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Neutron powder diffraction study of the phase transitions in deuterated methylammonium lead iodide

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Abstract

We report the results of a neutron powder diffraction study of the phase transitions in deuterated methylammonium lead iodide, with a focus on the system of orientational distortions of the framework of PbI_6 octahedra. The results are analysed in terms of symmetry-adapted lattice strains and normal mode distortions. The higher-temperature cubic–tetragonal phase transition at 327 K is weakly discontinuous and nearly tricritical. The variations of rotation angles and spontaneous strains with temperature are consistent with a standard Landau theory treatment. The lower-temperature transition to the orthorhombic phase at 165 K is discontinuous, with two systems of octahedral rotations and internal distortions that together can be described by 5 order parameters of different symmetry. In this paper we quantify the various symmetry-breaking distortions and their variation with temperature, together with their relationship to the spontaneous strains, within the formalism of Landau theory. A number of curious results in the low-temperature phase are identified, particularly regarding distortion amplitudes that decrease rather than increase with lowering temperature.

Keywords: hybrid perovskites, Landau theory, neutron diffraction, spontaneous strain, phase transitions

(Some figures may appear in colour only in the online journal)

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1. Introduction

Methylammonium lead iodide, $(CH_3NH_3)PbI_3$ (denoted as MAPbI₃), forms a classic perovskite structure, with cornerlinked PbI₆ octahedra and with the methylammonium (MA) cation in the larger A site with 12 iodine neighbours. MAPbI₃ has attracted a huge interest in recent years because it shows a relatively high photovoltaic efficiency. Much of this is described in a special collection of papers entitled 'Lead halide perovskites for solar energy conversion' edited by Zhu [1], which includes reviews of work of the atomic structure, phase transitions and atomic dynamics [2, 3] as well as many other practical issues associated with the using MAPbI₃ in photovoltaic applications.

At ambient pressure MAPbI₃ displays three different phases, with transition temperatures of 327 K and 165 K. The crystal structures of the three phases are shown in figure 1. The high-temperature phase has the ideal cubic structure, with space group $Pm\overline{3}m$ [4]. The orientations of the MA cations are highly disordered in this phase, because the site symmetry $(m\overline{3}m)$ is much higher than the molecular symmetry (3m). The extent of the orientational disorder has been studied by ourselves through neutron total scattering and the reverse Monte Carlo method (to be submitted), showing that there is almost complete isotropic disorder.

The intermediate phase has tetragonal symmetry, space group I4/mcm, with rotations of the PbI₆ octahedra about the tetragonal axis and alternate layers having opposite rotations [5, 6], as seen in figure 1(b). In terms of the Glazer notation [7, 8], the distortion in the intermediate-temperature phase is denoted as $a^0a^0c^-$. There is evidence for progressive ordering of the orientations of the MA cations, although complete order is still not permitted by symmetry.

The low-temperature phase has orthorhombic symmetry, space group *Pnma* [5, 6], and the phase transition is discontinuous because there is no symmetry group–subgroup relationship between the structures of the orthorhombic and tetragonal phases. The octahedra now have rotations about the crystallographic [010] axis that are the same for adjacent layers, and equal rotations about the other two axes with opposite rotations in neighbouring layers, as described by Glazer notation $a^-b^+c^-$. The MA cations have ordered orientations in this phase, as can be seen in figure 1(c).

In addition to the initial diffraction studies to determine the crystallographic structures of the three phases [5], there has been one study of the variation of the elastic response of the crystal structure with temperature [9], and another study of the octahedral rotation in the intermediate-temperature phase [6]. In this paper we perform a more detailed analysis of the distortions of the PbI₃ network across the range of temperatures from 10-330 K, encompassing both phase transitions, using neutron powder diffraction measurements analysed with the Rietveld method. We identify the spontaneous strains and a number of ordered parameters associated with the distortion of the PbI₃ network, and use the framework of Landau theory to determine the symmetry-constrained relationships between strains and order parameters. We do not comment here on the orientational order. The details of orientational order determined by ourselves using neutron total scattering will be reported elsewhere.

2. Methods

2.1. Sample preparation

The sample of deuterated MAPbI₃ was synthesised using a method similar to that of method 1 described by Baikie et al [10]. A flask containing DI solution in D_2O (60% w/w; 4.56 g, 21.2 mmol) was cooled using liquid nitrogen and connected, by opening a tap, to a balloon containing anhydrous methylamine-d₅ gas, CD₃ND₂. The flask was allowed to warm to approximately 0 °C, after which 1.555 g (43.1 mmol) of methylamine was found to have condensed in it. An additional portion of DI solution in D₂O (60% w/w; 3ml) was then added. Separately, PbI2 (17.0 g, 36.9 mmol) was dissolved in DI solution in D₂O (60% w/w; 37.0 ml) and heated to 100 °C with protection from atmospheric moisture by a calcium chloride tube. The CD3ND3I solution was added to the PbI₂ solution and the mixture was allowed to cool to 55 °C over 75 min. The precipitate that had formed was then filtered off and dried in an oven at 100 °C overnight to give CD₃ND₃PbI₃ (10.17 g, 44%) as a black solid. Some iodine (purple vapour) was lost by sublimation as the product was dried.

2.2. Neutron powder diffraction experiments

The neutron powder diffraction measurements were performed on the POLARIS diffractometer [11] at the ISIS pulsed spallation neutron source in the United Kingdom. The sample temperature was controlled using a cryostat for temperatures below 300 K and a furnace for temperatures above 300 K. Measurements of the powder diffraction pattern were obtained for temperatures between 10–330 K in steps of 10 K. Data reduction procedures to give a set of diffraction patterns for each bank of detectors were performed using the Mantid software [12].

No attempt was made to account for beam attenuation by the sample or sample environment in the conversion of the data to a form suitable for Rietveld refinement.

2.3. Rietveld refinement method

Rietveld refinements were performed using the GSAS package [13] with the EXPGUI interface [14], using data from several different banks of detectors. The shapes of the Bragg peaks were modelled using the peak profile type 3, as described in the GSAS manual [13]. The background functions associated with each detector bank were described using Chebychev polynomials.

We used the structure model of Weller *et al* [5] as our starting point in each case, but with hydrogen (H) replaced by deuterium (D). To allow for the possibility of incomplete deuteration, our approach was to first perform a refinement on the data at 10 K (*Pnma* space group) with the aim to determine a set of effective H/D ratios for different atomic sites. This



Figure 1. Crystal structures of (a) $Pm\overline{3}m$ phase, (b) I4/mcm phase, and (c) Pnma phase of MAPbI₃, viewed down the [100], [001] and [010] axes respectively. Carbon and nitrogen atoms are shown as black and blue spheres, but in the case of the I4/mcm and $Pm\overline{3}m$ phases these sites are used for fitting only and are not expected to be good representations of the distribution of positions. The PbI₆ octahedra are shown as shaded polyhedra, showing no rotations for the high-temperature $Pm\overline{3}m$ phase, showing in-plane rotations with opposite rotations for adjacent layers in the intermediate I4/mcm phase, and showing rotations about all three axes in the low-temperature Pnma phase with adjacent layers in the plane of the diagram having the same rotations about the vertical [010] axis. The deuterium atoms are shown only for the *Pnma* phase, where their positions are ordered, and are coloured pink.

starting point was chosen both because of the high degree of order and because the effects of thermal vibrations are lowest; it is often found that there is a strong correlation between atomic displacement parameters and site occupancies. This refinement started with 100% occupancy of the D/H sites by D, and we allowed the site occupancies to vary subject to the constraints of identical site occupancies for all H/D atoms bonded to carbon atoms and, separately, all those bonded to nitrogen atoms. It was found that the sites bonded to carbon were fully occupied by D within the standard error given by the refinement, and so we repeated the refinement allowing site occupancies of only the D/H sites connected to nitrogen. This gave a fractional occupation by D of 0.654 ± 0.003 . These site occupancies were then held at these values for subsequent Rietveld refinements of data at all temperatures.

The data for temperatures 300–330 K showed a mixture of both tetragonal and cubic phases, consistent with previous work [6].

In truth, Rietveld refinement does not give significant information on the MA cations in the two disordered phases, because, of necessity, the continuous distribution of molecular orientations has to be represented by a set of discrete atomic sites. However, Rietveld refinement enables us to extract information about the PbI₃ network and of the lattice parameters, which are the focus of this study.

The results from the refinements of the crystal structures are given in appendix A, in tables A1–A7. The quality of the fits achieved is illustrated for each phase in figure A1, with agreement factors given in table A8. It should be pointed out that we did not attempt to refine an absorption coefficient, which means that the refined values of the atomic displacement parameters will be systematically lower than they should be, even negative at low temperatures. Nevertheless we report our refined values because they demonstrate well the systematic trend of increasing in value on heating as expected.

3. Results, analysis and discussion

3.1. Lattice parameters and spontaneous strains

The variations of the lattice parameters with temperatures are plotted in figure 2(a), where they are scaled by factors of 2 or $\sqrt{2}$ to better compare with each other and with the lattice parameters of the cubic phase. In the tetragonal phase we define the extrapolation of the cubic lattice parameter as $a_0 = (2a + c)/3$. We extrapolate a_0 to low temperature by using a function of the form [15]

$$a_0(T) = a_1 + a_2\Theta \coth(\Theta/T) \tag{1}$$

which describes both the linear dependence on temperature at high temperature and the limiting behaviour $\partial a_0/\partial T \rightarrow$ 0 as $T \rightarrow 0$. We chose a value $\Theta = 55$ K—we discuss this choice in the next subsection when we consider the spontaneous strains—and obtained fitted values $a_1 = 6.2168$ Å and $a_2 = 2.5 \times 10^{-4}$ Å K⁻¹. The value of a_2/a_1 represents the coefficient of linear thermal expansion at high temperature, equal to $3.9 \pm 0.1 \times 10^{-5}$ K⁻¹. This is similar in size to the coefficient of thermal expansion of the cubic phase of CsPbI₃, which has value $5.2 \pm 0.1 \times 10^{-5}$ K⁻¹ [16].

3.2. Spontaneous strains

The three regular spontaneous tensile strains associated with the two lower-symmetry phases are defined as

$$\epsilon_1^{I4/mcm} = \frac{a - \sqrt{2}a_0}{\sqrt{2}a_0};$$

$$\epsilon_2^{I4/mcm} = \frac{b - \sqrt{2}a_0}{\sqrt{2}a_0};$$

$$\epsilon_3^{I4/mcm} = \frac{c - 2a_0}{2a_0}$$
(2)



Figure 2. (a) Lattice parameters for the three phases of methylammonium lead iodide, where for the tetragonal phase we show $a/\sqrt{2}$ and c/2, and for the orthorhombic phase we show $a/\sqrt{2}$, b/2 and $c/\sqrt{2}$. Black filled circles represent *a*, blue filled circles represent *b* and red filled circles represent *c* in each phase. The open black circles represent the values of a_0 extrapolated from the cubic phase by means of the equation $a_0 = (2a + c)/3$ within the tetragonal phase, and the black curve represents the fitted extrapolation using equation (1). (b) Temperature-dependence of the axial strains ϵ_1 , ϵ_2 and ϵ_3 as defined in equations (2) and (3). (c) Temperature dependence of the symmetry adapted strains ϵ_a as defined by equation (4), ϵ_{tz} in the tetragonal phase (also equation (4)), and strains ϵ_5 and ϵ_{ty} in the orthorhombic phase as defined in equations (5). Open circles represent the corresponding strains formed by fitting with the order parameters as described in the text: equations (8)–(10).

Table 1. Symmetry mode analysis of possible distortions that contribute to the phase transition from space group $Pm\overline{3}m$ to Pnma, obtained using the AMPLIMODES tool [18]. The first two lines give the atomic structures in the two higher-symmetry phases. The amplitudes (normalised, units of Å) are those calculated for the crystal structure at 10 K, table 2.

IR	Space group	I1	I2	Amplitude	Comment
	Pm3m Pnma	(1/2, 1/4, 0) $(1/2 - \delta, 1/4, -\delta')$	(1/4, 0, 1/4) $(1/4 - \gamma, n, 1/4 - \gamma')$		
$\overline{M^+}$	D4/mbm	(1/2 1/4 0)	$(1/4 - 2^{i}) = (1/4 - 2^{i})$	1.16	Potation about [010]
R_4^+	Imma	(1/2, 1/4, 0) $(1/2, 1/4, -2\delta)$	$(1/4 - \gamma, 0, 1/4 - \gamma)$ $(1/4, \delta, 1/4)$	0.55	Rotations about [100] and [001]
R_5^{+}	Imma	$(1/2, 1/4, -2\delta)$	$(1/4, -\delta, 1/4)$	0.13	Distortions of the polyhedra
X_{5}^{+}	Cmcm	$(1/2 - \delta, 1/4, 0)$	(1/4, 0, 1/4)	0.15	Distortions of the polyhedra
M_2^+	P4/mbm	(1/2, 1/4, 0)	$(1/4+\gamma,0,1/4-\gamma)$	0.02	Distortions of the polyhedra

and

$$\epsilon_{1}^{Pnma} = \frac{a - \sqrt{2}a_{0}}{\sqrt{2}a_{0}};$$

$$\epsilon_{2}^{Pnma} = \frac{b - 2a_{0}}{2a_{0}};$$

$$\epsilon_{3}^{Pnma} = \frac{c - \sqrt{2}a_{0}}{\sqrt{2}a_{0}}.$$
(3)

By symmetry, in the tetragonal phase $\epsilon_1^{I4/mcm} = \epsilon_2^{I4/mcm}$. These three strains for both phases are shown in figure 2(b).

In the tetragonal phase we can define (now dropping the space group superscript labels) two symmetry-adapted spontaneous strains [17]:

$$\epsilon_{a} = \epsilon_{1} + \epsilon_{2} + \epsilon_{3}; \qquad \epsilon_{tz} = \frac{1}{\sqrt{3}}(2\epsilon_{3} - \epsilon_{1} - \epsilon_{2}).$$
 (4)

 ϵ_a represents the totally-symmetric volume strain, and ϵ_{tz} represents a shear strain that generates the tetragonal distortion with z as the unique axis. It has symmetry E_g , its partner being the orthorhombic strain $e_o = \epsilon_1 - \epsilon_2$, which is clearly of zero value in this case. Similarly, in the orthorhombic phase,

where the special axis is now *y*, we define the corresponding strains [17]

$$\epsilon_{\rm ty} = \frac{1}{\sqrt{3}} (2\epsilon_2 - \epsilon_1 - \epsilon_3); \qquad \epsilon_5 = \epsilon_1 - \epsilon_3. \tag{5}$$

We also have the volume strain ϵ_a defined in the same way as for the tetragonal phase. Here ϵ_{ty} is the corresponding tetragonal strain but now, using the standard definition of the space group setting, with what was the tetragonal axis now being along y. The symmetry is lowered to orthorhombic by the shear strain ϵ_5 .

The values of the symmetry-adapted spontaneous strains are shown in figure 2(c). At this stage, we want to make a point about the definition of Θ used in equation (1). Depending on the value of Θ , the symmetric volume strain ϵ_a can have a dependence on temperature that gives it a lower or higher negative value in the limit $T \rightarrow 0$. The choice of $\Theta = 55$ K was made to make the value of ϵ_a more-or-less constant at low temperature. This is, of course, somewhat arbitrary, and thus ϵ_a cannot be considered to be a reliable quantity for detailed analysis. On the other hand, the value of a_0 cancels in the definitions of the other symmetryadapted strains, which are therefore independent of the choice of Θ .



Figure 3. Atomic images of the five distortion modes associated with the structural transition from space group $Pm\overline{3}m$ to Pnma. All views are down the cubic [001] axis, although in the distorted phase these are given different directions by convention. The black lines show the outlines of the new unit cells generated by these distortions. Atomic coordinates are given in table 1. The distortions are deliberately exaggerated for display purposes.

Table 2. Normalised amplitudes of the distortions of the *Pnma* PbI_3 structure associated with each irreducible presentation as calculated from the atomic coordinates (table A3) by the AMPLIMODES tool [18].

T (K)	R_4^+	<i>T</i> (K)	$M_{3}^{+}(q_{2})$	$R_4^+(q_4)$	$R_{5}^{+}(q_{7})$	$X_5^+(q_8)$	M_2^+
170	0.9121	10	1.1619	0.5479	0.1276	0.1486	0.0190
180	0.8900	20	1.1682	0.5478	0.1358	0.1439	0.0256
190	0.8864	30	1.1539	0.5530	0.1243	0.1448	0.0238
200	0.8900	40	1.1419	0.5510	0.1150	0.1448	0.0144
210	0.8721	50	1.1473	0.5522	0.1264	0.1403	0.0161
220	0.8685	60	1.1402	0.5644	0.1155	0.1403	0.0304
230	0.8471	70	1.1241	0.5579	0.1295	0.1457	0.0357
240	0.8471	80	1.1232	0.5706	0.1131	0.1510	0.0313
250	0.8185	90	1.1116	0.5574	0.1161	0.1403	0.0214
260	0.8078	100	1.0991	0.5622	0.1037	0.1564	0.0250
270	0.7953	110	1.0955	0.5639	0.1072	0.1448	0.0232
280	0.7738	120	1.0839	0.5655	0.0979	0.1501	0.0331
290	0.7381	130	1.0839	0.5661	0.0885	0.1653	0.0206
300	0.6898	140	1.0580	0.5655	0.0979	0.1608	0.0286
310	0.6536	150	1.0517	0.5737	0.0910	0.1385	0.0402
320	0.6934	155	1.0481	0.5541	0.0941	0.1599	0.0366
330	0.6394						

3.3. Analysis of order parameters

For many phase transitions in perovskites, the primary distortions involve rotations of the octahedra, but symmetry also allows some deformations of these octahedra. Here we perform a detailed analysis of the complete set of symmetrically-independent distortions of the PbI₃ network through both phase transitions. The concomitant ordering or partial ordering of the MA molecular ions is not included in this analysis.

We have used the AMPLIMODES tool [18] to identify the full set of symmetry-adapted atomic displacements that lower the symmetry, in combination, from $Pm\overline{3}m$ to Pnma[19]. These are given, with the corresponding irreducible representation labels appropriate for analysis with the octahedral site at the origin of the cubic unit cell, in table 1, and shown in figure 3. Based on the actual crystal structure presented to the AMPLIMODES tool, the amplitude of each mode present in the given crystal structure can be calculated, and the perature of 10 K are given in table 1. The two significant modes for the phase transition from $Pm\overline{3}m$ to Pnma are the rotational modes labelled M_3^+ and R_4^+ . The first is the rotation about the orthorhombic [010] axis, where neighbouring layers parallel to (010) have identical rotations. The modulation corresponds to that of a phonon of wave vector $\mathbf{k} = [1/2, 0, 1/2]$, which is labelled M. This distortion leads to the doubling of the lattice repeat distance in the [100] and [001] directions but does not double the repeat distance in the [010] direction. In Glazer notation [7, 8] this is described as $a^0b^+a^0$. On the other hand, the R_4^+ distortion, giving rotations in this case around both the orthorhombic [101] and [101] directions (that is, around the Pb-I bonds perpendicular to [010]), with Glazer notation $a^{-}b^{0}a^{-}$. This distortion doubles the periodicity in all three directions. This is conventionally described in terms of an *I*-centred unit cell in which the axes are rotated by 45° about [010]. The two modes M_3^+ and R_4^+ together give the distortion

amplitudes of each mode for the crystal structure at the tem-



Figure 4. Temperature-dependence of the symmetry adapted deformations associated with the two phase transitions in methylammonium lead iodide, labelled according to their irreducible representations of the cubic $Pm\overline{3}m$ space group.

of the low-temperature *Pnma* phase that is described in Glazer notation as $a^-b^+a^-$.

What is clear, however, is that the structure of the orthorhombic phase is not completely described in terms of rotations of PbI₆ octahedra only, but instead some of the structure change involves some distortions of the PbI₆ octahedra. The AMPLIMODES tool shows that there are three additional modes that involve deformations of the octahedra, which are also given in table 1 and shown in figure 3. It can be seen, based on the relative amplitudes presented in table 1 that two of these distortion modes are relatively important at around 1/4 of the amplitude of the R_4^+ mode, namely the X_5^+ and R_5^+ modes, and the third, M_2^+ , has amplitude that is smaller by a further order of magnitude.

For the transition from $Pm\overline{3}m$ to I4/mcm there is only one distortion, which is described completely by the mode of symmetry R_4^+ , but in this case, operating around one axis (the tetragonal [001] axis) rather than around two as in the *Pnma* structure, to give the distortion $a^0a^0c^-$.

The temperature dependence of the five distortion modes of the orthorhombic phase and of the one mode of the tetragonal phase are shown in figure 4. Data are given in table 2. It can be seen that there is continuous variation of the amplitude of the R_4^+ with temperature in the intermediate I4/mcm phase, but since the symmetry of the low-temperature *Pnma* phase is not a subgroup of the I4/mcm phase, the variation of the order parameters in the *Pnma* phase have a discontinuous change at the phase transition. In fact the M_3^+ mode, which is the largest distortion, shows a variation with temperature characteristic of a standard first-order phase transition, and so too does the smaller X_5^+ mode, but the R_4^+ and R_5^+ mode amplitudes show very little variation with temperature, and even show a slight decrease on cooling.

3.4. Landau free energy function for the transition from cubic to orthorhombic

The ISOTROPY tool [20-22] was used to give a free energy function for the transition from cubic $Pm\overline{3}m$ to orthorhombic Pnma. Here we exclude components of the multipledimensional irreducible representations that remain zero in the low-symmetry phase, together with the M_2^+ term since experimentally this is very small (table 2). We follow ISOTROPY write $q_2 = Q(M_3^+)$, $q_4 = Q(R_4^+)$, $q_7 = Q(R_5^+)$ and to $q_8 = Q(X_5^+)$, mostly to make writing the following equations easier. Furthermore, we only include terms up to the fourth power in order parameter. Of course, the first-order discontinuity of the phase transition, and the weak discontinuity of the phase transition from $Pm\overline{3}m$ to I4/mcm that we will discuss below, would require expansion to sixth order, but this does not serve our current purpose of investigating couplings between order parameters and strain. We also do not include terms that are quadratic (or of higher power) in strain. All together this leads to the following free energy function:

$$F = \frac{1}{2} \left(a_2 q_2^2 + a_4 q_4^2 + a_7 q_7^2 + a_8 q_8^2 \right) + \frac{1}{4} \left(b_2 q_2^4 + b_4 q_4^4 + b_7 q_7^4 + b_8 q_8^4 \right) + \frac{1}{4} q_2^2 \left(b_{24} q_4^2 + b_{27} q_7^2 + b_{28} q_8^2 \right) + \frac{1}{4} q_4^2 \left(b_{47} q_7^2 + b_{48} q_8^2 \right) + \frac{1}{4} \left(b_{78} q_7^2 q_8^2 + dq_4 q_7^3 + d' q_4^3 q_7 + gq_4 q_7 q_8^2 \right) + \frac{1}{2} \epsilon_a \left(\lambda_a^{(2)} q_2^2 + \lambda_a^{(4)} q_4^2 + \lambda_a^{(7)} q_7^2 + \lambda_a^{(8)} q_8^2 \right) + \frac{1}{2} \epsilon_{ty} \left(\lambda_{ty}^{(2)} q_2^2 + \lambda_{ty}^{(4)} q_4^2 + \lambda_{ty}^{(7)} q_7^2 + \lambda_{ty}^{(8)} q_8^2 + \lambda_{ty}^{(47)} q_4 q_7 \right) + \frac{1}{2} \epsilon_5 \left(\lambda_5^{(4)} q_4^2 + \lambda_5^{(47)} q_4 q_7 \right) + \frac{1}{4} \left(C_{11}^0 - C_{12}^0 \right) \epsilon_{ty}^2 + \frac{1}{6} \left(C_{11}^0 + 2C_{12}^0 \right) \epsilon_a^2 + \frac{1}{2} C_{44}^0 \epsilon_5^2$$
(6)

where *a*, *b*, *d*, *g* and λ are parameters, and C_{ij}^0 are the regular elastic constants of the cubic phase. Minimisation of the free energy with respect to the three strain variables yields the relationships

$$\epsilon_{\rm a} = -\frac{\lambda_{\rm a}^{(2)} q_2^2 + \lambda_{\rm a}^{(4)} q_4^2 + \lambda_{\rm a}^{(7)} q_7^2 + \lambda_{\rm a}^{(8)} q_8^2}{\frac{2}{3} \left(C_{11}^0 + 2C_{12}^0 \right)} \tag{7}$$

$$\epsilon_{\rm ty} = -\frac{\lambda_{\rm ty}^{(2)} q_2^2 + \lambda_{\rm ty}^{(4)} q_4^2 + \lambda_{\rm ty}^{(7)} q_7^2 + \lambda_{\rm ty}^{(8)} q_8^2 + \lambda_{\rm ty}^{(47)} q_4 q_7}{\left(C_{11}^0 - C_{12}^0\right)} \tag{8}$$

$$\epsilon_5 = -\frac{\lambda_5^{(4)}q_4^2 + \lambda_5^{(47)}q_4q_7}{2C_{44}^0}.$$
(9)



Figure 5. Comparison of experimental strains ϵ_{ty} , ϵ_5 and ϵ_{tz} with corresponding values of strains calculated from equations (8) and (9) for the *Pnma* phase (a)–(d), and equation (10) for the *I*4/*mcm* phase (e) and (f), with coefficients obtained by least-squares fitting as described in the text. The left side (a), (c) and (e) compares the dependence on temperature of the three strains as obtained experimentally from the measured lattice parameters and as calculated. The right side (b), (d) and (f) compares directly the experimental strains and the calculated strains. The straight lines in figures (b), (d) and (f) are of unit gradient.

Table 3. Fitted values of the coefficients linking the three strains ϵ_{ty} , ϵ_5 and ϵ_{tz} to the various quadratic functions of the order parameters as given in equations (8)–(10).

q	$\epsilon_{\rm ty}$ equation (8)	ϵ_5 equation (9)	ϵ_{tz} equation (10)
q_{2}^{2}	0.013(2)		
$q_4^{\overline{2}}$	0.03(1)	0.106(6)	0.0272(6)
q_7^2	-0.1(4)		
q_8^2	0		
$q_4 q_7$	0.05(15)	-0.03(2)	



Figure 6. Fitted temperature-dependence of the strain ϵ_{tz} in the I4/mcm phase fitted from the minimum of a first-order Landau free energy function.

In figures 5(a)–(d) we demonstrate the extent to which the data for strains ϵ_{ty} and ϵ_5 and order parameters in the *Pnma* phase are consistent with relationships 8 and 9. We have fitted the values of the coefficients in these two equations—such as $-\lambda_{ty}^{(2)}/(C_{11}^0 - C_{12}^0)$ for q_2^2 in equation (8)—using the experimental strain data shown in figure 2(c) and the experimental data for the values of the order parameters given in table 2. With the set of coefficients we then calculated the expected strain values from the values of the order parameters. In figures 5(b) and (d) we compare directly the expected and experimental values of strain, finding that the expected data follow closely the experimental data. In figure 5(a) and (c) we compare the temperature dependence of both the expected and experimental strains ϵ_{ty} and ϵ_5 respectively. Coefficients of the fitting are given in table 3.

The strain ϵ_{ty} has a temperature dependence that is typical of a first-order phase transition, with a large discontinuity at the phase transition (smallest values of ϵ_{ty}) and only a small variation with temperature. In the fitting it was found that the strain is almost completely described by order parameters q_2^2 and q_4^2 , with contributions from q_7^2 , q_8^2 and q_4q_7 being of low statistical significance (equation (8) and table 3).

More unusual is the variation of the strain ϵ_5 with temperature, figure 5(c). This primarily depends on order parameter q_4^2 , with a smaller contribution from the coupled product q_4q_7 (equation (9) and table 3). From figure 4 we see that the mode q_4 (R_4^+) also has unusual temperature dependence, as discussed above. From figures 5(c) and (d) we see that the temperature dependences of q_4 and ϵ_5 are consistent with each other. We should remark that the q_4q_7 contribution to ϵ_5 (equation (9) and table 3) is much smaller than that of q_4^2 , but has greater statistical significance than the contributions of q_7^2 , q_8^2 and q_4q_7 to ϵ_{ty} discussed above.

3.5. Tetragonal-cubic phase transition

The tetragonal-cubic phase transition in methylammonium lead iodide is nearly continuous, as can be seen in the plots of spontaneous strain (figure 2(c)) and of the order parameter (figure 4). In this phase we expect to find the relationship

$$\epsilon_{\rm tz} = eq_4^2 \tag{10}$$

similar in fact to the significant dependence of ϵ_{ty} on q_2^2 (equation (8)). This relationship is clearly demonstrated in figure 5, where the agreement across the range of temperatures and values of ϵ_{ty} is good except at temperatures close to the transition temperature, where the effects of systematic (and hence uncertain) errors may be largest in the determination of the atomic displacements.

The transition from the $Pm\overline{3}m$ to I4/mcm phase has been interpreted in terms of a tricritical phase transition [6, 9], where the order parameter varies with temperature as $Q \propto (T_{\rm c} - T)^{\beta}$, where $\beta = 1/4$. Previous experimental data were fitted to give a value of $\beta = 0.27 \pm 0.01$ [6, 9], which suggests that the transition is properly tricritical. However, two pieces of experimental evidence suggest that this interpretation is an approximation. One is that there is a coexistence of the tetragonal and cubic phase for a range of temperatures close to the transition point, both in our work and in references [6, 9](where the coexistence was alternatively attributed to a fast heating rate [6] in their experiments, but here we allowed equilibration for 10 min before each run). The second evidence is the existence of a latent heat [23, 24]. Both points suggest that the phase transition is first order. First-order phase transitions can be modelled with a Landau free energy function of the form

$$F(Q) = \frac{1}{2}a(T - T_0)Q^2 - \frac{1}{4}bQ^4 + \frac{1}{6}cQ^6$$
(11)

where Q is the order parameter, T is the temperature, and a, b, c and T_0 are parameters. The transition temperature T_c and the jump in order parameter at the phase transition are

$$T_{\rm c} = T_0 + \frac{3b^2}{16ac}; \qquad \Delta Q^2 = \frac{3b}{4c}.$$
 (12)

The temperature dependence of the order parameter is obtained by minimisation of the free energy as

$$Q^{2} = \frac{b}{2c} + \frac{\sqrt{b^{2} - 4ac(T - T_{0})}}{2c}.$$
 (13)

Treating ϵ_{tz} as an accurate measurement of Q^2 , we fitted equation (13) to the data for ϵ_{tz} . The resultant fit is shown in figure 6. From the results we obtained $T_c - T_0 = 2.1 \pm 0.2$ K, which is (from equation (12)) essentially indicating that the parameter *b* in equation (11) is small and hence the phase transition is nearly tricritical, as suggested previously.

4. Conclusions

In this paper we have reported detailed measurements of the crystal structure of MAPbI3 with small steps in temperature across the range of temperatures encompassing the two phase transitions. We have decomposed the atomic displacements due to the phase transitions into symmetrically-independent order parameters, and analysed how they couple to the symmetry-adapted spontaneous strains. The higher-temperature phase transition is characterised by a single order parameter, and its behaviour with temperature and as coupled to the spontaneous strain follows the form of a weakly first-order phase transition consistent with the description of a standard Landau free energy function. The lowertemperature phase is described by a group of order parameters, some of which show the unusual behaviour of decreasing in value on cooling. This is also seen in one of the spontaneous strains. The origin of this behaviour presumably arises from the relatively complex form of the Landau free energy function, including coupling terms of several different powers, but this has not been explored here.

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Data availability statement

The raw data that support the findings of this study are openly available at the following URL/DOI: https://doi.org/10.5286/ISIS.E.RB1510530.

Appendix A. Summary of results from Rietveld analysis

The quality of the fit to the Rietveld results can be seen visually from inspection of the fitted profiles shown in figure A1. These data are all from bank 4 of the POLARIS diffractometer, which has a nominal scattering angle of 90° , and therefore shows data to reasonably high resolution and covers a wide range of *d*-spacings [11].

The results from the Rietveld refinement for each of the phases are given in tables A1-A7. Tables A1 and A2 report refined values of lattice parameters, fractional coordinations and isotropic atomic displacement parameters for the Pb and I atoms in the cubic and tetragonal phases respectively. Corresponding values for the orthorhombic phase are given in tables A3 and A4. Tables A5–A7 give the refined values of the fractional coordinates and isotropic atomic displacement parameters for the C/N and H atoms. Only for the orthorhombic phase do these data have significance; for the cubic and tetragonal phases the atomic positions are chosen to model the disorder. Models with atomic coordinates for the atoms in the MA ions in these two phases are given by both Weller et al [5] and Whitfield et al [6]. These two models differ slightly in their treatment of the disorder, and in this regard we follow the model of Weller et al [5], but we consider that because of the significant disorder there is little importance in the choice. Finally, agreement factors for all refinements are given in table A8.



Figure A1. Example of the quality of the fitting of calculated to experimental neutron powder diffraction pattern given by use of the Rietveld method. Each figure shows data from the detector bank with scattering angle of nominally 90°. The χ^2 values for the refinements at 100 K, 280 K and 400 K from table A8 are 0.86, 0.93 and 0.84 respectively, and profile *R*-factors R_p are 3%, 4% and 4% respectively.

Table A1. Lattice parameters and atomic displacement parameters (ADPs) for the Pb and I atoms in the cubic phase of methylammonium lead iodide (space group $Pm\overline{3}m$), obtained from Rietveld refinement of the neutron powder diffraction data. The Pb atom has fractional coordinates (0, 0, 0), and the I atom has fractional coordinates (1/2, 0, 0). We report the refined coordinates of the atoms in the MA molecular cation in table A4.

T (K)	<i>a</i> (Å)	Pb 100 \times $U_{\rm iso}$ (Å ²)	I $100 \times U_{11} (\text{\AA}^2)$	I $100 \times U_{22} (\text{\AA}^2)$
300	6.3145(13)	9.4(18)	-6.7(6)	20.9(29)
310	6.2997(6)	5.2(6)	-4.9(5)	16.5(10)
320	6.2973(3)	3.3(6)	14.6(11)	14.6(11)
330	6.2988(2)	3.40(17)	15.5(4)(4)	15.5(4)
340	6.3023(1)	2.94(9)	1.4(3)	16.1(3)
350	6.3052(1)	3.04(9)	2.2(3)	16.5(3)
360	6.3077(1)	3.16(9)	1.9(3)	15.8(3)
370	6.3106(1)	3.18(10)	2.1(3)	16.3(3)
380	6.3133(1)	3.06(9)	2.6(3)	16.2(3)
390	6.3158(1)	3.39(10)	2.3(3)	16.2(3)
400	6.3184(1)	3.55(10)	2.5(3)	15.6(3)

Table A2. Lattice parameters, fractional coordinates and ADPs for the Pb and I atoms for the tetragonal phases of methylammomium lead iodide (space group I4/mcm), obtained from Rietveld refinement of the neutron powder diffraction data. Pb has fractional coordinates (0, 0, 0), I1 has fractional coordinates (x, 1/2 - x, 1/2), and I2 has fractional coordinates (1/2, 1/2, 3/4). We report the refined coordinates of the atoms in the MA molecular cation in table A4.

T (K)	<i>a</i> (Å)	<i>c</i> (Å)	Pb 100 × $U_{\rm iso}$ (Å ²)	I1 x	I1 100 × $U_{\rm iso}$ (Å ²)	I2 100 × $U_{\rm iso}$ (Å ²)
170	8.7930(3)	12.6985(5)	0.97(8)	0.1992(3)	3.0(1)	2.3(2)
180	8.7966(3)	12.6970(5)	1.2(1)	0.2000(4)	2.7(1)	2.4(2)
190	8.8014(3)	12.6974(6)	0.9(1)	0.1999(4)	3.2(1)	2.7(2)
200	8.8078(3)	12.6998(6)	1.4(1)	0.1999(4)	3.0(1)	2.2(2)
210	8.8132(3)	12.6976(6)	1.3(1)	0.2003(4)	3.1(2)	2.1(2)
220	8.8186(3)	12.6981(6)	1.5(1)	0.2008(4)	3.4(2)	2.7(2)
230	8.8232(3)	12.6972(6)	1.7(1)	0.2026(4)	3.9(2)	2.7(2)
240	8.8297(3)	12.6945(6)	1.5(1)	0.2020(4)	3.7(2)	2.8(2)
250	8.8359(3)	12.6957(6)	1.8(1)	0.2038(5)	4.4(2)	2.7(2)
260	8.8415(3)	12.6923(7)	2.0(1)	0.2048(5)	4.5(2)	3.4(3)
270	8.8469(3)	12.6863(7)	2.0(1)	0.2055(5)	4.7(2)	3.5(3)
280	8.8548(3)	12.6858(7)	1.9(1)	0.2067(5)	4.7(2)	4.0(3)
290	8.8614(3)	12.6802(7)	2.0(1)	0.2087(5)	5.0(2)	4.0(3)
300	8.8681(3)	12.6737(7)	2.7(2)	0.2114(7)	7.0(3)	6.5(5)
310	8.8671(3)	12.6623(7)	2.3(1)	0.2136(5)	7.8(3)	7.4(3)
320	8.8771(5)	12.6569(10)	2.5(3)	0.2112(10)	7.2(4)	7.8(7)
330	8.8890(10)	12.6509(18)	2.1(2)	0.2143(17)	6.1(5)	9.3(15)

Table A3.	Lattice parameters and refined values	of the atomic displacement	parameters for the Pb and I	atoms for the orthorhombic phases
of methyla	mmomium lead iodide (space group)	Pnma), obtained from Rietve	eld refinement of the neutron	powder diffraction data.

T (K)	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	Pb 100 × $U_{\rm iso}$ (Å ²)	I 100 × $U_{\rm iso}$ (Å ²)
10	8.8139(2)	12.5963(2)	8.5640(2)	-0.15(2)	-0.03(3)
20	8.8164(3)	12.5961(3)	8.5625(3)	-0.13(4)	-0.01(5)
30	8.8204(3)	12.5976(3)	8.5626(3)	-0.14(4)	0.03(5)
40	8.8253(3)	12.6002(4)	8.5617(3)	-0.02(4)	0.11(5)
50	8.8301(3)	12.6031(4)	8.5616(3)	-0.05(4)	0.20(6)
60	8.8347(3)	12.6038(4)	8.5622(3)	0.02(5)	0.23(6)
70	8.8401(3)	12.6065(4)	8.5626(3)	0.08(5)	0.41(7)
80	8.8445(3)	12.6078(4)	8.5639(3)	0.15(5)	0.37(7)
90	8.8486(3)	12.6109(4)	8.5657(4)	0.15(6)	0.53(8)
100	8.8529(3)	12.6136(4)	8.5680(3)	0.19(6)	0.58(8)
110	8.8590(3)	12.6172(4)	8.5722(4)	0.36(6)	0.85(9)
120	8.8619(3)	12.6199(4)	8.5752(4)	0.22(6)	0.96(9)
130	8.8648(4)	12.6219(4)	8.5789(4)	0.30(6)	0.91(9)
140	8.8665(4)	12.6247(4)	8.5845(4)	0.42(7)	0.91(9)
150	8.8685(4)	12.6269(5)	8.5905(4)	0.26(6)	1.19(10)
155	8.8700(4)	12.6283(5)	8.5944(4)	0.39(7)	1.26(11)

Table A4. Lattice parameters, fractional coordinates and temperature factors for the Pb and I atoms for the orthorhombic phases of methylammomium lead iodide (space group *Pnma*), obtained from Rietveld refinement of the neutron powder diffraction data. Pb has fractional coordinates (1/2, 0, 0), I1 has fractional coordinates (x, 1/4, z). Data for the atoms in the MA cation are given in table A5.

	T 1	T1	10	12	10
<i>T</i> (K)	$\prod x$	11 <i>z</i>	12 x	12 y	12 z
10	0.4834(3)	-0.0535(3)	0.1860(2)	0.0166(1)	0.1839(2)
20	0.4839(5)	-0.0541(5)	0.1861(3)	0.0163(2)	0.1832(4)
30	0.4838(5)	-0.0536(5)	0.1868(3)	0.0170(2)	0.1841(4)
40	0.4838(5)	-0.0527(5)	0.1870(3)	0.0172(2)	0.1853(4)
50	0.4843(6)	-0.0537(5)	0.1867(4)	0.0168(2)	0.1849(4)
60	0.4843(6)	-0.0538(5)	0.1879(4)	0.0178(2)	0.1845(4)
70	0.4837(6)	-0.0544(6)	0.1891(4)	0.0170(3)	0.1851(4)
80	0.4831(7)	-0.0541(6)	0.1889(4)	0.0181(3)	0.1854(4)
90	0.4843(7)	-0.0533(6)	0.1890(4)	0.0175(3)	0.1866(5)
100	0.4825(7)	-0.0527(6)	0.1899(4)	0.0181(3)	0.1871(5)
110	0.4838(8)	-0.0531(7)	0.1900(5)	0.0181(3)	0.1874(5)
120	0.4832(8)	-0.0525(7)	0.1912(5)	0.0185(4)	0.1875(5)
130	0.4815(8)	-0.0518(7)	0.1905(5)	0.0189(4)	0.1882(5)
140	0.4820(9)	-0.0525(7)	0.1924(5)	0.0185(4)	0.1892(5)
150	0.4845(10)	-0.0526(8)	0.1934(5)	0.0191(4)	0.1889(6)
155	0.4821(10)	-0.0513(8)	0.1934(6)	0.0182(4)	0.1893(6)

Table A5. Fractional coordinates and temperature factors for the C and N atoms of the MA ion in the three phases of methylammomium lead iodide, obtained from Rietveld refinement of the neutron powder diffraction data. For the low-temperature *Pnma* phase the positions are defined without any sense of disorder. In the intermediate-temperature tetragonal phase the C and N atoms both have fractional occupancies of 1/4. In the high-temperature cubic phases the C and N atoms are assigned the same positions and have fractional occupancies of 1/3 each.

T (K)	C x	C y	C z	N x	N y	N z	C 100 \times $U_{\rm iso}$	N 100 \times $U_{\rm iso}$
		L	ow-temperature p	bhase, orthorhom	bic space group	Pnma		
10	0.9197(2)	1/4	0.0654(3)	0.9406(2)	3/4	0.0264(2)	0.44(5)	0.69(4)
20	0.9201(4)	1/4	0.0650(4)	0.9400(3)	3/4	0.0263(4)	0.53(8)	0.74(6)
30	0.9206(4)	1/4	0.0645(5)	0.9390(3)	3/4	0.0260(4)	0.68(9)	0.95(7)
40	0.9209(4)	1/4	0.0638(5)	0.9387(32)	3/4	0.0264(4)	0.65(9)	1.01(7)
50	0.9201(4)	1/4	0.0633(5)	0.9394(3)	3/4	0.0265(4)	0.64(9)	1.28(8)
60	0.9207(5)	1/4	0.0621(6)	0.9383(4)	3/4	0.0269(5)	0.97(11)	1.48(9)
70	0.9218(5)	1/4	0.0608(6)	0.9366(4)	3/4	0.0269(5)	1.21(12)	1.80(10)
80	0.9203(5)	1/4	0.0605(7)	0.9384(4)	3/4	0.0276(6)	1.24(12)	2.29(12)
90	0.9212(6)	1/4	0.0610(7)	0.9374(5)	3/4	0.0269(6)	1.38(14)	2.04(12)
100	0.9233(6)	1/4	0.0599(8)	0.9356(5)	3/4	0.0283(6)	2.05(16)	2.35(13)
110	0.9227(7)	1/4	0.0571(9)	0.9352(6)	3/4	0.0292(8)	2.48(19)	3.15(16)
120	0.9229(7)	1/4	0.0566(9)	0.9347(6)	3/4	0.0292(8)	2.52(19)	3.26(17)
130	0.9229(8)	1/4	0.0588(10)	0.9357(7)	3/4	0.0285(8)	2.70(20)	3.57(17)
140	0.9231(9)	1/4	0.0556(11)	0.9347(8)	3/4	0.0302(9)	2.87(22)	4.16(20)
150	0.9207(9)	1/4	0.0501(11)	0.9368(8)	3/4	0.0351(11)	2.32(22)	5.20(23)
155	0.9214(9)	1/4	0.0527(12)	0.9362(9)	3/4	0.0326(12)	2.59(23)	5.65(25)
		Intern	nediate-temperat	ure phase, tetrag	onal space group	I4/mcm		
170	0.522(1)	-0.022(1)	0.234(2)	0.4155(10)	0.0849(9)	0.2880(7)	10.315()	3.67(25)
180	0.524(5)	-0.024(5)	0.244(14)	0.4102(10)	0.0898(10)	0.2869(9)	11.4(25)	3.84(27)
190	0.525(6)	-0.025(6)	0.238(8)	0.4090(11)	0.0910(11)	0.2847(10)	11.2(30)	3.85(28)
200	0.520(11)	-0.020(11)	0.246(31)	0.4103(13)	0.0897(13)	0.2873(11)	14(4)	4.52(34)
210	0.527(5)	-0.027(5)	0.234(5)	0.4062(11)	0.0938(11)	0.2842(11)	10.4(29)	4.38(33)
220	0.5311(26)	-0.0311(26)	0.2297(28)	0.4054(11)	0.0946(11)	0.2820(11)	8.4(20)	5.1(4)
230	0.523(13)	-0.023(13)	0.264(10)	0.4057(11)	0.0943(11)	0.2851(11)	15(5)	5.3(4)
240	0.527(6)	-0.027(6)	0.260(10)	0.4038(12)	0.0962(12)	0.2806(12)	11.9(32)	6.2(5)
250	0.5360(14)	-0.0360(14)	0.736(16)	0.4010(11)	0.0990(11)	0.2815(13)	6.3(11)	7.7(5)
260	0.5367(12)	-0.0367(12)	0.2740(15)	0.4015(12)	0.0985(12)	0.2807(14)	5.7(10)	7.5(5)
270	0.531(4)	-0.031(4)	0.2715(32)	0.4016(16)	0.0984(16)	0.2803(15)	10.4(25)	7.6(6)
280	0.5357(16)	-0.0357(16)	0.2756(16)	0.4031(19)	0.0969(19)	0.2802(19)	6.9(13)	8.7(7)
290	0.537(4)	-0.037(4)	0.258(13)	0.3999(19)	0.1001(19)	0.2769(19)	0.138(29)	8.5(7)
300	0.537(6)	-0.037(6)	0.274(5)	0.4070(26)	0.0930(26)	0.270(4)	15(4)	14.1(12)
310	0.533(3)	-0.033(3)	0.274(2)	0.3994(20)	0.1005(20)	0.277(2)	9.4(18)	11.0(7)
320	0.5385(23)	0.0385(23)	0.269(4)	0.3954(27)	0.1046(27)	0.268(4)	8.6(21)	11.1(11)
330	0.509(8)	-0.009(8)	0.261(7)	0.4180(29)	0.0820(29)	0.281(4)	9.5(7)	15(2)
			High-temperatu	are phase, cubic s	space group $Pm\overline{3}$	m		
310	0.384(3)	1/2	1/2				12.3(16)	
320	0.393(2)	1/2	1/2				14.8(7)	
330	0.366(5)	1/2	1/2				15.0(2)	
340	0.3922(23)	1/2	1/2				15.0(2)	
350	0.3890(17)	1/2	1/2				13.7(1)	
360	0.3903(19)	1/2	1/2				14.2(1)	
370	0.392(4)	1/2	1/2				17.7(2)	
380	0.3885(18)	1/2	1/2				14.1(1)	
390	0.3866(19)	1/2	1/2				15.2(2)	
400	0.3872(20)	1/2	1/2				15.2(2)	

Table A6. Fractional coordinates and temperature factors for the H/D atoms of the MA ion in the high-temperature cubic $(Pm\overline{3}m)$ and intermediate-temperature tetragonal I4/mcm) phases of methylammomium lead iodide, obtained from Rietveld refinement of the neutron powder diffraction data. In the high-temperature cubic phases the C and N atoms are assigned the same positions and have fractional occupancies of 1/8. In the intermediate-temperature tetragonal phase the H/D atoms have fractional occupancies of 1/4.

T (K)	D1 x	D1 y	D1 <i>z</i>	D2 <i>x</i>	D2 y	D2 z	D 100 $ imes$ $U_{\rm iso}$
		Hig	h-temperature pha	se, cubic space gro	$Pm\overline{3}m$		
310	0.3101(25)	0.522(8)	0.401(4)				9.2(13)(24)
320	0.3043(15)	0.484(7)	0.393(2)				9.8(6)
330	0.3100(28)	0.462(4)	0.4093(30)				13.5(12)
340	0.3110(8)	0.4497(18)	0.4034(19)				11.3(6)
350	0.3107(8)	0.4454(15)	0.4002(18)				10.6(6)
360	0.3102(8)	0.4462(17)	0.4024(19)				10.8(6)
370	0.3121(11)	0.4501(21)	0.4028(22)				12.3(7)
380	0.3105(8)	0.4455(16)	0.3999(19)				11.0(6)
390	0.3116(10)	0.4493(20)	0.4013(20)				12.6(7)
400	0.3116(11)	0.4503(22)	0.4011(20)				13.1(8)
		Intermedia	te-temperature pha	ase, tetragonal spac	ce group I4/mcm		
170	0.035(1)	0.360(1)	0.2153(7)	0.447(1)	0.0530(9)	0.345(1)	14.6(3)
180	0.0516(17)	0.3613(14)	0.2301(13)	0.4478(15)	0.0522(15)	0.3445(16)	17.5(7)
190	0.0543(17)	0.3631(15)	0.2304(13)	0.4462(15)	0.0538(15)	0.3452(16)	16.7(7)
200	0.0513(19)	0.3649(17)	0.2315(17)	0.4465(17)	0.0535(17)	0.3453(17)	18.1(1)
210	0.0497(18)	0.3648(15)	0.2321(15)	0.4487(15)	0.0513(15)	0.3455(17)	16.3(8)
220	0.0249(22)	0.3667(16)	0.2093(11)	0.4484(14)	0.0516(14)	0.3413(16)	15.1(7)
230	0.012(4)	0.3643(15)	0.2115(13)	0.4493(19)	0.0507(19)	0.3428(18)	18.8(7)
240	0.0172(32)	0.3702(15)	0.2080(11)	0.4501(15)	0.0499(15)	0.3426(16)	15.0(6)
250	0.0100(29)	0.3707(15)	0.2073(11)	0.4479(15)	0.0521(15)	0.3420(17)	15.8(6)
260	0.0011(27)	0.3721(15)	0.2073(11)	0.4487(15)	0.0513(15)	0.3436(19)	15.9(7)
270	0.0017(31)	0.3712(16)	0.2082(12)	0.4509(18)	0.0491(18)	0.3413(18)	16.6(8)
280	-0.0074(28)	0.3737(15)	0.2101(12)	0.4505(17)	0.0495(17)	0.3426(18)	16.0(8)
290	-0.0083(27)	0.3750(15)	0.2084(11)	0.4510(16)	0.0490(16)	0.3446(18)	15.0(8)
300	-0.001(5)	0.3733(22)	0.2058(18)	0.4597(32)	0.0403(32)	0.3466(26)	21.6(13)
310	0.000(2)	0.3808(16)	0.2045(11)	0.4529(18)	0.0471(18)	0.3436(18)	17.0(6)
320	-0.002(5)	0.3753(23)	0.2000(20)	0.4550(25)	0.0450(25)	0.3364(29)	15.9(9)
330	-0.022(4)	0.3774(33)	0.1986(25)	0.436(4)	0.063(4)	0.327(5)	14.2(9)

Table A7. Fractional coordinates and temperature factors for the H/D atoms of the MA ion in the orthorhombic (*Pnma*) phase of methylammomium lead iodide, obtained from Rietveld refinement of the neutron powder diffraction data. In the refinement the concentrations were set at approximate. The atomic positions are defined without any sense of disorder.

T (K)	D1 <i>x</i>	D1 y	D1 z	D2 <i>x</i>	D2 y	D2 z	D 100 \times $U_{\rm iso}$
		Low-terr	perature phase (CD	3), orthorhombic spa	ace group Pnma		
10	0.9483(4)	1/4	0.188 83(35)	0.854 31(22)	0.18030(18)	0.037 48(3)	2.294(34)
20	0.9488(7)	1/4	0.1891(6)	0.8538(4)	0.18076(31)	0.0369(4)	2.28(6)
30	0.9484(7)	1/4	0.1879(6)	0.8541(4)	0.180 53(31)	0.0372(4)	2.58(6)
40	0.9474(8)	1/4	0.1876(7)	0.8551(4)	0.180 49(34)	0.0348(4)	2.83(7)
50	0.9470(8)	1/4	0.1866(7)	0.8560(5)	0.1803(4)	0.0344(5)	3.12(7)
60	0.9464(9)	1/4	0.1871(7)	0.8558(5)	0.1803(4)	0.0340(5)	3.32(8)
70	0.9466(10)	1/4	0.1856(8)	0.8559(5)	0.1814(4)	0.0325(6)	3.92(9)
80	0.9467(11)	1/4	0.1849(8)	0.8577(6)	0.1807(4)	0.0321(6)	4.10(10)
90	0.9461(12)	1/4	0.1842(9)	0.8581(6)	0.1811(5)	0.0308(7)	4.55(11)
100	0.9491(12)	1/4	0.1844(9)	0.8580(6)	0.1821(5)	0.0305(7)	4.97(11)
110	0.9469(14)	1/4	0.1815(10)	0.8578(7)	0.1817(5)	0.0315(7)	5.50(13)
120	0.9458(14)	1/4	0.1820(11)	0.8581(7)	0.1821(5)	0.0309(8)	5.85(14)
130	0.9438(15)	1/4	0.1817(11)	0.8595(8)	0.1817(5)	0.0298(8)	6.29(14)
140	0.9446(16)	1/4	0.1807(12)	0.8612(8)	0.1806(6)	0.0313(9)	6.53(16)
150	0.9403(17)	1/4	0.1762(12)	0.887 11(9)	0.1757(6)	0.0314(9)	6.73(18)
155	0.9441(19)	1/4	0.1775(13)	0.8709(9)	0.1768(6)	0.0313(10)	7.43(19)
		Low-terr	perature phase (ND	3), orthorhombic sp	ace group Pnma		
10	0.1241(4)	0.183 17(34)	-0.0009(5)	0.9615(7)	0.75	0.1474(6)	
20	0.1227(7)	0.1830(6)	-0.0017(9)	0.9582(13)	0.75	0.1452(10)	
30	0.1225(8)	0.1830(6)	-0.0016(9)	0.9580(13)	0.75	0.1444(10)	
40	0.1216(8)	0.1824(6)	-0.0008(10)	0.9555(15)	0.75	0.1439(10)	
50	0.1233(9)	0.1840(7)	-0.0009(11)	0.9567(16)	0.75	0.1457(11)	
60	0.1233(9)	0.1845(7)	-0.0019(11)	0.9556(17)	0.75	0.1450(11)	
70	0.1214(10)	0.1835(7)	0.0017(12)	0.9474(20)	0.75	0.1449(12)	
80	0.1235(11)	0.1851(8)	0.0005(13)	0.9507(11)	0.75	0.1445(13)	
90	0.1243(12)	0.1847(9)	-0.0011(15)	0.9501(24)	0.75	0.1440(13)	
100	0.1214(12)	0.1834(8)	0.0028(15)	0.9395(26)	0.75	0.1464(14)	
110	0.1222(13)	0.1837(9)	0.0020(16)	0.9423(29)	0.75	0.1471(15)	
120	0.1227(14)	0.1842(10)	0.0042(17)	0.9427(30)	0.75	0.1456(15)	
130	0.1224(14)	0.1848(10)	-0.0010(18)	0.9404(33)	0.75	0.1446(16)	
140	0.1285(16)	0.1894(11)	0.0037(18)	0.9415(35)	0.75	0.1475(16)	
150	0.1437(15)	0.2005(10)	0.0008(19)	0.9480(35)	0.75	0.1525(18)	
155	0.1439(26)	0.1991(11)	-0.0041(22)	0.947(4)	0.75	0.1491(19)	

Table A8. Agreement factors for all Rietveld refinements reported in tables A1–A7.					
T (K)	Reduced χ^2	Rp	$R_{ m wp}$		
10	1.621	0.0197	0.0107		
20	0.8606	0.0311	0.0170		
30	0.8001	0.0315	0.0169		
40	0.8354	0.0329	0.0172		
50	0.8479	0.0316	0.0171		
60	0.8729	0.0322	0.0173		
70	0.8427	0.0306	0.0170		
80	0.8755	0.0330	0.0172		
90	0.9011	0.0318	0.0182		
100	0.8431	0.0291	0.0174		
110	0.8607	0.0304	0.0174		
120	0.8615	0.0301	0.0174		
130	0.8405	0.0305	0.0170		
140	0.8496	0.0298	0.0172		
150	0.9046	0.0327	0.0178		
155	0.8878	0.0323	0.0179		
170	0.8610	0.0389	0.0179		
180	0.8727	0.0428	0.0181		
190	0.9054	0.0407	0.0182		
200	0.8747	0.0392	0.0179		
210	0.8844	0.0427	0.0179		
220	0.8590	0.0407	0.0179		
230	0.8575	0.0420	0.0181		
240	0.8326	0.0396	0.0174		
250	0.8515	0.0393	0.0175		
260	0.8757	0.0396	0.0179		
270	0.8652	0.0424	0.0179		
280	0.8583	0.0401	0.0176		
290	0.8326	0.0396	0.0174		
300	0.8020	0.0447	0.0207		
310	0.8442	0.0447	0.0208		
320	0.8201	0.0402	0.0200		
330	0.7708	0.0429	0.0200		
340	0.8385	0.0394	0.0198		
350	0.8455	0.0420	0.0206		
360	0.8212	0.0416	0.0200		
370	0.8851	0.0423	0.0203		
380	0.8466	0.0430	0.0208		
390	0.8286	0.0432	0.0200		
400	0.8381	0.0416	0.0203		

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