Perovskite Crystal Structure

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Short-Range Order of Methylammonium and Persistence of Distortion at the Local Scale in $MAPbBr_3$ Hybrid Perovskite

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Abstract: *Short-range investigation by means of variable-temperature neutron total scattering and pair distribution function analysis revealed that the local environment around the methylammonium (MA) cation in $MAPbBr_3$ hybrid perovskite is maintained through the different phase transitions observed as a function of temperature. In addition, the orthorhombic distortion of the lattice is present at any temperature. Local structure around MA changes from static to configurationally averaged or dynamic with temperature but the local structure of the low-temperature orthorhombic phase is preserved.*

The geometrical arrangement of the organic (methylammonium, $CH_3NH_3^+$, MA) group in hybrid organic–inorganic perovskites and the relative influence of lattice distortions are object of intense theoretical and experimental investigations.[1–4] Such information is crucial in defining the electronic properties of hybrid perovskites such as band-gap nature and carrier lifetimes.

Until now the structural data on hybrid perovskites have been obtained by means of X-ray and neutron diffraction studies. In general, for the MA lead halides, three phases have been detected moving from low- to high-temperature, namely, orthorhombic, tetragonal and cubic phase.[1,2,5] Together with the different long-range order of the various crystalline phases, also the orientation and mobility of the MA group changes. For example, in the cubic phase of $MAPbI_3$ and $MAPbBr_3$ perovskites (space group $Pm\bar{3}m$) it has been reported a fast rotation of the MA group around the C–N bond while in the orthorhombic *Pnma* symmetry there is an orientational ordering of the MA ion.[1,6]

Recently there has been an increasing recognition of possible distortion in cubic hybrid perovskites and preferred orientation of the organic cation.[4,7,8] Motta and co-workers, for example, observed that, in cubic $MAPbI_3$, if the MA ion orients along specific crystallographic directions, i.e., (001)-like, the PbI_6 octahedra cage distorts and the band-gap can become indirect. In their work they also observed that the relaxation of the MA cation leads to geometries where the PbI_6 octahedra are distorted.[4] Also from the experimental point of view, there has been some suggestions that the actual symmetry of the cubic phases may be different and that Pb could be shifted with respect to the (0,0,0) position expected in the $Pm\bar{3}m$ space group.[1] In addition, while the cubic symmetry indicates a fully disordered MA group, the suggestion of alternative symmetries may imply that the MA groups are tumbling more along specific crystallographic directions.[1]

In order to unveil the possible distortion at the local scale in hybrid perovskites and to shed light on the correlation between short-range and long-range order between the different polymorphs, we carried out a variable-temperature neutron total scattering experiment coupled to pair distribution function (PDF) analysis. This has been performed on a fully deuterated $MAPbBr_3$ sample by collecting data as a function of temperature from 5 K to 300 K, i.e., by crossing the different crystalline phases found in this material. The sample has been synthesized according to the procedure reported in the Supporting Information (SI) which also includes the refined laboratory X-ray diffraction pattern of the deuterated $MAPbBr_3$ sample (Figure S1 in the SI). Room temperature data refinement confirms the $Pm\bar{3}m$ space group for the methylammonium lead bromide with a lattice parameter of 5.9123(2) Å, in agreement with previous literature data.[9] The sample is single-phase without any trace of impurities.

From the total scattering $S(Q)$ collection, after the proper data corrections procedure, described in the SI, the data were Fourier transformed to obtain the PDFs and analyzed in real-space by means of the PDFgui software.[10,11]

Figure 1a shows the neutron PDFs for the deuterated $MAPbBr_3$ sample as a function of temperature in the 1–10 Å range, while Figure 1b shows the same PDF in the reduced range between 1 and 5 Å.

From the qualitative analysis of the PDFs reported in Figure 1 it is already possible to draw some conclusions. First of all, according to the literature data and our diffraction and calorimetric measurements (Figure S2 in the SI), the sample is in the cubic form at 300 K while at 225 K, 175 K and 150 K the actual phase is the tetragonal *I*4/*mcm*.[5] Finally, the data at 100 K, 50 K and 5 K correspond to temperatures where the $MAPbBr_3$ is in the orthorhombic phase (*Pnma*).[5]

As a matter of fact, by reducing temperature, some differences can be found in the PDFs but this is true only for *r*-values greater than ca. 2.8 Å (see the vertical bar in Figure 1b). Below this value, the PDFs seem to be very scarcely

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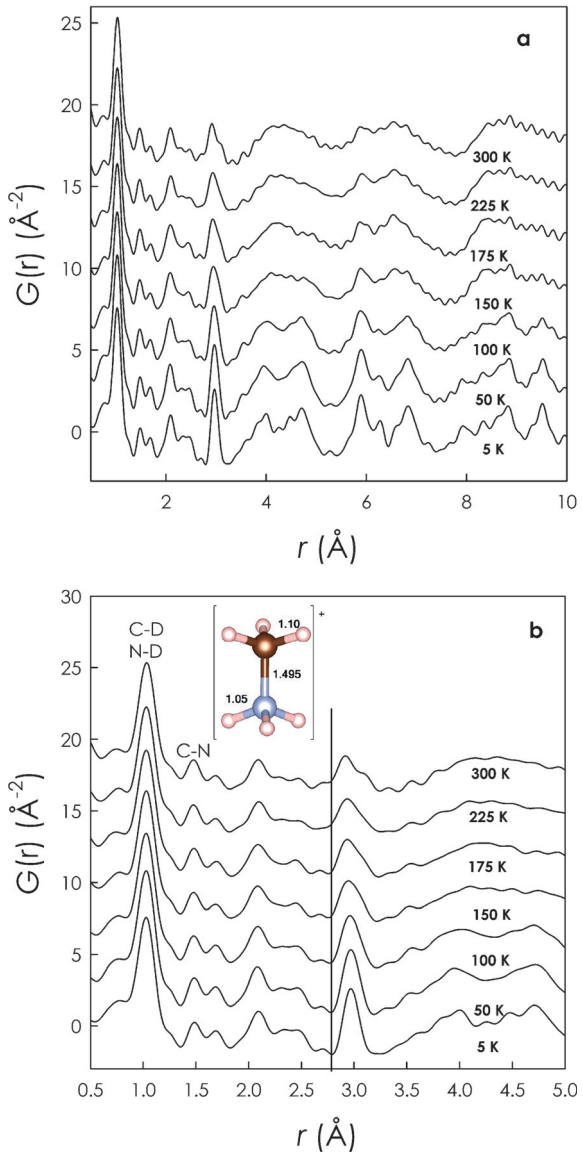

Figure 1. a) Neutron PDFs for $MAPbBr_3$ as a function of temperature in the 1–10 Å range. b) Neutron PDFs for MAPbBr3 as a function of temperature in the 1–5 Å range. Inset: structure of the methylammonium ion, taken from Ref. [12].

affected by the temperature variation and by the fact that the material is changing from a cubic symmetry at 300 K to a distorted orthorhombic structure at 5 K. The range of *r*-values where the data are insensitive to the temperature and, more importantly, lattice symmetry changes, contains bond pair contributions of the $CD_3ND_3^+$ group (methylammonium) and interaction between this group and the Br coordination environment. For example, the first most intense peak in the PDFs reported in Figure 1 contains atom–atom interactions coming from the N–D and C–D bonds, while the N–C pair is found around 1.47 Å, according to the chemical structure of the MA cation shown in the inset of Figure 1 b (taken from Ref. [12]). The first bond pairs involving the $MABr_{12}$ environment are found at about 2.50 Å and correspond to two sets of D···Br bonds with the deuterium atoms of the ND_3^+ group. Interaction of Br with the D atoms attached to the C atoms are found around 2.90 and 3 Å. Around 3 Å are also found the Pb–Br bond lengths of the octahedron. All these considerations about the bond pairs are based on the available model for the orthorhombic structure in the *Pnma* space group and the reason for taking into account this argument will be clarified in the following.

It should be noted that the clear similarity between the PDFs at the different temperatures, corresponding to at least three different long-range structures, has not only a direct relevance regarding the MA group but also with respect to the $PbBr_6$ octahedra. This comes from the fact that the bond pairs involving the hydrogen bond between D and Br indirectly influence the structure of the $PbBr_6$ octahedra as well as the orientation of the MA group within the space left in the perovskite structure.[6] All these qualitative observations strongly support a situation where the MA group maintains a nearly constant arrangement and connection with the Br cage irrespective to the long-range structure.

The data reported in Figure 1 have been refined against the available models for the different crystal structures. We start our discussion from the low-*T* data, i.e., the PDF at 5 K. Figure 2 reports the fit, in the 1–10 Å range of the neutron

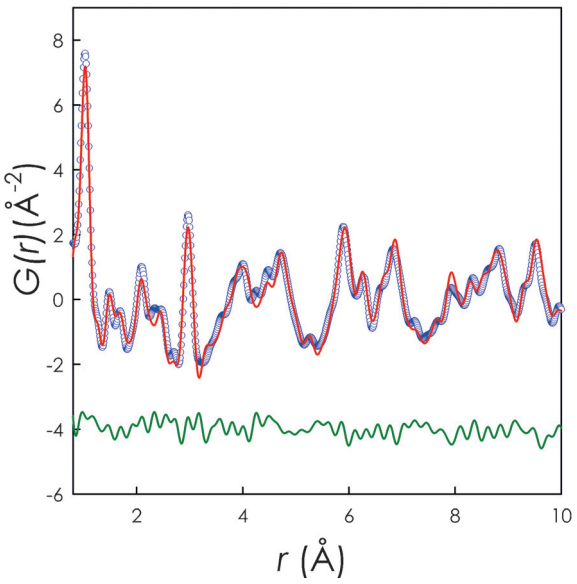

Figure 2. Fit for the 5 K data against the *Pnma* structure. Empty blue circles: experimental data; red line: fitted structure; green line: residual. Residuals have been shifted by −4.

PDF of the fully deuterated $MAPbBr_3$ at 5 K against the orthorhombic *Pnma* structural model used as input model structure.[6] Parameters fitted in the structure were unit cell parameters, scale factor, correlation parameter, atomic positions and isotropic thermal displacement parameters (U_{iso}) for all the atoms. The refined parameters for the fit of Figure 2 are reported in Table S1 in the SI. The R_{wp} of the fit is 17.1 % and no correlation between the parameters has been observed. Moreover, the *U* values have been found to be very reasonable for all the atoms.

As can be appreciated from the fit and the refinements results, the orthorhombic *Pnma* structure properly describes the 5 K data both for the heavy atoms (Br and Pb) and, most importantly, for the MA group. The results of our refinement are in good agreement with the neutron powder diffraction data reported by Swainson et al. in Ref. [6] carried out on a $CH_3ND_3PbBr_3$ sample. A sketch of the structure refined in Figure 2 is reported in the following Figures 3a and b. The

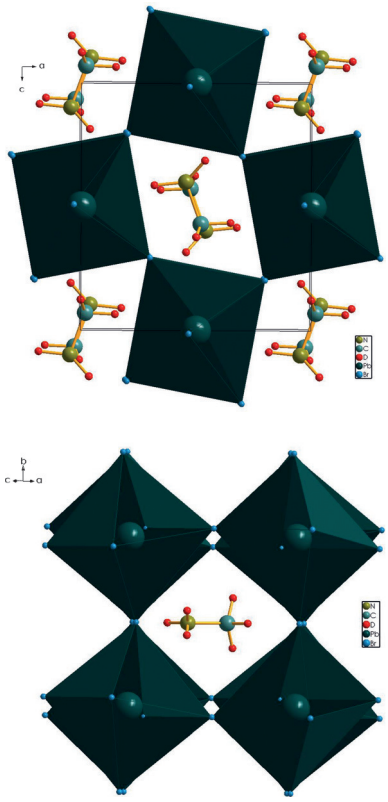

Figure 3. Sketch along two different projections of the crystal structure of MAPbBr3 as obtained from the refinement of the 5 K data in the *Pnma* space group. Color code (ball-and-stick model): green, N; blue-gray, C; red, D; (polyhedron model): dark blue, Pb; light blue, Br.

MA group is normal to the *b*-axis and can be viewed to lie in a position parallel to a pseudo-cubic unit cell as represented by Figure 3b. Moreover, there are interaction between the D and Br atoms that are a key ingredient in defining the octahedral arrangement (and distortion) within the structure. The three bond lengths of the $PbBr_6$ octahedron are 2.99-(1) Å, 2.963(7) Å and 2.96(1) Å.

Having properly refined the 5 K data it is now possible to discuss the data at higher temperatures. While the 50 K and 100 K data still lie in the orthorhombic long-range structure and can be adequately refined with this model, the fundamental question is how to model the data with the tetragonal and cubic symmetries also considering the very close similarity between the PDFs as a function of temperature, particularly in the low-*r* range pertaining to the MA group bond pairs and the interaction within the $MABr_{12}$ framework (see Figures 1a and b).

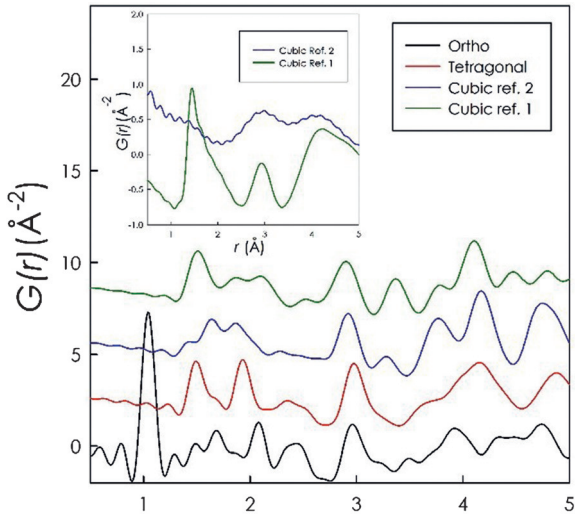

Figure 4. Calculated PDFs for the different crystal structures available for the $MAPbBr_3$ perovskite.

Figure 4 displays the calculated PDFs in the 1–5 Å range for the orthorhombic, tetragonal and cubic structures according to the available models, i.e., Ref. [6] for the orthorhombic, Ref. [2] for the tetragonal and Refs. [1] and [2] for the cubic structures. In order to make the comparison reliable, all the structures have been calculated considering a U value of 0.005 $Å^2$ for all the atoms and replacing the H with D. The data reported in Figure 4 are just calculated from the literature and have not been refined against any data. The most striking aspect of the comparison of Figure 4 is that none of the higher-symmetry models, i.e., tetragonal and cubic structures, are able to describe the peak located at about 1 Å which pertains to N–D and C–D distances of the MA group. This results from the smearing of the intensity due to the location of D atoms on high-multiplicity sites with fractional coordinates.

In addition, let us note that in the cubic models derived from neutron diffraction data available in the current literature, that is, Refs. [1] and [2], the refined U_{iso} pertaining to the MA units are very high (up to 1.5–1.7 $Å^2$), that is, values without any physical meaning. If used, such parameters would lead to a totally smeared PDF as shown in the inset of Figure 4. The main problem relating to the use of a long-range probe such as neutron diffraction to study hybrid perovskites, is the presence of a significant diffuse scattering contribution that is discarded in the analysis of the Bragg peaks.[1,2] Only by means of a short-range order probe such as PDF and collecting neutron total scattering data, including diffuse scattering, on deuterated samples, it is possible to address the structural problem of these materials.[11]

Considering the results reported in Figure 4 it is clear that no one of the available models for the tetragonal and cubic structures can be used to treat the data at higher temperatures. Already considering the results reported up to now for the refinement of the 5 K and the previous discussion, one can already highlight a striking result of our investigation: the local arrangement of the MA group does not significantly change as the long-range symmetry of $MAPbBr_3$ changes

being the PDFs at low-*r* very similar at all the temperatures investigated.

Based on the considerations above, the data at all the remaining temperatures have been refined according to the orthorhombic model. Figure 5 shows the fit of the 300 K data in the 1–10 Å and 1–5 Å ranges for the $MAPbBr_3$ perovskite.

The fit reported in Figure 5, which results are reported in Table S2 in the SI, is capable of describing the short-range order of the $MAPbBr_3$ hybrid perovskite taking into account the bond pairs involving the MA group and the interaction of this group with the surrounding coordination environment with the Br anions. It is interesting to note that the location of the MA within the $MABr_{12}$ network is only marginally affected by the temperature increase (see Figure S3 in the SI). While still keeping the orthorhombic crystal structure, the overall distortion of the system reduces. The pseudo-cubic lattice parameters for the 5 K data are $a = 5.6041$ Å, $b = 5.9013$ Å, and $c = 6.0213$ Å, while at 300 K they become $a = 5.8562$ Å, $b = 5.9610$ Å, and $c = 6.1300$ Å, thus reducing the difference between the three axes. Concerning the $PbBr_6$ octahedron, it can be seen that moving from 5 K to 300 K the bond angles tend to converge towards closer values, that is, 82.6(1)°, 88.8(1)° and 85.4(1)° at 5 K and 88.1(1)°, 86.2(1)° and 88.1(1)° at 300 K. On the other hand, the three distinct bond lengths of the $PbBr_6$ octahedron become slightly more separated at higher temperature going to 2.95(1) Å, 3.00(2) Å and 3.10(1) Å at 300 K while at 5 K they are 2.99(1) Å, 2.963(7) Å and 2.96(1) Å. This splitting of the distinct bond lengths of the octahedron by increasing temperature is worth of relevance, and suggests some local rearrangement of the octahedron upon temperature increases that should be investigated further and which may be related to the strain induced by the MA group at higher temperatures, as suggested by theoretical works.[4]

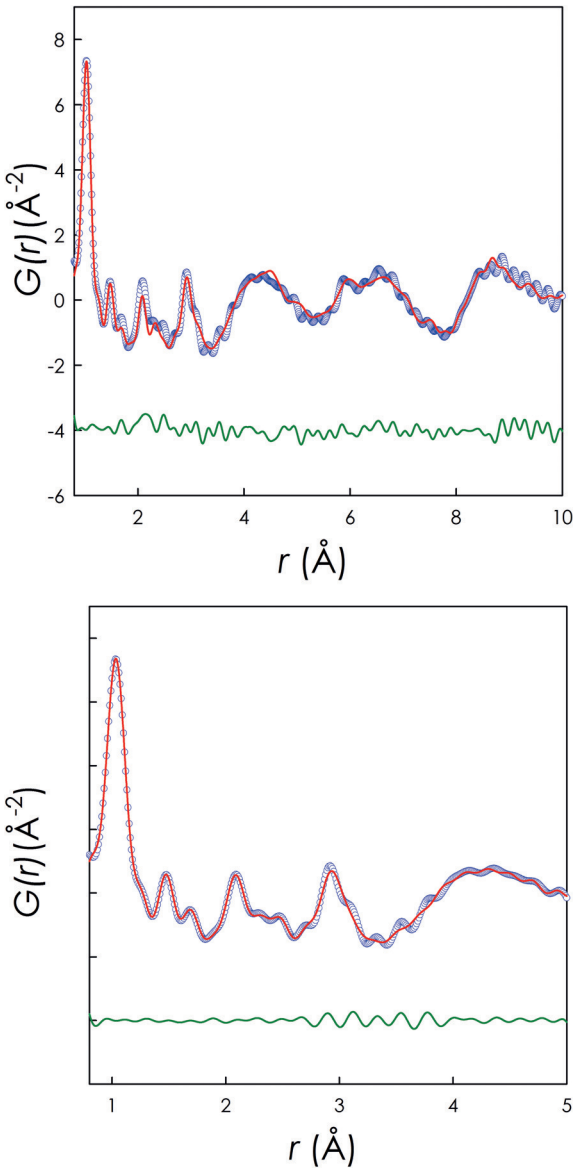

Figure 5. Fits for the 300 K data against the *Pnma* structure a) in the 1–10 Å range and b) in the 1–5 Å range. Empty blue circles: experimental data; red line: fitted structure; green line: residual. Residuals have been shifted by −4. R_{wp} of the fit 15.6%.

The results reported in this work clearly show that, by taking into account the diffuse scattering found in the neutron diffraction data on hybrid perovskites, it is possible to provide a clear picture of the short-range order in these materials. The case study presented here on $MAPbBr_3$ has shown a very important result. The MA group, which is capable of rotation around its axis in the cubic phase, is not actually disordered as proposed by means of long-range order probes such as diffraction. On the other hand, we have clearly shown that the arrangement of the methylammonium group remains essentially the same upon crossing the different phase transitions in $MAPbBr_3$. What is changing by increasing temperature is the configurational degeneracy of the MA ion within the structure, but the local arrangement of this moiety is analogous in the orthorhombic, tetragonal and cubic phases. The very close similarity between the PDFs at all temperatures, and in particular in the low-*r* range affected by the MA bond pairs and MA interactions with the Br cage, together with the presented refinements of the data, clearly indicate that, at the local structure scale, the symmetry of the system is orthorhombic and that, most probably, this result is connected to the constant arrangement of the MA group within the perovskite lattice and its interaction by hydrogen bonding with Br ions. As the key conclusion of this work, it can be stated that by increasing temperature, the local environment and position of the MA group changes from static to configurationally averaged while preserving the same local arrangement as in the orthorhombic unit cell. Whether this is accommodated dynamically, or within an order–disorder structural motif is an open question. As a matter of fact, all the experimental and theoretical works carried out until now considering the MA group completely disordered within the perovskite lattice, should be re-considered taking into account that the MA cation has a defined position within the structure for all the phases found. What is changing, by increasing *T*, is its access to the available rotation degrees of freedom while preserving a well-defined local structure.

The experimental results reported in this work support a recent theoretical investigation[4] which suggests that the high efficiency of hybrid perovskite solar cells may come from

the strain exerted by the organic cation leading to a distortion of the PbX_6 octahedra and by the fact that the cation adopts specific positions in space which is in agreement with the present experimental observation of a configurationally averaged while locally well-defined MA arrangement.

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[1] T. Baikie, N. S. Barrow, Y. Fang, P. J. Keenan, P. R. Slater, R. O. Piltz, M. Gutmann, S. G. Mhaisalkar, T. J. White, *J. Mater. Chem. A* **2015**, *3*, 9298.
[2] M. T. Weller, O. J. Weber, W. P. Henry, A. M. Di Pumpo, T. C. Hansen, *Chem. Commun.* **2015**, *51*, 4180.
[3] J. J. Choi, X. Yang, Z. M. Norman, S. J. L. Billinge, J. S. Owen, *Nano Lett.* **2014**, *14*, 127.
[4] C. Motta, F. El-Mellouhi, S. Kais, N. Tabet, F. Alharbi, S. Sanvito, *Nat. Commun.* **2015**, *6*, 7026.
[5] D. Weber, A. Poglitsch, *J. Chem. Phys.* **1987**, *11*, 6373.
[6] I. P. Swainson, R. P. Hammonf, C. Soulliere, O. Knop, W. Massa, *J. Solid State Chem.* **2003**, *176*, 97.
[7] Y. Ren, I. W. H. Oswald, X. Wang, G. T. McCandless, J. Y. Chan, *Cryst. Growth Des.* **2016**, *16*, 2945.
[8] I. Deretzis, B. Di Mauro, A. Alberti, E. Smecca, A. La Magna, *Sci. Rep.* **2016**, *6*, 24443.
[9] A. Mancini, P. Quadrelli, C. Milanese, M. Boiocchi, A. Sironi, M. Patrini, G. Guizzetti, L. Malavasi, *J. Solid State Chem.* **2016**, *240*, 55.
[10] T. Egami, S. J. L. Billinge, *Underneath the Bragg Peaks: Structural Analysis of Complex Materials*, Pergamon, Amsterdam, **2003**.
[11] C. L. Farrow, P. Juhás, J. W. Liu, D. Bryndin, E. Božin, J. Bloch, T. Proffen, S. J. L. Billinge, *J. Phys. Condens. Matter* **2007**, *19*, 335219.
[12] G. Giorgi, J.-I. Fujisawa, H. Segawa, K. Yamashita, *J. Phys. Chem. C* **2015**, *119*, 4694.

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