Large dynamic scissoring mode displacements coupled to band gap opening in Hybrid Perovskites

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Hybrid perovskites are a rapidly growing research area, having reached photovoltaic power conversion efficiencies of over 25%. We apply a symmetry-motivated analysis method to analyse X-ray pair distribution function data of the cubic phases of the hybrid perovskites MAPbX$_3$ ($X = I$, Br, Cl). We demonstrate that the local structure of the inorganic components of MAPbX$_3$ ($X = I$, Br, Cl) are dominated by scissoring type deformations of the PbX$_6$ octahedra. We find these modes to have a larger amplitude than equivalent distortions in the A-site deficient perovskite ScF$_3$ and demonstrate that they show a significant departure from the harmonic approximation. Calculations performed on an all-inorganic analogue to the hybrid perovskite, FrPbBr$_3$, show that the large amplitudes of the scissoring modes are coupled to an opening of the electronic band gap. Finally, we use density functional theory calculations to show that the organic MA cations reorientate to accommodate the large amplitude scissoring modes.

I. INTRODUCTION

Molecular perovskites, also known as hybrid perovskites, are a fast growing research area in photovoltaics, due to their low cost to make and rapid increase in efficiency (from 3.9% in 2009 to > 25% today). These materials have the general structure and chemical formula of traditional perovskites (ABX$_3$), but where they differ is that the A site cation is organic. The most frequently studied of this class of materials are the methylammonium (MA) lead halides, which have the general formula CH$_3$NH$_3$PbX$_3$ ($X = I$, Br, Cl), commonly abbreviated to MAPbX$_3$. In addition to their high conversion efficiency, this class of hybrid perovskites have other desirable photovoltaic properties, such as long charge carrier lifetimes, mobility, and diffusion lengths, a high absorption coefficient, and a direct band gap. These properties couple together to create a device that has a high density of charge carriers with a strong barrier against recombination, all whilst needing much less material than traditional solar cell materials, and without the need for a high energy input manufacturing process.

Whilst perovskite oxides are a well studied class of materials due to the wide range of desirable properties exhibited by them, less is understood about the structure-property relationship in halide perovskites, particularly the hybrid perovskite family. Having a methylammonium ion rather than a metal ion at the A site results in the A site possessing an electric dipole moment rather than a point charge, so the dynamics of these ions are the focus of a lot of research in these hybrid perovskites. In the higher temperature tetragonal and cubic phases, the alignment of the ions appears to be disordered, however they could form small domains below the length scale required for coherent diffraction where the molecules are aligned. The dynamics of their rotations, and any local order, could have a large contribution to the properties of the material. For example, the interaction between phonons and the rotational degrees of freedom of the MA cations has been shown to have an impact on thermal conductivity. The changes in dynamics are thought to be closely linked to the structural changes of the material with temperature, and it is still unknown how the dynamics affect the properties of this material as a photovoltaic. Another question that has still not been fully solved is whether the configuration of the MA cations lead to this class of materials being ferroelectric.

Use of X-ray single crystal and powder diffraction has led to a good understanding of the different structural phases of these materials. Similarly to a large number of perovskites, all of the single-halide MAPbX$_3$ materials have cubic symmetry at high temperatures and undergo symmetry-lowering phase transitions to tetragonal and orthorhombic structures at lower temperatures. Most experimental studies agree that there are 3 structural phases for MAPbI$_3$ and MAPbCl$_3$, however there is a 4$^{th}$ phase for MAPbBr$_3$ which is preferred for a small temperature range (ca. 150-155 K), commonly thought to be an incommensurate phase. In the cubic phase, the MA cation is thought be fully disordered, with recent advances made using techniques such as NMR and
quasi-elastic neutron scattering showing that the MA cation is close to having the orientational freedom of a free MA cation. As the inorganic framework undergoes structural phase transitions, lowering the average symmetry from cubic $Pm3m$, the orientational freedom of the MA cation is restricted, becoming fully ordered in the orthorhombic phases. This shows that the organic molecular and inorganic framework dynamics in MAPbX$_3$ are inherently linked. In addition to experimental studies, computational methods have seen a lot of use in this, and other, areas of research in hybrid perovskites. Both classical molecular dynamics and DFT simulations have demonstrated a link between the different phases of MAPbI$_3$ and the preferred orientations of the MA cation. Work from Quarti et al. demonstrated that the configuration of the MA cations has a significant effect on the properties of the material, such as its electronic band structure. This underlines why it is important to fully understand the structure-property relationship in these materials. Despite the knowledge that the organic molecular and inorganic framework dynamics are linked via hydrogen bonding interactions, it is currently unclear how this interaction affects the dynamics as a whole.

The bands forming the top of the valence bands and the bottom of the conduction band in the electronic structure of the methylammonium lead halides will be dominated by Pb and X ($X = I$, Br, Cl) electrons. Therefore, regardless of the role of the MA cation in stabilising particular distortions, it is necessary to establish good models for the dynamic distortions in the PbX$_3$ framework. In this work, we aim to probe the dynamics of the inorganic framework of the cubic phases of the three single-halide MAPbX$_3$ materials. We have recently demonstrated how by using a symmetry motivated approach to analysing PDF data we can gain extra information on disorder and dynamics within a system. Our study on BaTiO$_3$ has shown that this method is very sensitive to primary order parameters and is a powerful tool to analyse order-disorder phase transition. Both this study and our more recent work on the negative thermal expansion materials ScF$_3$ and CaZrF$_6$ has demonstrated that this method is also sensitive to soft phonon modes and has also revealed substantial deviations from the crystallographic average structure in these materials. Here, we use X-ray total scattering data, which is much more sensitive to the inorganic framework than the molecular cations, to probe the characters of the low lying excitations of the cubic phases of the methylammonium lead halides.

II. EXPERIMENTAL DETAILS AND DATA ANALYSIS

MAPbI$_3$ was prepared using the inverse temperature crystallisation method. Briefly, equal molar amounts of MAI and PbI$_2$ were dissolved in a solvent (γ-butyrolactone) at room temperature. Then the obtained MAPbI$_3$ solution was heated to 110 °C for the crystal growth. Powder samples of MAPbBr$_3$ were prepared by the reaction of stoichiometric amounts of lead acetate and methylamine hydrobromide in hydrobromic acid. The excess acid was then evaporated to leave an orange colored product which was washed with diethyl ether. Powder samples of MAPbCl$_3$ were prepared out of a solution of methylamine hydrochloride and lead acetate dissolved in hydrochloric acid. An excess of an approximately 8-10 molar ratio of methylamine hydrochloride was required to obtain these phase pure samples. The resulting powder was washed with diethyl ether.

For MAPbBr$_3$, synchrotron radiation X-ray total scattering experiments were conducted at the synchrotron facility PETRA III (beamline P02, DESY, Hamburg). A wavelength $\lambda = 0.2070$ Å was used to collect data. Data were collected at temperatures of 125, 140, 147, 152 K and at intervals of 25 K from 175 to 450 K.

For MAPbI$_3$ and MAPbCl$_3$, Synchrotron radiation X-ray total scattering experiments were conducted at the synchrotron facility Diamond Light Source (beamline I15-1). A wavelength of $\lambda = 0.161669$ Å was used to collect data. Data were collected at 20 K intervals over the temperature ranges 100 - 460 K (MAPbCl$_3$) and 100 - 460 K (MAPbI$_3$).
Figure 2. For each compound, the best individual fitting statistic is plotted for each irrep at each temperature. The R-factor is shown relative to the R-factor for the refinement with no symmetry adapted displacement modes active in the refinement, and the temperature shown is relative to the cubic phase transition as reported in the literature. The cubic transition temperature for each compound is indicated on the plot. The irreps are labelled as follows: colour denotes the k-transition temperature for each compound, with blue referring to the M-point, green to the X-point, pink to R and yellow to Γ; marker shape denotes the irrep number, with a circle referring to 1, an upward-pointed triangle to 2, a star to 3, a square to 4 and a downward-pointed triangle to 5; linestyle denotes the parity of the irrep, with a solid line referring to a “+” irrep, and a dashed line referring to a “−” irrep.

- 560 K (MAPbI₃).

The obtained 2D images were masked and radially integrated using the DAWN software. G(r) and D(r) functions were computed using GudrunX using Q_{max} values of 21, 30 and 28 Å⁻¹ for MAPbBr₃, MAPbCl₃ and MAPbI₃ respectively. GudrunX was also used to perform background subtraction, sample absorption and fluorescence corrections.

Analysis of the pair distribution functions was carried out using the symmetry-adapted PDF analysis (SAPA) method described in ref. 32. For each sample, a 2 × 2 × 2 P1 supercell of the Pm3n aristotype PbX₃ with Pb at (0.5, 0.5, 0.5) and X at (0.5, 0.5, 0) was generated and parameterised in terms of symmetry adapted displacements using the ISODISTORT software. The generated mode listings were output in .cif format and then converted to the .inp format of the TOPAS Academic software v6 using the Jedit macros. In total, there were 96 modes which transformed according to one of 19 irreducible representations. These supercells were generated without the organic A-site cation included, since the contribution of pairs involving the organic components of the structure will have a negligible contribution to the overall PDF due to their comparatively weak scattering power for X-rays. This lack of sensitivity of X-ray total scattering to the organic elements of hybrid perovskites can be seen by comparing recent publications by Malavasi et al. For each irreducible representation (irrep) at each temperature, refinements of the corresponding modes were started from random starting mode amplitudes. This was repeated 500 times. For all samples, the refinements were carried out with a fitting range of 1.7 to 20 Å. Refinements were also tested using a fitting range with a maximum of 10 Å and found to be broadly similar.

The DFT calculations were performed using the Vienna Ab Initio Simulation Package (VASP) version 5.4.4. We employed the optB86b-vdW exchange correlation potential which includes VdW corrections previously found to suit hybrid perovskites. Projector augmented-wave (PAW) pseudopotentials were utilised, as supplied within the VASP package. A plane wave basis set with a 1100 eV energy cutoff and a 4 × 4 × 4 Monkhorst-Pack k-point mesh with respect to the parent cubic primitive cell (scaled accordingly for other supercells) were found suitable. The energy landscape of the various modes in the hybrid system were studied by fixing the halide framework while allowing for Pb and MA to relax until the forces were less than 5 meV/Å. Results were compared with FrPbBr₃, which we used as a hypothetical inorganic analogue to the hybrid perovskite, since Fr best matches the ionic radii of MA.

III. RESULTS AND DISCUSSION

A key aspect of the local structure of the MAPbX₃ (X = I, Br, Cl) family of hybrid perovskites is that the first four peaks of the inorganic component of the PDF do
Figure 3. (a-c) A breakdown of the atomic basis that spans the $X_5^+$ irreps. Shown in (d) is the structure resulting from a refinement of the $Pnma$ order parameter direction of the $X_5^+$ irreps. (e) Mode energies with varying distortion mode amplitude for the $Pnma$ order parameter direction of FrPbBr$_3$. Harmonic (2$^{\text{nd}}$ order) and anharmonic (4$^{\text{th}}$ order) fits to the potential well are shown. (f) Mean displacement values for the general $X_5^+$ order parameter direction.

not change much beyond that expected for simply changing the temperature, i.e a change in peak width corresponding to a change in thermal energy, and a change in peak position corresponding to thermal expansion. For MAPbBr$_3$ (Fig. 1) and MAPbCl$_3$, the peaks stay the same from the low temperature orthorhombic phase into the high temperature cubic phase. For MAPbI$_3$, there is a slight change upon the transition between the tetragonal and orthorhombic phases, but the peaks from the tetragonal phase persist in the cubic phase (see SI). This has been taken to imply that the cubic phase consists of local symmetry-broken domains and there has been recent work to support this hypothesis.

This would suggest that the distortions most responsible for the local structure should be the rigid-unit modes (RUMs) that drive these phase transitions.

To gain a more robust understanding of the local structure of MAPbX$_3$ ($X$ = I, Br, Cl), we perform a symmetry-adapted PDF analysis (SAPA) to elucidate the character of the dominant lattice dynamics associated with the inorganic cage. We note that we are insensitive to MA orientation and displacement modes in the present X-ray PDF study, and so no attempt is made to model these against the experimental data. The symmetry-adapted displacements which show the most improvement in the $R_w$ for the models against the PDFs for all compounds and all temperatures are those which transform according to irreps that permit a scissoring motion of the X anions, i.e., the Br–Pb–Br bond angles are distorted away from 90° but the Pb–Br bond lengths remain undistorted. This result of the SAPA analysis does not imply that the RUMs are high energy modes, it simply means that the majority of the motion of the halide anions arise from these scissoring modes. This is supported by competitive two-phase refinements of the PDFs, in which we allow the $X_5^+$ displacements to refine in one phase and the displacements for one of the RUMs ($R_5^-$ or $M_2^-$) in the other. These refinements show a preference for scissoring modes compared to the RUMs for all 3 samples, as evident from the refined scale factors of the two phases which show an approximate scissoring:rotation ratio of 2.3:1 (see SI for more details). For context, this ratio is approximately 4:1 in ScF$_3$, which is isostructural to the inorganic framework of MAPbX$_3$. The lower ratio compared to ScF$_3$ reflects a lower flexibility due to the presence of an A-site cation, which can interact with the inorganic framework via hydrogen bonding. However, it is clear from our results that the majority of the halide anion motion still arises from scissoring-type deformations of the octahedra.

The above results are in line with a recent reverse Monte Carlo (RMC) analysis of neutron PDFs of MAPbI$_3$ between 10 and 400 K. This study demonstrates that a bending of the Pb-I-Pb bond angle dominates the local distortions of the PbI$_6$ octahedra. Our results show that the four best fitting modes all have
scissoring character, of which it is the $X_3^+$ (Fig. 3a, c and d) that performs best across all three compositions and temperatures. This could be due to the fact that there are more parameters for the $X_3^+$ irrep than the other three (18 modes transform as the $X_3^+$ irrep, compared to 12 for $M_5^-$ and 6 for $X_5^-$ and $M_6^+$), but the improvement could arise from the anti-polar Pb displacements that enter into the irrep $X_3^+$, although this is unlikely since they only have a small contribution to the overall displacements. The three distortions that span this irrep are shown in Fig 3a.

We find the amplitudes of these scissoring modes to be quite large; refinements of $X_5^-$ and $X_5^+$ in the tetragonal phase of MAPbBr$_3$ resulted in supercell-normalised mode amplitudes of $\approx 1.35 \text{ Å}$. This is close in magnitude to the equivalent amplitude of the $R_5^-$ distortion ($\approx 1.65 \text{ Å}$) which is frozen into the structure in the tetragonal phase.

Given how large the local deviations are from the average structure, it is reasonable to assume they will have a substantial effect on the band structure. We used DFT calculations to investigate the impact that the scissoring modes could have on the electronic band structure of the hybrid perovskites. We chose to analyse MAPbBr$_3$, since it is cubic at room temperature where experimental band gap values have been reported, and to focus on the two X point modes that do the best job at describing the deviations away from local cubic symmetry, as evident in the PDF data. For a completely unrestrained order parameter direction transforming as $X_5^+$, there are a rather large number of degrees of freedom (18 in total), so, to make our results more robust, and to facilitate a direct comparison to $X_5^-$, we take results from refinements using higher symmetry OPDs with no more than 5 parameters. We use structures from refinements against our data with $X_5^-$ OPDs with $Pnma$ and $Cmcm$ symmetry ($(0, a; b, 0; 0, c)$ and $(0, a; b, b, a, 0)$ respectively) and the $X_5^-$ OPD with $C2/c$ symmetry ($(a, b, c; -c, -b, -a)$) as input to our band structure calculations. For the two $X_5^-$ OPDs, only Br anion displacements were refined when generating the CIFs for the band structure calculations, although by symmetry, Pb displacements also enter into the irrep. For $X_5^-$, Pb displacements are forbidden by symmetry. We also sampled points of different overall distortion amplitude along the $X_5^-$ OPD with $Pnma$ symmetry and calculated the energy. These energy calculations were performed for the FrPbBr$_3$ structures used to calculate the band structure.

In the undistorted structure, the calculated band gap was 1.717 eV, which is slightly higher than other calculated band gaps for cubic MAPbBr$_3$ (1.64 eV$^{[55]}$) at the same level of theory, and is direct. Previous work has shown that substitution of Fr for MA opens up the band gap slightly in orthorhombic MAPbI$_3$.$^{[22]}$ For each distortion, the band gap opens up significantly to values of 2.025, 2.138 and 2.162 eV for the $C2/c$, $Cmcm$ and $Pnma$ distortions with an amplitude of 0.8× the maximum amplitude refined from PDF data for the $X_5^-$ distortions and 1.1× the maximum amplitude for $X_5^-$, respectively, and remains direct. These relative amplitudes were chosen so all 3 distortions were at similar mode amplitudes. These values are closer to the experimentally determined band gaps for MAPbBr$_3$ of $\approx 2.3$ eV at room temperature$^{[53]}$, although this is likely due to a cancellation of errors. The distortions result in a reduced orbital overlap between Pb and Br p-orbitals, leading to a lower band curvature and therefore an increased effective mass in the distorted band structures (Fig. 3a and SI). The mobility of polarons is inversely proportional to the electron band effective mass$^{[50]}$, and this increased effective mass in the distorted structures may explain the discrepancy between experimental and calculated values.$^{[56]}$

Spin-orbit coupling (SOC) interactions, which play a large role in systems involving Pb, have not been accounted for. Consequently, the exact shape of the electron bands and size of the band gap won’t be accurate, since inclusion of SOC has been shown to lead to unconventional dispersion relations.$^{[27]}$ The effects from SOC on band gap size in halide perovskites tend to be canceled out by full treatment of electron Coulomb interactions beyond DFT$^{[50,59]}$. Therefore, the trends we detect due to the different distortion modes will remain the same.

In the two $X_5^+$ distortions, the degeneracy of the bands at the conduction band minimum (CBM) at the Γ point are broken, leading to fewer available states at the CBM. Contrastingly, the $X_5^+$ $Pnma$ distortion appears to have the largest DOS at the valence band maximum due to the reduced bandwidth. Fluctuations in the band gap of hybrid perovskites due to their highly dynamic structure has been previously predicted.$^{[12]}$ and is expected to assist the initial stages of charge separation. In addition, an increase of the band gap coinciding with a transverse displacement of I ions in MAPbI$_3$ due to an external strain field has been reported.$^{[13]}$

Our refinements against the PDF data show that all three modes have a large amplitude, with supercell-normalised mode amplitudes of 1.84, 1.82 and 1.36 Å for OPDs with $Pnma$, $Cmcm$ and $C2/c$ symmetries, respectively. These mode amplitudes correspond to maximum Br displacements of 0.486, 0.410 and 0.350 Å. Note that the refined distortions correspond to a time-averaged view of the structure, so these maximum Br displacements are a factor of $\sqrt{2}$× greater, in the harmonic approximation, than those found in the refined structures. As a consequence of their large amplitudes, the distortions would be expected to be anharmonic in nature, which is supported by the potential energy well we calculate for the $X_5^+$ $(0, a; b, 0; 0, c)$ OPD in FrPbBr$_3$ (Fig. 3f), which has a significant quartic component when fit with a 4th order polynomial fit ($\Delta E = 127x^4 + 79.7x^2$, where $x$ is the distortion mode amplitude relative to its maximum value at 400 K). This breakdown in the harmonic approximation would then allow the scissoring modes of the inorganic framework to couple directly to the anharmonic modes that correspond to the organic cation dynamics.$^{[60,61]}$ Despite the presence of an A-site in these materials, the amplitude of these scissoring modes
are greater than those in ScF₃, suggesting the MA cations move to accommodate the large-amplitude modes. The implication of this, then, is that the band gap opening we detect as a response to the scissoring modes is likely influenced by the dynamics of the MA cations, although our refinements are only sensitive to the inorganic framework.

To investigate the above hypothesis, we consider the X₃² OPD with Pnma symmetry. This breaks the equivalency of the < 100 > directions and leads to two distinct A-site symmetries (see SI). Therefore, if the inorganic and organic dynamics are coupled together, we would expect to see the MA cations located at different points of the unit cell to respond differently to the distortion mode, to reflect the different local environments they would experience. To test this, we relaxed the MA cations from an initial anti-polar configuration with the C-N bonds aligned with the [1 0 0] direction, in a structure with a 0.8 × X₃²⁺ (0, a; b, 0; 0, c) distortion (relative to the maximum amplitude at 400 K) frozen in. The MA cations showed significant reorientation, with the “edge” ((0.5, 0, 0) and equivalents) and “corner” ((0, 0, 0)) cations rotating to include significant components along c. There is a split amongst the “face” cations, with two (at (0.5, 0.5, 0) and (0, 0.5, 0)) rotating to include smaller components along the b- and c-axes. The remaining “face” cation and the cation located at the centre of the supercell both rotate to include a significant component along c and a smaller component along b. In all, there are 5 distinct C-N bond alignments, which may reflect the 5 distinct Br sites. In addition, all cations show a slight displacement from the high-symmetry-unique positions. Full details can be found in the SI. This demonstrates that the MA cations can rotate to accommodate the distortions of the inorganic framework, indicating that the dynamics of the two components of the structure may be linked. However, it is important to note that our calculations are effectively performed at 0 K, where the ground state is the fully ordered orthorhombic phase. It is quite possible that the configurational entropy associated with the MA orderings may effectively act to decouple these dynamics at higher temperatures in the cubic phase. Indeed, there is evidence to suggest the organic and inorganic dynamics are decoupled in MAPbCl₃. Additionally, a similar computational result in CsPbBr₃ showing coupling between large amplitude distortions of the Br ions and head-to-head Cs motion suggest this feature may not be exclusive to hybrid inorganic systems. We have also shown that acoustic phonon lifetimes for the all-inorganic CsPbBr₃ are very similar to those in MAPbCl₃, further supporting the idea that at high temperatures the MA rotational modes may have little effect on the lattice phonon modes.

There has been recent literature support for the idea that cubic halide perovskites, rather than being treated as a single repeating unit, should be thought of as a network of polymorphs showing different symmetry-lowering deformations of the average structure, such as varying degrees of octahedral tilting or differing amplitudes of B-site displacement. Our work is broadly consistent with this picture. The stereochemical behaviour of the Pb cation, in conjunction with the coupling between organic cation and inorganic framework dynamics, is likely to have a large impact on the possible polymorphs the material exhibits within this hypothesis of the nature of the structure of halide perovskites.

In summary, we have shown that large scissoring modes of the halide ions describe the dominant deviations from the average structure in the cubic phases of the hybrid perovskites. These modes have a similar amplitude to those of the static RUMs below the phase transition temperature. These distortions have the effect of opening up the band gap of the electronic structure. In addition, we have shown that the organic cations can move to accommodate the distortions of the inorganic framework, suggesting the dynamics of the two components could be inherently linked, and that the inorganic lattice is likely to be significantly distorted from the average at a local level. These dynamic structures should be accounted for in simulations performed on the hybrid perovskites, since they can have a significant effect on the calculated properties.

Figure 4. The calculated electronic band structure of FrPbBr₃ for the undistorted structure (a), the Pnma and Cmcm order parameter directions of the X₃²⁺ irrep (b and c, respectively) and the C2/c order parameter direction of the X5ᵬ irrep (d). These figures were created using sumoc.

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