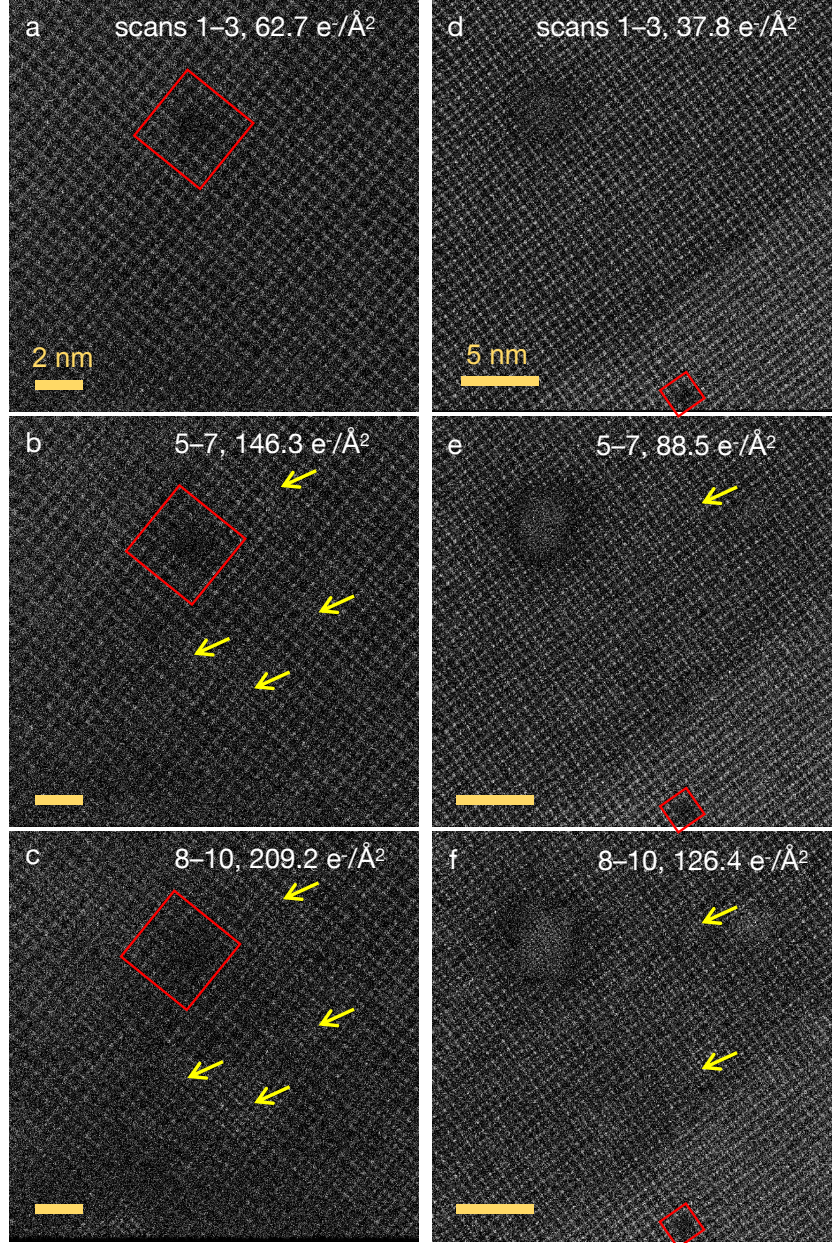
Estimating the net ionic charge of these defect centres we find the unstable defects are positively charged while the unstable defects are negatively charged. The estimates are based on the estimated occupations of their atomic columns, as described in the



SFig. 48 Two additional unstable defects in the internal regions. **a–c**, ePIE images from the 1st, 2nd, and 10-12th scans of a defect. **d–e**, Power spectra corresponding to **a** and **c**, respectively. **f–h**, ePIE images of another defect from the 1st scan, and scans 1–3, 1–9. The damaged structures of these two defects are most likely Pb particles, as determined by the lattice spacings. **i–j**, Power spectra corresponding to **f** and **h**, respectively.

next section. We hypothesise that the net positive charge associated with the loss of negatively charged I ions, the only negatively charged species present, facilitates halide ion migration which accelerates structural degradation. Conversely, when more positively charged Pb atoms are lost compared to I atoms, the resulting net negative charge seems likely to suppress halide ion migration, and therefore slow structural collapse. The more severe the I deficiency of a region the more negatively charged it will be and the more rapidly it is likely to degrade.

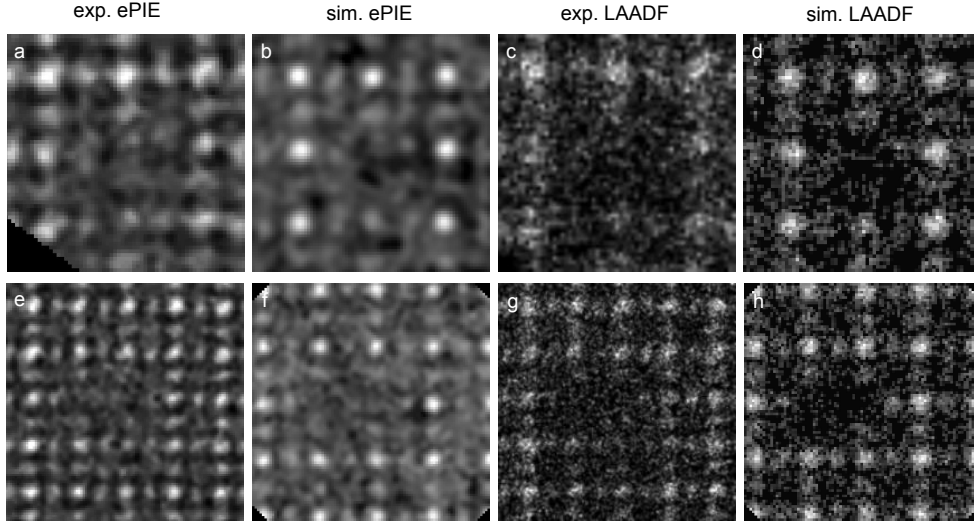
In interior regions where no defects are initially apparent, some areas gradually transition to PbI_2 . In this transition the columns of light MA molecules are replaced by heavier Pb and I atoms to form Pb-I columns. This behaviour is most clearly observed



SFig. 49 Phase change from MAPbI₃ to PbI₂ illustrated by LAADF images. The left column shows the area around the Fig. 4g,h defect, while the right shows the area adjacent to the Fig. 4d,e defect. The yellow arrows indicate locations where PbI₂ is generated, and the red boxes in a and d corresponds to the locations used in Fig. 4h, and Fig. 4e, respectively. The numbers before the electron dose represent which scans are summed to increase the signal to noise ratio.

in the Z-contrast LAADF images. An example is seen in SFig. 42 in the region highlighted in the red box. SFig. 49 also shows regions of PbI₂ forming. Although some form relatively near the obvious defects we discussed earlier, they do not appear to be an obvious result of the expansion of the defects themselves. It seems more likely these are the result of separate I vacancy formation, and their appearance in regions not connected with the obviously already defected regions suggests this transformation is an easily occurring common phenomenon. In contrast, in regions with severe iodine deficiency, the lack of sufficient iodine to form PbI₂ leads to the eventual formation of elemental Pb crystallites as we observe at unstable defects such as those in SFig. 48.

Overall, it appears that I vacancies are the dominant force controlling the rate of damage with high concentrations leading to rapid damage at doses as low as $11 \text{ e}^-/\text{\AA}^2$,



SFig. 50 Comparison of simulated and experimental imaging for the two stable defects shown in Fig. 4 using the models shown there. **a–d**, show the Fig. 4d,e defect with -0.86 charge. **e–h**, show the Fig. 4g,h defect with -0.13 charge. The simulated dose is $100 \text{ e}^-/\text{\AA}^2$.

whereas regions without obvious iodine vacancies remain stable to significantly higher doses. In these more stable regions, I vacancies eventually form leading to the gradual formation of PbI_2 above at least $65 \text{ e}^-/\text{\AA}^2$ as the primary decomposition product. The variation in damage rates and decomposition products provides indirect evidence of a variation in the I distribution that may be inherent to the material.

Estimation of defect charge states

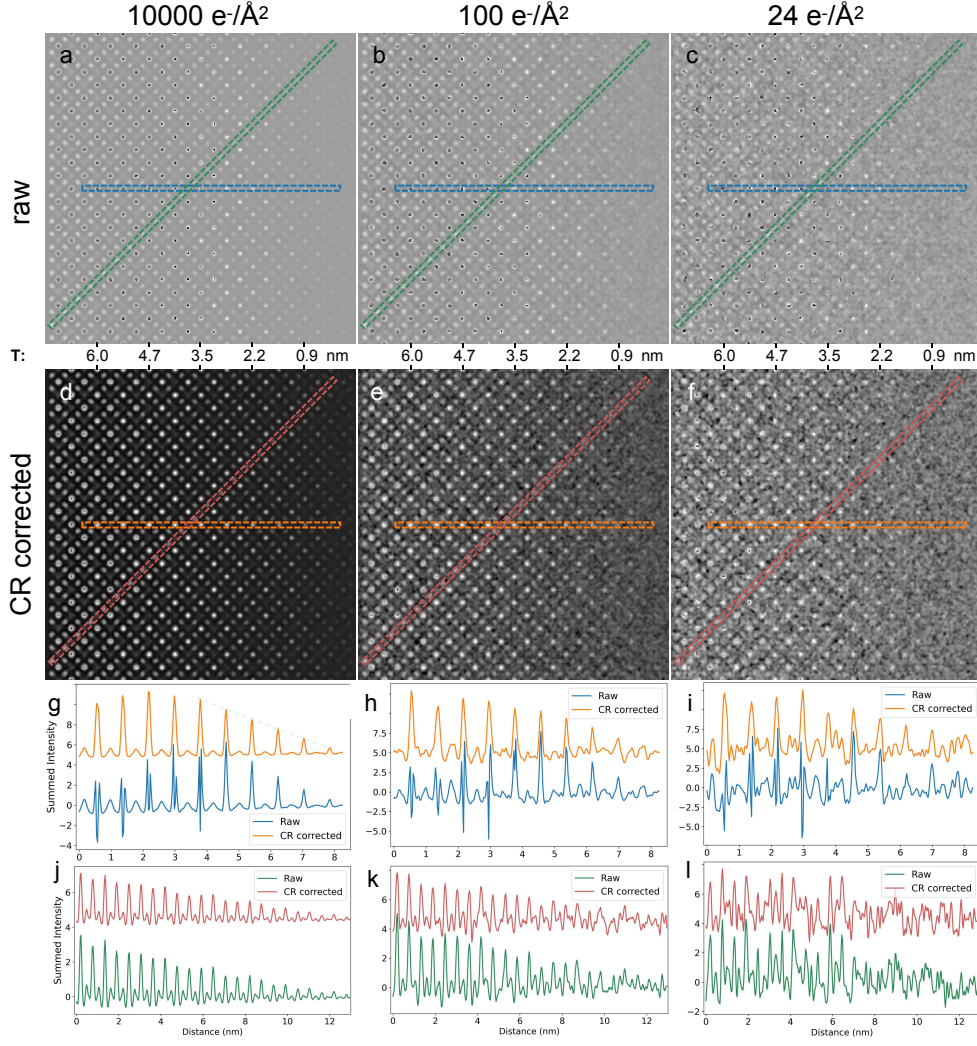
Given the ionic nature of MAPbI_3 , composed of MA^+ , Pb^{2+} , and I^- ions organized into MA^+ , PbI^+ , and I^- columns in the projection in which imaging was performed, we can obtain an estimate of the overall charge of a defect based on the loss of cations and anions.

To quantify the occupations in the defects relative to those in the pristine material based on the phase images we made three key assumptions:

1. The pristine area outside the defect used for our quantification is of uniform thickness, and the phase variations within the same column type in the pristine region are primarily due to noise.
2. The pristine region can be assigned a net charge of zero.
3. The atom columns exhibiting higher intensities represent a higher probability of containing more atoms.

While phase images can be complex, simulations show that the phase in ptychography images generally does increase with the number of atoms in an atomic column aside from any unaddressed issues with contrast reversals. This can already be seen in our simulations of vacancies, and in previous papers^{27,28} In the present case the contrast reversals have generally been removed by the phase offset method, and with the thin nanosheets the scope for the total numbers of atoms removed from a column is limited.

However, to assess the phase–thickness relationship in more detail, we simulated the ePIE images shown in SFig. 51 with the wedge shaped model shown in SFig. 14. At the relatively high dose of $10,000 \text{ e}^-/\text{\AA}^2$ the raw phase exhibits little noise, and increases linearly up until 2.8 nm in thickness for all types of columns. Above this contrast reversals occur in the centre of the Pb-I columns, reducing their overall phase. However, once we apply the phase offset we optimized for the thickness of our sample and use in our images unless otherwise noted, the phase becomes linear for all columns



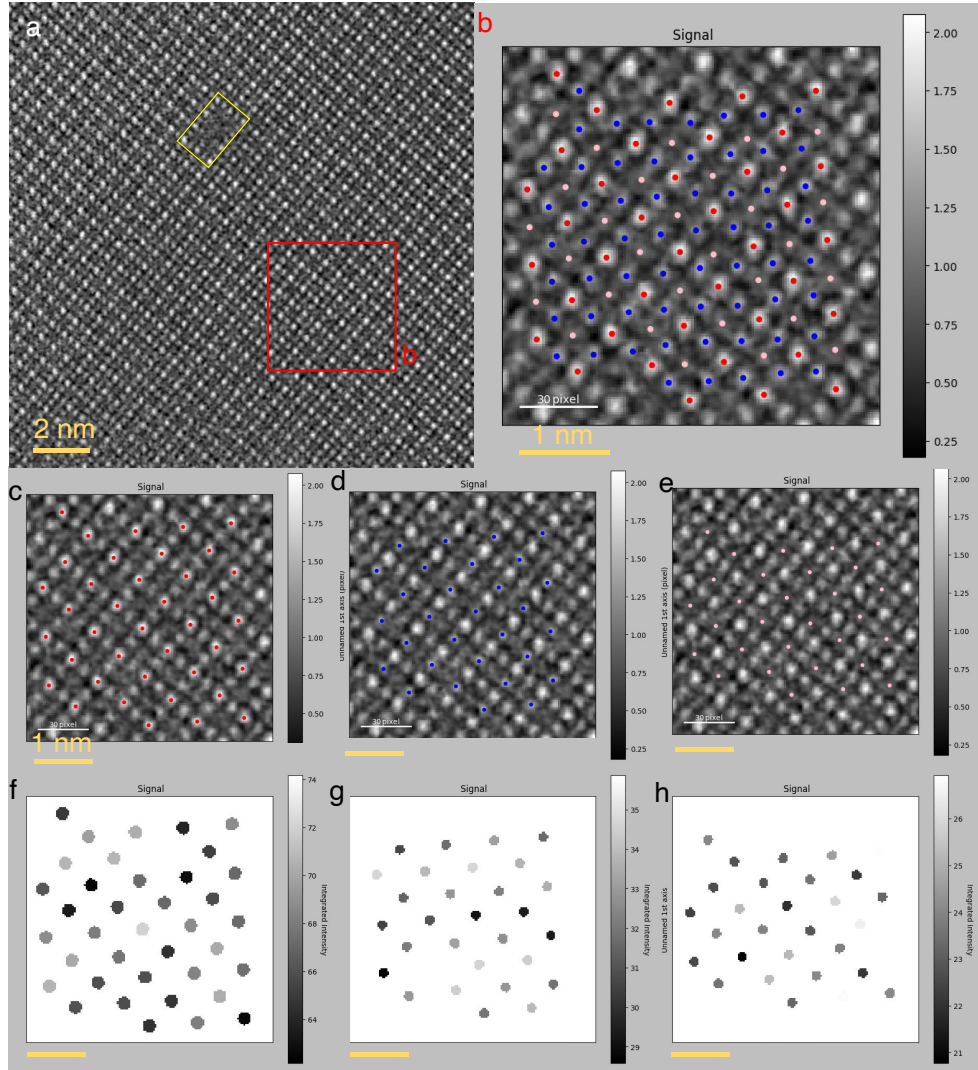
Sfig. 51 Ptychographic simulations of the wedge-shaped model, with thickness (T) decreasing from left to right. **a–c**, Raw ptychographic phase images simulated at different electron doses. **d–f**, Contrast reversal corrected versions. Profiles from thick to thin across the **g–i** Pb-I and MA columns and **j–l** I and MA columns before and after contrast reversal correction at each dose. The regions used for the profiles are marked in **a–f** with matching colours.

for all thicknesses up to that of our sample, 3.8 nm, and significantly beyond. The contrast reversals do start to reappear as the thickness increases sufficiently beyond the thickness in our experiments. A single phase offset clearly only works for a finite range of thickness, as seems only to be expected given how the correction works. Therefore the phase of the Pb-I columns also begins to decrease above about 4.7 nm, but this does not matter for our present purposes as our sample does not reach this thickness. Therefore the contrast reversal correction ensures that the ptychography responds to the linear increase in thickness with a linear increase in phase across all column types in the range of thickness of our sample.

Naturally, as the dose is reduced the images become more noisy, but continue to display an overall linear decrease of the phase with the decreasing thickness as expected. The individual line profiles sample only a single column of each type at each thickness, and therefore are more susceptible to displaying deviations from linearity due to noise than the whole images. However, the $100 \text{ e}^-/\text{\AA}^2$ profiles remain relatively strong, and even the $24 \text{ e}^-/\text{\AA}^2$ profiles, which are naturally much more noisy, show an overall decreasing trend from the 3.8 nm thickness of our sample. Therefore assumption 3 seems sufficiently valid for the purposes of our estimates.

Quantitative analysis method

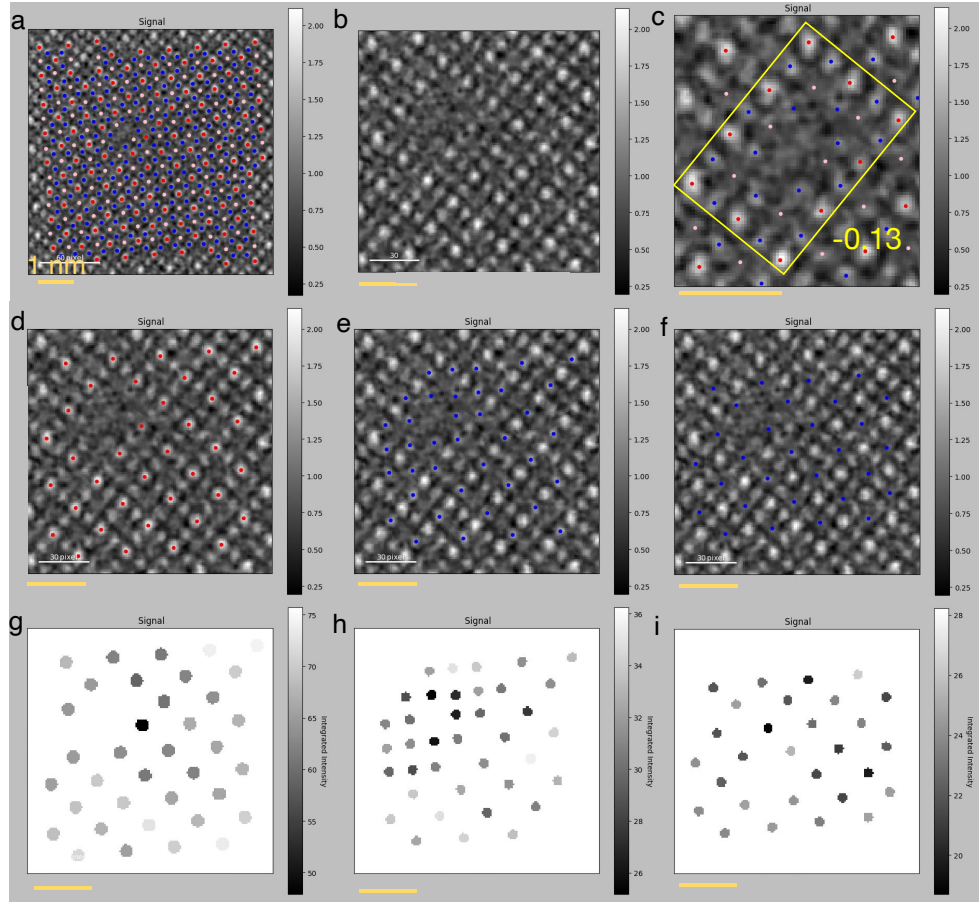
Atomic columns were located by computing the centre of mass of individual atomic columns in the phase offset corrected data using the Atomap package as illustrated in S Figs. 52 and 53, which show the same internal defect as in Fig. 4g of the main text, but also without cropping, so that the larger pristine area surrounding it is visible. Atomap was then used to assign an “intensity” to each atomic column based on the phase. The integration radii were set to 4 pixels (0.13 nm) for Pb-I columns, and 3 pixels (0.10 nm) for I and MA columns.



S Fig. 52 Atomap identification of the atomic column centres and quantification of their “intensities” for the region containing the defect shown in Fig. 4g. **a**, A wider field of view version of the ePIE image shown in Fig. 4g with the defect highlighted in the yellow box. **b**, Enlarged view of the indicated pristine region in **a**. Red, blue, and pink dots indicate the centres of the Pb-I, I, and MA atomic columns as determined by Atomap. The individual Atomap results are shown for the Pb-I **c,f**, I **d,g** and MA **e,h** columns with the quantified “intensities” showing the summed intensities. Note that the brightest columns are white and therefore are not visible in the quantification results.

Estimation of Pristine Column Standard Deviations with an Ideal Model

Based on the assumption of uniform thickness, we constructed an atomically flat model of the structure at the experimental thickness and performed image simulations at a variety of doses as shown in S Fig. 54. Using Atomap, we quantified the ‘intensity’ distributions of the different atomic columns (MA, Pb-I, and I) and calculated the



SFig. 53 Atomap identification of the atomic column centres and quantification of their “intensities” for the defect shown in Fig. 4g. **a**, Atomap identification of the column centres in the area of the defect with red, blue, and pink dots for Pb-I, I, and MA respectively. **b**, Enlarged view of the defect containing area. **c**, Further enlarged view of the defect centre with the bounding box used for the calculation of its charge in yellow. **d–f**, Identification of the centres of Pb-I, I, and MA atomic columns. **g–i**, The intensity distribution of Pb-I, I, and MA atomic columns. Note that Atomap displays the highest intensity columns in white and these are therefore not visible.

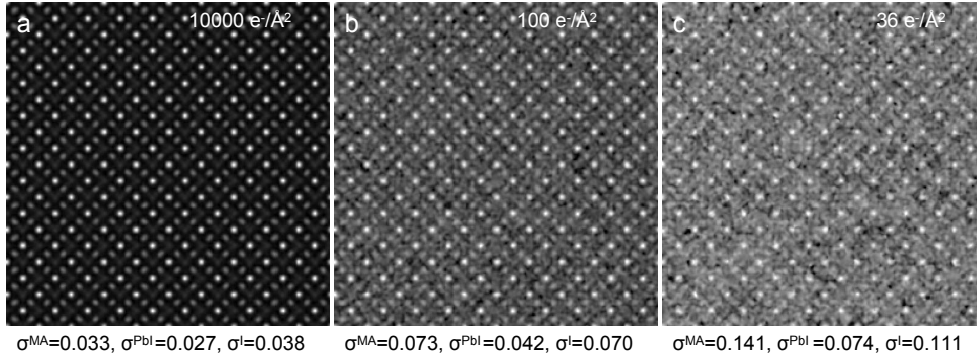
corresponding standard deviations (σ^{MA} , σ^{PbI} , and σ^{I}), which represent measurement error caused purely by Poisson statistical noise.

Estimation of Experimental Column Standard Deviations

Analysis of defect-free regions in experimental images yields experimental standard deviations of $\sigma^{\text{MA}} = 0.12$, $\sigma^{\text{PbI}} = 0.065$, $\sigma^{\text{I}} = 0.086$ for the data used in Fig. 4a using a total dose of $32.1 \text{ e}^-/\text{\AA}^2$. The standard deviations seem in reasonably good agreement with the $\sigma^{\text{MA}} = 0.141$, $\sigma^{\text{PbI}} = 0.075$, $\sigma^{\text{I}} = 0.111$ of the $36 \text{ e}^-/\text{\AA}^2$ simulation. Note that we do not expect a perfect agreement given the experimental structure is likely not perfectly flat, and there is also significant potential for small amounts of mistilt with a very thin sample such as this.

The data used for the images displayed in Figs. 4d and 4g use roughly $100 \text{ e}^-/\text{\AA}^2$. Comparing to the $\sigma^{\text{MA}} = 0.073$, $\sigma^{\text{PbI}} = 0.042$, $\sigma^{\text{I}} = 0.070$ of the $100 \text{ e}^-/\text{\AA}^2$ simulation, the experimental standard deviations in pristine regions of these datasets again appear generally inline with the experiments. For the dataset corresponding to Fig. 4d we obtain $\sigma^{\text{MA}} = 0.078$, $\sigma^{\text{PbI}} = 0.036$, $\sigma^{\text{I}} = 0.055$, and $\sigma^{\text{MA}} = 0.092$. For that of Fig. 4g, we obtain $\sigma^{\text{MA}} = 0.092$, $\sigma^{\text{PbI}} = 0.057$, $\sigma^{\text{I}} = 0.075$.

Quantitative Estimation of the Net Charge of Defect Regions



SFig. 54 Standard deviation analysis from simulated ptychography. **a–c**, Normalized phase images simulated using the wedge-shaped model under different electron doses. σ^{MA} , σ^{PbI} , and σ^{I} represent the standard deviations corresponding to the MA, Pb-I, and I atomic columns, respectively.

For each column type we sum the quantified intensities of all the columns within a box defining our region of interest, applying the rule of scaling edge intensities by 1/2 and corner intensities by 1/4 to account for the boundary excluding parts of columns. The total intensity for each type of column within the box is divided by the average intensity of that column type in a pristine region to give the effective number of fully occupied columns of that type within the box, C ,

$$N_{\text{eff}}^{\text{C}} = \sum_{i=1}^{N^{\text{C}}} \frac{I_i^{\text{C}}}{I_{\text{PA}}^{\text{C}}}, \quad (1)$$

where N^{C} is the number of column type C in the box, I_i^{C} is the integrated intensity of the i th column type C inside the box and I_{PA}^{C} is the average intensity of column type C in the pristine region. For example if our box contains 4 I columns that are fully occupied, we will obtain approximately $N_{\text{eff}}^{\text{C}} = 4$ after we sum the intensities of the I columns within the box and divide by the average I column intensity in the pristine region. If, however, we have 4 I columns that are half occupied we will obtain at total of 2 because they have half the occupancy. However, it should be noted that $N_{\text{eff}}^{\text{C}}$ can also take on non-integer values.

An estimate of the net charge of the region of interest, the defect, can then be obtained multiplying the effective number of columns, $N_{\text{eff}}^{\text{C}}$, of each type by their net charge and summing the result. In equation form we can write the net charge of the defect

$$Q = q^{\text{PbI}} \sum_{i=1}^{N^{\text{PbI}}} \frac{I_i^{\text{PbI}}}{I_{\text{PA}}^{\text{PbI}}} + q^{\text{I}} \sum_{j=1}^{N^{\text{I}}} \frac{I_j^{\text{I}}}{I_{\text{PA}}^{\text{I}}} + q^{\text{MA}} \sum_{k=1}^{N^{\text{MA}}} \frac{I_k^{\text{MA}}}{I_{\text{PA}}^{\text{MA}}} \quad (2)$$

where q^{C} is the charge on each column of type C, N^{C} is the total number of columns within the region of interest box of type C, I_i^{C} represents the integrated intensity of the i th column of type C within the box, and I_{PA}^{C} represents the average intensity of the column type as determined from a pristine region in the same dataset. Using the charges of $q^{\text{PbI}} = 1$, $q^{\text{I}} = -1$, and $q^{\text{MA}} = 1$ this can be recast as

$$Q = \sum_{i=1}^{N^{\text{PbI}}} \frac{I_i^{\text{PbI}}}{I_{\text{PA}}^{\text{PbI}}} - \sum_{j=1}^{N^{\text{I}}} \frac{I_j^{\text{I}}}{I_{\text{PA}}^{\text{I}}} + \sum_{k=1}^{N^{\text{MA}}} \frac{I_k^{\text{MA}}}{I_{\text{PA}}^{\text{MA}}}, \quad (3)$$

or more concisely

$$Q = N_{\text{eff}}^{\text{PbI}} - N_{\text{eff}}^{\text{I}} + N_{\text{eff}}^{\text{MA}}, \quad (4)$$

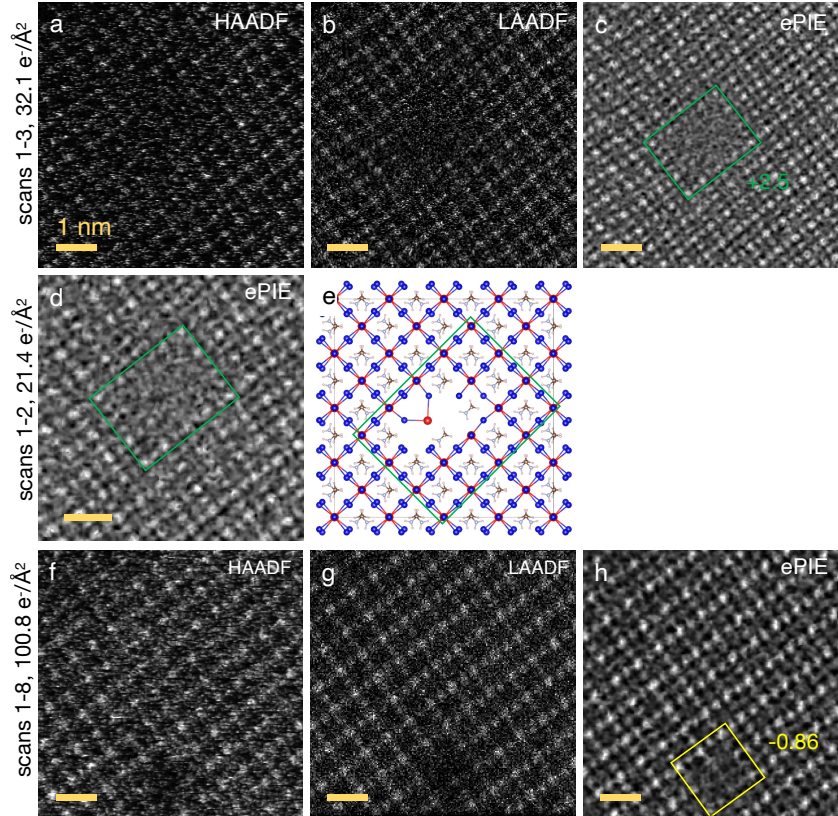
and the uncertainty can be expressed as

$$\sigma_Q = \left[\sum_{i=1}^{N^{\text{PbI}}} \left(\sigma^{\text{PbI}} \frac{I_i^{\text{PbI}}}{I_{\text{PA}}^{\text{PbI}}} \right)^2 + \sum_{j=1}^{N^{\text{I}}} \left(\sigma^{\text{I}} \frac{I_j^{\text{I}}}{I_{\text{PA}}^{\text{I}}} \right)^2 + \sum_{k=1}^{N^{\text{MA}}} \left(\sigma^{\text{MA}} \frac{I_k^{\text{MA}}}{I_{\text{PA}}^{\text{MA}}} \right)^2 \right]^{\frac{1}{2}}. \quad (5)$$

The estimated net charges are calculated to be 2.5 ± 0.56 for the defect in Fig. 4a, -0.86 ± 0.20 for the defect in Fig. 4d and -0.13 ± 0.31 for the defect in Fig. 4g. The defect in Fig. 4d is clearly negative, and while the error bar for that of Fig. 4g extends into positive charge, the most likely charge for the defect is also negative. The uncertainty is significantly larger for Fig. 4a than the others because of its much lower dose, but is clearly significantly positively valued and well separated from the Fig. 4d and g defects.

Additional images and model for the defects shown in Fig. 4

SFig. 55 shows the defects of Fig. 4a and d within the context of the wider areas in which they are contained. The green and yellow boxes indicate the bounding regions used for each for the charge calculations. SFig. 55e shows a model of the discernible atoms within the Fig. 4a defect. Due to the limited contrast and resolution at a dose of only $32.1 \text{ e}^-/\text{\AA}^2$, the proposed configuration should be interpreted with caution. As the dose is significantly lower than those used for Fig. 4d and Fig. 4g, the proposed structure here is less reliable than those in Fig. 4f and Fig. 4i for the other defects in Fig. 4.



SFig. 55 HAADF, LAADF, and ePIE imaging of the wider areas containing the defects shown in **a–d** Fig. 4a and **f–h** Fig. 4d. The green and yellow boxes indicate the bounding boxes used for estimating the net ionic charge. The dose is both the accumulated dose and that used for the images. **e**, A possible defect structure inferred from low signal-to-noise ptychographic images.

References

- [1] Whitfield, P. *et al.* Structures, phase transitions and tricritical behavior of the hybrid perovskite methyl ammonium lead iodide. *Scientific reports* **6**, 35685 (2016).
- [2] Rothmann, M. U. *et al.* Atomic-scale microstructure of metal halide perovskite. *Science* **370**, eabb5940 (2020).
- [3] Zhang, S. *et al.* Deterministic synthesis of a two-dimensional mapbi3 nanosheet and twisted structure with moiré superlattice. *Journal of the American Chemical Society* **146**, 27861–27870 (2024).
- [4] Yang, H. *et al.* Simultaneous atomic-resolution electron ptychography and z-contrast imaging of light and heavy elements in complex nanostructures. *Nature Communications* **7**, 12532 (2016).
- [5] Gao, C. *et al.* Overcoming contrast reversals in focused probe ptychography of thick materials: An optimal pipeline for efficiently determining local atomic structure in materials science. *Applied Physics Letters* **121** (2022).
- [6] Zhang, S. *et al.* Moiré superlattices in twisted two-dimensional halide perovskites. *Nature Materials* **23**, 1222–1229 (2024).
- [7] Egerton, R. F. *Electron energy-loss spectroscopy in the electron microscope* (Springer Science & Business Media, 2011).
- [8] Jannis, D. *et al.* Event driven 4d stem acquisition with a timepix3 detector: Microsecond dwell time and faster scans for high precision and low dose applications. *Ultramicroscopy* **233**, 113423 (2022).
- [9] Song, K. *et al.* Atomic-resolution imaging of halide perovskites using electron microscopy. *Advanced Energy Materials* **10**, 1904006 (2020).
- [10] Li, Y. *et al.* Unravelling atomic structure and degradation mechanisms of organic-inorganic halide perovskites by cryo-em. *Joule* **3**, 2854 (2019).
- [11] Chen, S. *et al.* Transmission electron microscopy of organic-inorganic hybrid perovskites: myths and truths. *Science Bulletin* **65**, 1643–1649 (2020).
- [12] Rothmann, M. U. *et al.* Structural and chemical changes to $\text{CH}_3\text{NH}_3\text{PbI}_3$ induced by electron and gallium ion beams. *Advanced Materials* **30**, 1800629 (2018).
- [13] Velazco, A., Béch , A., Jannis, D. & Verbeeck, J. Reducing electron beam damage through alternative STEM scanning strategies, Part I: Experimental findings. *Ultramicroscopy* **232**, 113398 (2022).
- [14] Jannis, D., Velazco, A., B   , A. & Verbeeck, J. Reducing electron beam damage through alternative STEM scanning strategies, Part II: Attempt towards an empirical model describing the damage process. *Ultramicroscopy* **240**, 113568 (2022).
- [15] McGovern, L., Futscher, M. H., Muscarella, L. A. & Ehrler, B. Understanding the Stability of MAPbBr_3 versus MAPbI_3 : Suppression of Methylammonium Migration and Reduction of Halide Migration. *The Journal of Physical Chemistry Letters* **11**, 7127–7132 (2020).
- [16] Nandal, V. & Nair, P. R. Predictive Modeling of Ion Migration Induced Degradation in Perovskite Solar Cells. *ACS Nano* **11**, 11505–11512 (2017).

- [17] Mkhoyan, K. A., Silcox, J., Ellison, A., Ast, D. & Dieckmann, R. Full recovery of electron damage in glass at ambient temperatures. *Phys. Rev. Lett.* **96**, 205506 (2006).
- [18] Allen, L., McBride, W., O’Leary, N. & Oxley, M. Exit wave reconstruction at atomic resolution. *Ultramicroscopy* **100**, 91–104 (2004).
- [19] Van Dyck, D., Jinschek, J. R. & Chen, F.-R. ‘big bang’ tomography as a new route to atomic-resolution electron tomography. *Nature* **486**, 243–246 (2012).
- [20] Yuan, B. & Yu, Y. High-resolution transmission electron microscopy of beam-sensitive halide perovskites. *Chem* **8**, 327–339 (2022).
- [21] Lu, Y. *et al.* Imaging electron beam-sensitive twisted hybrid perovskite bilayers at one-angstrom resolution. *ACS nano* **19**, 4279–4288 (2025).
- [22] Shi, H., Lu, Y., Wang, Z., Zhang, S. & Yu, Y. An improved soft-thresholding exit wave reconstruction for imaging beam-sensitive materials. *Ultramicroscopy* 114154 (2025).
- [23] Nellist, P. D. & Pennycook, T. J. Making the link between adf and 4d stem: Resolution, transfer and coherence. *Chinese Physics B* **33**, 116803 (2024).
- [24] Varnavides, G. *et al.* Iterative Phase Retrieval Algorithms for Scanning Transmission Electron Microscopy arXiv:2309.05250 (2024).
- [25] Maiden, A., Johnson, D. & Li, P. Further improvements to the ptychographical iterative engine. *Optica* **4**, 736–745 (2017).
- [26] Odstrčil, M., Menzel, A. & Guizar-Sicairos, M. Iterative least-squares solver for generalized maximum-likelihood ptychography. *Optics Express* **26**, 3108 (2018).
- [27] Yang, H. *et al.* Electron ptychographic phase imaging of light elements in crystalline materials using wigner distribution deconvolution. *Ultramicroscopy* **180**, 173–179 (2017).
- [28] Clark, L. *et al.* The effect of dynamical scattering on single-plane phase retrieval in electron ptychography. *Microscopy and Microanalysis* **29**, 384–394 (2023).
- [29] Hofer, C., Gao, C., Chennit, T., Yuan, B. & Pennycook, T. J. Phase offset method of ptychographic contrast reversal correction. *Ultramicroscopy* **258**, 113922 (2024).
- [30] O’Leary, C. *et al.* Phase reconstruction using fast binary 4d stem data. *Applied Physics Letters* **116** (2020).
- [31] Stroppa, D. G. *et al.* From stem to 4d stem: Ultrafast diffraction mapping with a hybrid-pixel detector. *Microscopy Today* **31**, 10–14 (2023).
- [32] Zhang, D. *et al.* Atomic-resolution transmission electron microscopy of electron beam-sensitive crystalline materials. *Science* **359**, 675–679 (2018).
- [33] Foroosh, H., Zerubia, J. B. & Berthod, M. Extension of phase correlation to subpixel registration. *IEEE transactions on image processing* **11**, 188–200 (2002).
- [34] Maiden, A., Humphry, M., Sarahan, M., Kraus, B. & Rodenburg, J. An annealing algorithm to correct positioning errors in ptychography. *Ultramicroscopy* **120**, 64–72 (2012).

- [35] O’Leary, C. M. *et al.* Contrast transfer and noise considerations in focused-probe electron ptychography. *Ultramicroscopy* **221**, 113189 (2021).
- [36] Lazić, I., Bosch, E. G. T. & Lazar, S. Phase contrast STEM for thin samples: Integrated differential phase contrast. *Ultramicroscopy* **160**, 265–280 (2016).