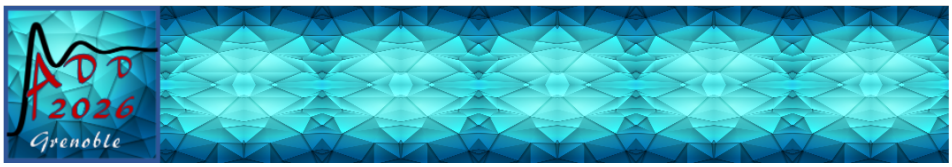

Abstract ID : **45**

Understanding local structure and dynamics in Prussian blue analogues

Content

Prussian blue analogues (PBAs) are an important and compositionally diverse class of hybrid frameworks with applications spanning a variety of different fields, including potassium-ion cathode materials and gas storage [1,2]. PBAs can contain a wide variety of different distortions and defect structures, including correlated octahedral tilts, Jahn–Teller (JT) distortions, and hexacyanometallate vacancies [3]. Gaining a better understanding of the interplay of the different distortion mechanisms is therefore important when seeking to optimise the performance of functional PBA materials.

Transition-metal hexacyanoplatinates, MPt(CN)6, are a compositionally simple subfamily of PBAs that are of interest due to their negative thermal expansion (NTE) behaviour [4]. We used a combination of X-ray pair distribution function (PDF) measurements, lattice dynamical calculations, and ab initio density functional theory (DFT) calculations to study the local structure and dynamics in various MPt(CN)6 PBAs. In order to link directly the local distortions captured by the PDF with the lattice dynamics of this family, we developed and applied a new Monte Carlo-driven, 'interaction-space' PDF refinement approach based on the optimisation of harmonic force constants, from which the (experiment-derived) low-energy phonon dispersion relations could be approximated [5]. Calculation of the corresponding Grüneisen parameters allowed us to identify correlated octahedral tilts as the key modes responsible for NTE in these materials.

Next, we sought to understand what rules might govern cooperative Jahn–Teller (CJT) order in PBAs. A simple model governing CJT order, based on the competition between strain and crystal-field stabilisation that can account for the extent of CJT order, crystallite strain, and stability measured experimentally, was developed [6]. This model shows how PBA compositions might be tuned in order to control the emergence and nature of CJT effects. Access to coarse-grained representations of JT orientations in JT-dilute and/or partially-vacant PBAs then allowed us for the first time to construct atomistic models of the local structure in these systems using the 'interaction-space' PDF refinement approach developed previously on the NTE PBAs.

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