Twinning in MAPbI₃ at room temperature uncovered through Laue neutron diffraction

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The crystal structure of MAPbI₃, the signature compound of the hybrid halide perovskites, at room temperature has been a reason for debate and confusion in the past. Part of this confusion may be due to twinning as the material bears a phase transition just above room temperature, which follows a direct group–subgroup relationship and is prone to twinning. Using neutron Laue diffraction, we illustrate the nature of twinning in the room temperature structure of MAPbI₃ and explain its origins from a group-theoretical point-of-view.

Hybrid halide perovskites have caused a nouvelle vague in the research of photovoltaic absorber materials.¹² Within 10 years of their first consideration as solar absorbers, perovskite solar cells have reached over 25% efficiency, close to the theoretical limit of such devices. While the rise in efficiency has provoked a huge interest in applied research—with some 4000 papers published on halide perovskites in 2019,³ the efforts in structural elucidation have not always been commensurate. The crystal structure of methylammonium lead iodide (MAPbI₃), for instance, has been a matter of debate and several, partially contradicting studies since its introduction into solar cells, although MAPbI₃ clearly is the signature compound of this family of materials.⁵⁻¹¹. One striking discrepancy in the structural characterisation of MAPbI₃ is the question as to whether it is ferroelectric at room temperature or not.¹²⁻²⁰ The generally accepted space group of MAPbI₃ at room temperature is I₄/mcm⁵,⁷,⁹,¹¹, a centrosymmetric space group that would not allow bulk ferroelectricity or further non-linear effects. However, there are striking reports of such behaviour and we have recently discussed a deviation from the centrosymmetric crystal structure to a polar one (in space group I₄cm) through the influence of the molecular cation on its surrounding iodide anions.²¹

One important factor in the structural elucidation of hybrid halide perovskites in general and MAPbI₃ in particular is their tendency for twinning. Commonly, this twinning can be associated with the phase transition from the high-temperature phase in the cubic aristotype to the lower temperature hettotypes. Ferroelectric compounds, for instance, do normally show heavy domain twinning, as this allows the compensation of the internal electric field through the formation of oppositely polarised domains. In the case of MAPbI₃, at room temperature, this would correspond to inversion twins in this case, as the inversion symmetry is lost between I₄/mcm and I₄cm. However, the observed domain structure of MAPbI₃ exhibits further twin laws, so that twinning solely due to the loss of inversion symmetry would not explain this fully. To account for this further twinning, namely ferroelastic twinning was proposed as primary driver.²³⁻²⁶ Nonetheless, it should be emphasised that ferroelasticity and ferroelectricity are not mutually exclusive but can exist in the same phase, as for instance in BiFeO₃.²⁷

At higher temperatures, MAPbI₃ crystallises in the cubic perovskite aristotype (space group Pm₃m). When cooling below 330 K, the crystal structure changes into a tetragonal hettotype in I₄cm or I₄/mcm, where the latter is the centrosymmetric and the former the polar space group choice. Since the question of centrosymmetry is not touched in this work, we give both options in the further discussion. It needs to be mentioned that the structural differences are small, which makes the distinction between the choices even more subtle. Finally, at 160 K, the crystal structure of MAPbI₃ transitions into an orthorhombic perovskite subgroup (space group Pnma)¹¹,¹². The high temperature phase transition is reasonably close to room temperature, and, consequently, below the typical synthesis temperature in conventional solution based processes as well as in other important techniques, such as the inverse temperature gradient method.³⁰ Therefore, MAPbI₃ necessarily undergoes a phase transition when synthesised through such a way. Herein, we studied a crystal that was synthesised at room

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temperature and that was never heated above the cubic-tetragonal phase transition. This study is
seconded by an in-depth explanation of twinning in MAPbI₃ in order to make the thematic approachable for
the wider scientific community.

Twinning in MAPbI₃ through the cubic-to-tetragonal phase transition. In a nutshell, twinned
crystals are not composed of one single orientation, but are built up from different individual or domains. These
domains or individual are, however, not randomly oriented but related through point symmetry elements, which
must not be element of the space group symmetry, and can be categorised through the twinning element in
inversion twins (related through inversion at a twin inversion centre), rotation twins (related through rotation
at a twin axis) or reflection twins (related through reflection at a twin plane). For twinning that occurs during
a phase transition, the twinning element needs to be a symmetry element of the high-symmetry structure,
which is lost during the phase transition. Therefore, it is crucial to understand the group-subgroup relationships
through the cubic-to-tetragonal phase transition in MAPbI₃. Prior work on twinning in the perovskite BaTiO₃
may be taken as a first guidance.

The phase transition from the cubic perovskite aristotype in Pn̅3m to the room temperature perovskite
structure in I4cm (I4/mcm) follows a direct group-subgroup relationship and hence makes a second order
phase transition possible. Even more importantly, the I3 translationengleiche symmetry descent from Pn̅3m to
P4/mmm (Fig. 1) gives rise to the formation of triple twinning along the lost symmetry elements, i.e. the four
threefold rotation axes. It is probably more illustrative to approach this from the unit cell dimensions (which
are, of course, a consequence of the symmetry operations): while all three unit-cell axes are constrained to be
equal in the cubic crystal system, only a and b have to fulfil this constraint in the tetragonal crystal system with
c being independent of the other two. When transitioning from cubic to tetragonal, the choice of which of the
three cubic unit-cell axes becomes the independent c-axis is arbitrary and hence three equivalent possibilities
exist, standing perpendicular to each other.

A complication of the cubic-to-tetragonal transition in MAPbI₃ is the symmetry descent from P4/mmm
into the body-centred klassengleiche subgroup I4cm (I4/mcm; Fig. 1). This transition is accompanied with a 45°
rotation of the unit cell in the ab-plane and thus a change of the lattice constants in the manner
a_{t-F} = \sqrt{2}a_c and c_{t-F} = 2c_c (where the index t – I signifies the tetragonal body centred structure and c the cubic one). This has as
consequence that direction and plane denominations change in a rather complex manner when transforming from
Pn̅3m to I4cm (I4/mcm). Therefore, we chose a non-standard setting of the tetragonal unit cell in F4mc
(F4/mmm), where a_{t-F} = 2a_c and c_{t-F} = 2c_c (with t – F standing for tetragonal face centred; Fig. 1). Although this
setting violates the Bravais rules of choosing the smallest possible unit cell, it has as major advantage that the
directions correspond to each other in the tetragonal and the cubic lattices. Where appropriate, we will give
directions and lattice planes for both settings. At room temperature, the lattice constants a and c with regard
to the non-standard setting F4mc (P4/mmm) are not greatly different (a_{t-F} = 12.507 Å, c_{t-F} = 12.622 Å)\(^2\), which
means that the diffraction spots of the different domains are close to each other to the extent that they nearly
overlap completely—similar to a pseudo-merohedral twinning.

The twinning element in the cubic-to-tetragonal descent can, essentially, be any symmetry element lost during
the phase transition. Most prominently, the aforementioned three-fold axes, which are defining the cubic
crystal system, can become the twinning element. However, rotation twinning through 90° rotations along the
<100>_c axes or 180° rotation along the <101>_c axes (Fig. 2) are also possible as well as reflection twinning on the [011]_c-planes\(^2\). These twin laws correspond to the respective four-fold and two-fold rotation symmetries that are lost when c becomes unequal from a and b in the transition from the cubic aristotype to the tetragonal
structure. However, these different twin laws are only seemingly contradictory, as they all represent the same phenomenon of axis permutations, i.e. of mapping the unique c axis on either a or b axis (Fig. 2). The difference between the different twin laws is the relative orientation of the a and b axes, which are symmetry equivalent in the tetragonal crystal system and are linked through four-fold rotation along the [001] axis and {100} mirror planes. Furthermore, a non-centrosymmetric space group would only be visible in the reflection intensities, not in their positions. A 120° rotation around one of the <111> directions would hence produce twins that look identical to 90° twins around the <100> directions or 180° twins around the <101> directions. The same also

Figure 2. View of the crystal structure of MAPbI₃ along the a-axis (with crystallographic axes according to the non-standard setting F4mc (F4/mmc)) (a). Representations of different rotation twin axes (red lines) in the cubic (blue) and non-standard tetragonal (green) unit cells (b–d), and the resulting crystal structures with the twinning elements acting upon the original crystal structure (e–g). The molecular cation is simplified as orange spheres for the sake of visibility.
applies to the [011], reflection twins, that have been reported for this system. Finally, it needs to be noted that the presence of these twin laws does not rule the possibility of further inversion twinning out and, therefore, does not allow a conclusion on the absence of ferroelectricity: Inversion twinning would only be discernible under very specific measurement conditions, for instance at the proximity of an element’s absorption edge, since Friedel’s law is not strictly valid for these cases.

Two structural effects occur during the cubic-to-tetragonal phase transition within the crystal structure of MAPbI₃: (1) the molecular cations are no longer completely disordered, but orient along a number of preferred orientations and (2) a tilting of the [PbI₆] octahedra, both of which phenomena are probably interlinked. (1) The molecular cation in the cubic crystal structure is completely disordered and rotates freely in its cuboctahedral void. In the room temperature crystal structure, though, it is still dynamically and structurally disordered but resides in well-defined preferential orientations in correspondence to its surrounding anions. (2) The network of corner-sharing octahedra is undistorted in the cubic aristotype, i.e. all Pb–I–Pb angles are at 180° as dictated by the cubic symmetry. At room temperature, however, the octahedra are still untilted in one direction, i.e. the Pb–I–Pb angles along the crystallographic c-axis remain at 180°, but they are tilted within the ab-plane. From a crystallographic point of view, the PbI₆ units no longer form exact octahedra in the tetragonal symmetry, but rather a square-planar bipyramid. The tilting of the inorganic [PbI₆] octahedra affects the size of the A-cation void (the place of the molecular MA+ cation) and on the electronic structure of the compound, which is mainly determined by the inorganic [PbI₆] octahedra network.

Neutron Laue diffraction on MAPbI₃. When applying diffraction methods, one is faced with two distinct problems: on the one hand powder diffraction techniques do not allow to distinguish between 4/mcm and 4/mcc as both belong to the same diffraction group, i.e. they bear exactly the same translation symmetry and hence have the exact same systematic extinctions. Therefore, the only reflections that could differ overlap entirely. Single crystal studies, on the other hand, are flawed by heavy twinning of the crystals under consideration, which is a consequence of the phase behaviour of this compound: MAPbI₃ shows several structural phase transitions as outlined above.

Applying neutron Laue diffraction to study twinning in methylammonium lead iodide has two major advantages: first, neutrons interact much less strongly with matter than X-rays as neutrons are scattered on the atomic nuclei only, while X-rays are scattered on the electron shell. This implies that larger samples are necessary for neutron diffraction, but also less absorption for the electron rich atoms, such as lead and iodine. The larger size of the samples in neutron diffraction is indeed an advantage for this study, as these crystals typically exhibit more pronounced twinning. Furthermore, the architecture of the instrument is adapted to the use of larger crystals, which is not typically the case for X-ray diffraction with normally much smaller beam sizes of f = 500 µm. The chosen setup allowed us to measure crystals of several millimetres size. Furthermore, Laue diffraction has a unique property: by using a polychromatic (“pink”) beam, each individual wavelength constructs its own Ewald sphere and, therefore, allows measurements with static detectors. In a typical single wavelength experiment—which is the standard in X-ray diffraction—the reflections move in and out of the detector plane (i.e. the plane in which the detector records) when the lattice constants change, for instance due to temperature. Therefore, it is generally necessary to measure a crystal during a rotation. In Laue diffraction, on the other hand, the polychromatic light produces reflection spots regardless of lattice parameter changes, and a crystal rotation is not necessary. Using powder diffraction does not allow the distinction of individual domains, since the three-dimensional information of the reflection position is merged into a single dimension, the scattering angle. However, the twinned reflections appear, because more than one domain overlay in a very specific way that is only discernible in three dimensions.

Due to the heavy twinning of these crystals, it was impossible to index the neutron Laue patterns using the unit cell parameters of the tetragonal room temperature crystal structure in the space group 4/mcm (I4:1/mcm) directly. However, indexation was successful on basis of the cubic aristotype, as the differences in the reflection positions between the cubic aristotype and the tetragonal room-temperature structure are rather small. The hkl indices of the cubic indexing are given in Fig. 3, and can be linked to the tetragonal ones through the group-subgroup relationship between the two space groups (comp. Fig. 1). To distinguish the hkl indices in this work, tetragonal body centred, tetragonal face centred and cubic hkl indices are marked with an index t–I, t – F or c, respectively. Furthermore, we checked the successful indexation using the tetragonal subgroup P4/nmmn (see “SI”), which is an intermediate space group in the symmetry descent but still bears approximately the same lattice constants as the cubic aristotype. In essence all three axis permutations appear as equally acceptable solutions for the indexation.

Using a static crystal in a special sample environment, we conducted temperature-dependent measurements using a specific crystal orientation. Due to the sample environment, we were limited in the choice of orientation, which is why the orientations at room temperature and at controlled temperature differ. The Laue patterns clearly show a twinning at room temperature in a pseudo-merohedral way: the double-maxima of the spots under consideration lie very close to each other (Fig. 4a). However, the Laue spots are clearly split at 300 K (Fig. 4b,c). On heating towards the tetragonal-to-cubic phase transition temperature at 330 K, the spots merge more and more into one single spot as the reflections of the twins become equivalent and hence the twinning domains are being merged during this process. The smooth merging of the domains can be taken as an indicator for the fact that this phase transition is actually an order–disorder phase transition.

In order to prove the nature of the twinning at room temperature, we recorded a series of diffraction images while turning the crystal in increments of 1° around the ω-axis (i.e. the axis, on which the crystal is mounted and that is perpendicular to the beam path) without the heating equipment. What is observed in such an experiment is the movement of the diffraction spots through the detector plane, caused by diffraction at the same lattice plane from different wavelengths at different crystal rotations. According to Bragg’s law, the separation of reflections...
depends on the wavelength (as a simplification, the wavelength of the twinned reflections with very similar 
\(d\)-spacings shall be taken as equal) and becomes larger at longer wavelengths, since \(d\) and \(\lambda\) are proportional 
to each other. It can be observed that most reflections show a separation indicative of twinning, since they bear two 
reflections that are almost, but not completely, identical in \(d\)-spacing. As an example, this behaviour can be very 
well observed for the \(110t\) (200t and 020t) and 002t (002t) reflections (equivalent to the 010, reflections, 
Fig. 5). However, the 111c reflection behaves differently in that no splitting can be observed. Since all the lattice 
planes \{111\} still exhibit the same \(d\)-spacing in the tetragonal phase \{202\t or \{222\t\}, they are diffracted 
by the same wavelength and hence do not vary in spot separation in the detector plane. Consequently, the 111c 
reflection does not exhibit a change in splitting over its full way through the detector plane, in line with rotation 
twinning along the three-fold \(<111>\) axes. As we grew the crystals used in this experiment at room temperature, 
the twinning clearly does not stem from running through the cubic-to-tetragonal phase transition. Instead, 
a different symmetry between the crystallisation nuclei and the bulk material may be an explanation for this 
behaviour, where the nuclei have a higher symmetry than the bulk material.

Conclusion
We demonstrated the particularities of twinning in MAPbI\(_3\) by means of neutron Laue diffraction and explained 
the peculiarities of twinning in MAPbI\(_3\) from a crystallographic point-of-view. We could show intrinsic twin-
ing in crystals grown at room temperature, which have not been heated to the existence region of the cubic 
phase prior to the experiments. This latter gives a powerful insight into the crystallisation and growth process 
of MAPbI\(_3\) and supports the assumption of cubic crystallisation nuclei. This finding is important as it may allow 
more targeted thin film production procedures in the future, and more targeted studies on the crystallographic 
nature of the earlier crystallisation states will be highly beneficial.

Materials and methods
Single crystals for this study were grown using an antisolvent room temperature method described before\(^{16,21}\). 
Crystals were covered in acrylic lacquer to prevent oxygen and moisture destruction of the crystal.

Neutron Laue patterns were collected using the FALCON (Fast Acquisition Laue Camera for Neutrons) Laue 
diffactrometer at BER II research reactor (HZB). FALCON consists of two area detectors in backscattering and 
transmission position with four iCDD cameras each and total scattering area of 400 \times 400 mm\(^2\). A “pink” neutron 
beam with wavelength \(\approx 0.9–3.2\) Å and a neutron flux of 8 \times 10\(^6\) n/cm\(^2\)s is applied. For variable temperature meas-
urements, a detector distance for the Laue patterns was 168 mm, pattern acquisition time was 60 s. Temperature 
dependent measurements were carried out by means of a Stirling cooler based closed cycle cryostat providing 
sample temperatures from 150 up to 450 K\(^{36}\). Room temperature measurements were performed at a detector 
distance of 120 mm with an acquisition time of 180 s. By means of a rotation stage, \(\omega\)-scans were performed 
within the range of \(-120°\) and \(120°\). For indexing of the Laue patterns “Cologne Laue Indexation programme” 
CLIP\(^{37}\) was applied. Successful indexing was possible assuming perovskite cubic aristotype with a unit cell 
dimension of \(a = 6.3\) Å. Further, indexation was performed in the tetragonal subgroup \(P4/mmm\), as this subgroup

Figure 3. Indexation of a MAPbI\(_3\) Laue image at room temperature in the cubic aristotype in space group 
\(Pm\overline{3}m\) with \(a = 6.3\) Å. The colormap of the image was modified to increase the visibility of the Laue spots. The 
unaltered Laue image may be found as supplementary information.
Figure 4. Indexation of the transmission Laue image of MAPbI₃ at 300 K in the cubic aristotype (a). The colormap was modified to increase spot visibility. The unaltered Laue image may be found as supplementary information. The inverted image of the area selected around the 001 reflection (grey frame in a) is shown at variable temperature (b). Rectangular profile integration at different temperatures (c) was performed for the selected area shown in b).
still bears approximately the same unit cell dimensions of the cubic space group (see “SI”), but clearly shows the twinning through axis permutation.

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Author contributions
J.B. and S.S. conceived the original idea of the study. All authors developed the experimental strategy, J.B. and M.T. conducted the experiments. J.B. wrote the manuscript with input from all authors.

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