

Supporting Information
of
Influence of the Halide Ion on the A Site Dynamics in FAPbX₃ (X
= Br and Cl)

V. K. Sharma^{1,2*}, R. Mukhopadhyay^{1,2}, A. Mohanty³, V. García Sakai⁴, M. Tyagi^{5,6}, D. D. Sarma^{3,7}

¹*Solid State Physics Division, Bhabha Atomic Research Centre, Mumbai 400085, India*

²*Homi Bhabha National Institute, Anushaktinagar, Mumbai 400094, India*

³*Solid State and Structural Chemistry Unit, Indian Institute of Science, Bengaluru 560012, India*

⁴ *ISIS Pulsed Neutron and Muon Facility, Science and Technology Facilities Council, Rutherford Appleton Laboratory, Didcot OX11 0QX, United Kingdom*

⁵*National Institute of Standards and Technology, Center for Neutron Research, Gaithersburg, MD 20899, United States*

⁶*Department of Materials Science and Engineering, University of Maryland, College Park, MD 20742, United States*

⁷*CSIR-National Institute for Interdisciplinary Science and Technology (CSIR-NIIST), Industrial Estate P.O., Pappanamcode, Thiruvananthapuram 695019, India*

*Corresponding Author: Email: sharmavk@barc.gov.in; vksphy@gmail.com Phone +91-22-25594604

It is reported by Govinda et al¹ that FAPbCl₃ undergoes two first order phase transitions at ca 258 K and 271 K as observed in DSC measurements. It is also shown that at low temperatures (200 K and 100 K) the system exists in orthorhombic (O) structure and at room temperature (295K) it is in cubic (C) phase. However, the structure in the region between these two transitions i.e. 258K to 271K was not reported and no such literature is available for this phase. As mentioned in the manuscript, by virtue of the presence of a small number of diffraction detectors in the IRIS spectrometer, diffraction patterns could be recorded simultaneously to the QENS data. However, these diffraction patterns are of limited *d*-spacing range. The neutron diffraction patterns for FAPbCl₃ so obtained are shown in Fig. S1 at three different temperatures, 250K (below the first transition), 265K (in between the two phase transitions) and 280 K (above the second transition). The data clearly show the

presence of three distinct phases at these temperatures. We have used these diffraction patterns to specify the structure of the intermediate phase (258 – 271 K). First, we have used the space group and lattice parameters obtained from the ref. 1 for cubic and orthorhombic phase and refined the lattice parameter using FullProf. Albeit not a full refinement due to the limited range accessed by IRIS, the observed diffraction patterns could be described well (Fig. S1), and the obtained lattice parameters (Table-S1) are found to be consistent with the earlier reported results¹. The $APbX_3$ ($A=MA, FA$) family of compounds, in general, forms orthorhombic structure at low temperature which goes to cubic phase via tetragonal phase¹⁻³. As there is no information available for the intermediate phase, we attempted to obtain the same using the structural parameters as reported for the tetragonal phase of $FAPbBr_3$ ² and refined the data, for the lattice parameters only. We find that at 265 K it is most likely to be a tetragonal structure (Fig. S1).

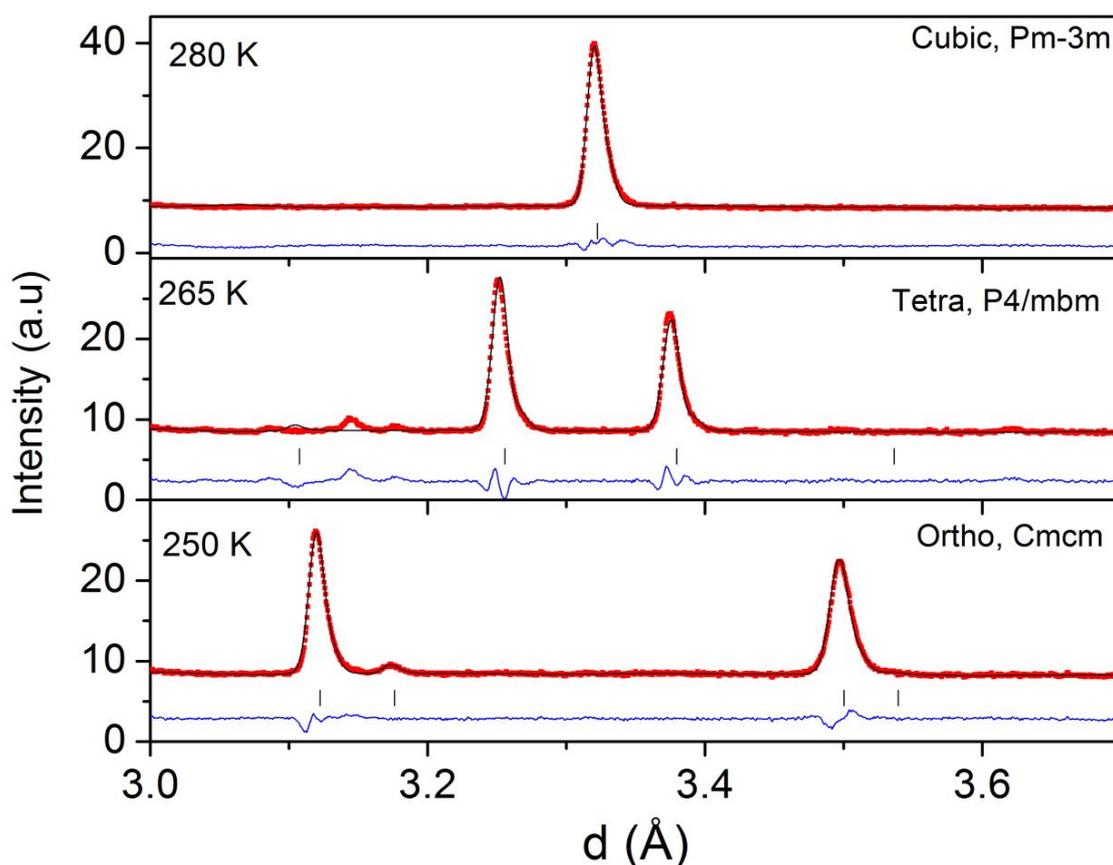


Fig. S1 The diffraction patterns for $FAPbCl_3$ recorded using IRIS spectrometer at 250K, 265K and 280K. Solid lines are the fits assuming orthorhombic ($Cmcm$), tetragonal ($P4/mbm$) and cubic ($Pm-3m$) phases^{1,2}.

Table S1: Structural parameters obtained from the refinement of diffraction patterns

T (K)	Crystal system	Space group	Lattice (Å)	Volume(Å ³)
250K	Orthorhombic	Cmcm	a=8.8266 b=7.4384 c= 11.4783	753.6161
265K	Tetragonal	P4/mbm	a=7.9077 b=7.9077 c= 6.5112	407.1563
280K	Cubic	P m-3m	a=5.7536	190.4706

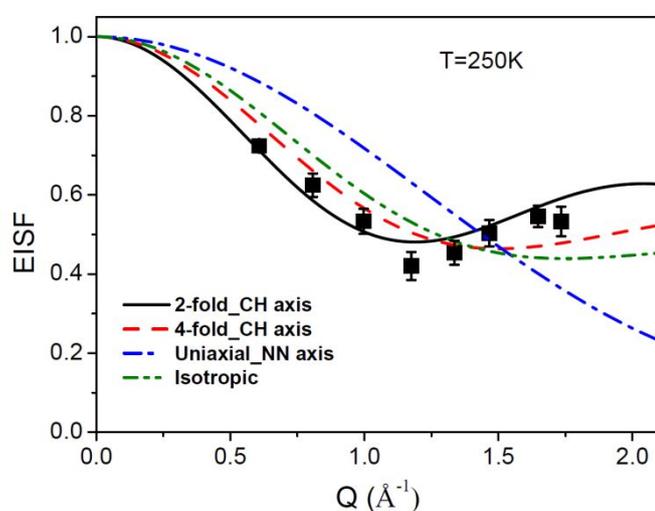


Fig. S2 Comparison of various possible models for the rotational motion of FA cation in orthorhombic phase at a typical temperature of 250 K. Solid (black), dashed (red), dash-dotted (blue) and dash double dotted (green) lines correspond to the least-squares fits assuming, 2-fold jump rotation about the C–H axis, 4-fold jump rotation about the C–H axis, uniaxial rotation around the N–N axis, and isotropic rotational diffusion models. It is evident that the 2-fold jump rotation about the C–H axis with about 88% mobile FA cations describes the experimental EISF the best.

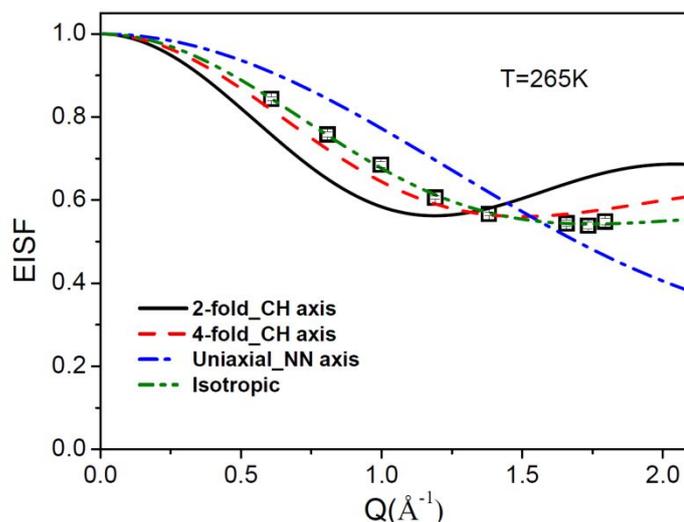


Fig. S3 Comparison of various possible models for the rotational motion of FA cation in tetragonal phase at a typical temperature of 265 K. Solid (black), dashed (red), dash-dotted (blue) and dash double dotted (green) lines correspond to the least-squares fits assuming, 2-fold jump rotation about the C–H axis, 4-fold jump rotation about the C–H axis, uniaxial rotation around the N–N axis, and isotropic rotational diffusion models. It is evident that isotropic rotational diffusion with 46% mobile FA cations describes the experimental EISF best.

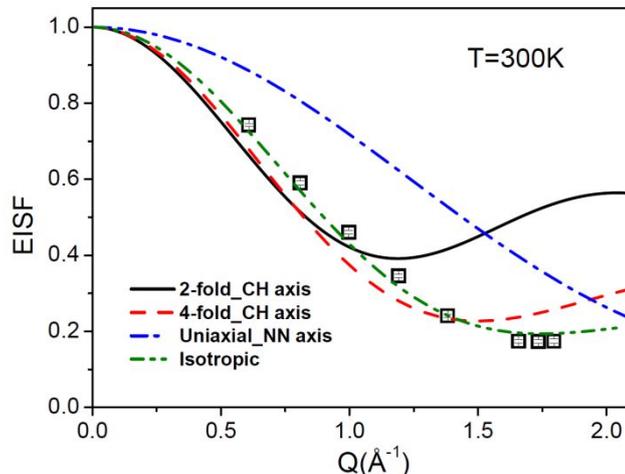


Fig. S4 Comparison of various possible models for the FA cation reorientation in the cubic phase at a typical temperature of 300 K. Solid (black), dashed (red), dash-dotted (blue) and dash double dotted (green) lines correspond to the least-squares fits assuming, 2-fold jump rotation about the C–H axis, 4-fold jump rotation about the C–H axis, uniaxial rotation around the N–N axis, and isotropic rotational diffusion models. It is evident that isotropic rotational diffusion with 81% mobile FA cations describes the experimental EISF best.

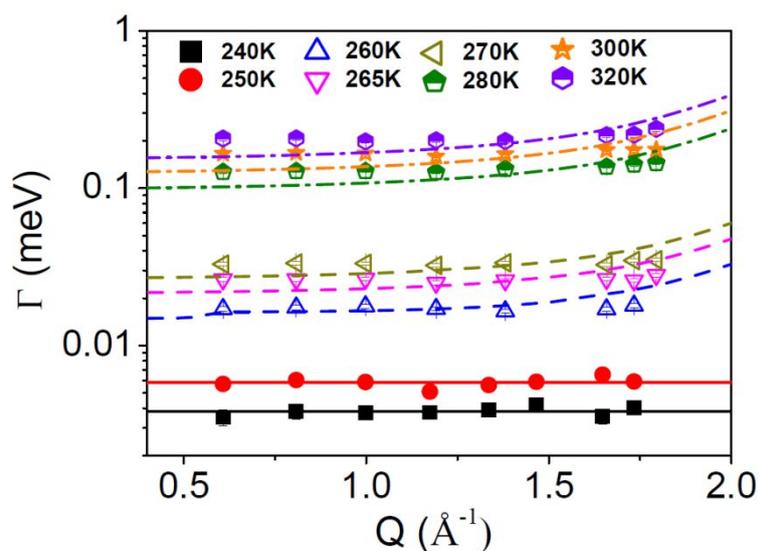


Fig.S5 Variation of HWHM for FAPbCl₃ with Q at different temperatures. It is evident that HWHM shows step jumps around both the crystallographic orthorhombic-tetragonal and tetragonal-cubic phase transitions. Solid and dashed lines are as per the fits assuming fractional 2-fold jump rotation with respect to the C-H axis (in the orthorhombic phase) and fractional isotropic rotational diffusion (in the tetragonal and cubic phases) models, respectively.

References

1. Govinda, S.; Kore, B. P.; Swain, D.; Hossain, A.; De, C.; Guru Row, T. N.; Sarma, D. D., Critical Comparison of FAPbX₃ and MAPbX₃ (X = Br and Cl): How Do They Differ? *The Journal of Physical Chemistry C* **2018**, *122* (25), 13758-13766.
2. A. Franz, D. M. T., F. Lehmann, M. Kärgeell and S. Schorr, The influence of deuteration on the crystal structure of hybrid halide perovskites: a temperature-dependent neutron diffraction study of FAPbBr₃. *Acta Crystallographica Section B* **2020**, *76* (2), 267-274.
3. Poglitsch, A.; Weber, D. Dynamic disorder in methylammoniumtrihalogenoplumbates (II) observed by millimeter-wave spectroscopy. *J. Chem. Phys.* **1987**, *87* (11), 6373-6378.