MUSHROOM Science Case Study 2

Development opportunity - Dynamics of functional materials under pressure

Measuring both phonon and magnon dispersion relations in metal organic framework (MOF) materials under pressure is attracting increasing scientific interest since these materials are substantially softer than their inorganic counterparts, and thus pressure experiments are an ideal way to probe and modulate their functional behaviour.

For example, barocaloric materials undergo order-disorder phase transitions with associated changes in entropy as a function of pressure, and therefore find application in environmentally friendly refrigeration. For adamantine, a barocaloric which is rare in being possible to grow in large enough single crystal form for INS experiments to be feasible with existing instruments (see figure 1), this transition occurs at 4.8 kbar. Characterisation of the lattice dynamics around these phase transitions has to be measured as a function of pressure throughout the Brillouin zone - which is only possible with inelastic neutron scattering (INS) because of the low X-ray scattering cross section for light elements prevalent in MOFs. In addition, the large detector coverage necessary to measure the full 3d dispersion relation is only available using INS which further removes the risk of damaging soft organic materials in contrast to high-energy X-ray beams.

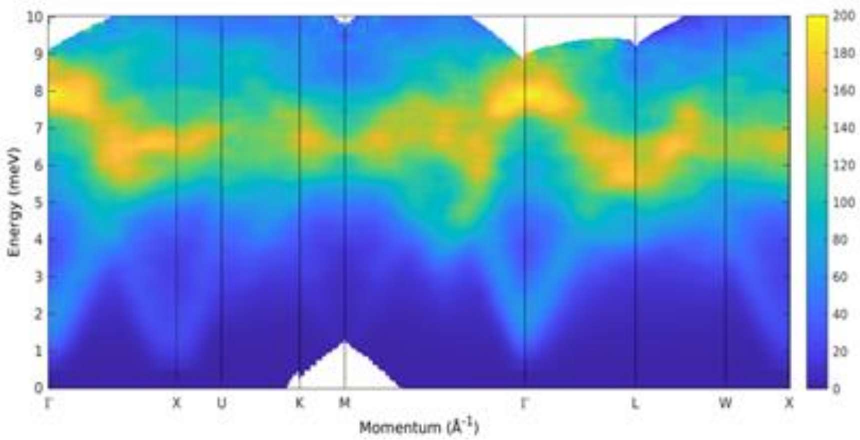

Figure 1: Low energy phonon dispersion relation of the barocaloric adamantane ($C_{10}D_{16}$) [1] measured at 220 K and 1 kbar.

Another example is that of pressure-dependent orbital-lattice coupling in organic magnets. Asymmetric ligand environments around the magnetic cation can result in strong coupling between the orbital orientation and the lattice. Application of external pressure can result in orbital reorientation, leading to dramatic changes in the magnetic interactions and structures of these materials. For example, in the coordination polymer $CuF_2(H_2O)_2(pyz)$ [2] there are two orbital orientation transitions at ~10 kbar and ~32 kbar (see figure 2) with associated transitions in the magnetic dimensionality. There is a clear opportunity here to use inelastic neutron scattering measurements to

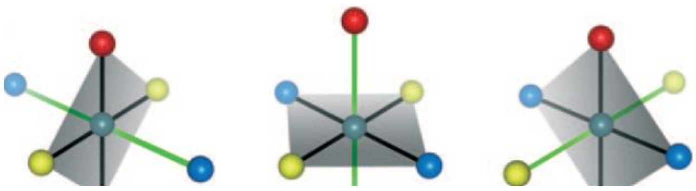

Figure 1: Pressure dependent switching of the local cation coordination in $CuF_2(H_2O)_2(pyz)$. The local elongated (Jahn-Teller) axis – shown in green – and the orbital planes – shown in grey – switch direction at ~10 and ~32 kbar.

characterise the interplay of lattice, orbital, and magnetic degrees of freedom because of the neutron's sensitivity to all three of these properties which will help understanding the structure–property relationship in this class of functional materials.

The feasibility of high-pressure INS studies is commonly constrained by the sizes of the available samples – which are often too small to be measured on state-of-the-art time-of-flight inelastic neutron spectrometers. Additionally, those crystals which *are* large enough to be attempted are too large for the available sample volumes in high pressure cells adapted for neutron scattering (e. g. Paris-Edinburgh cells). MUSHROOM provides a natural answer to these conflicting constraints, providing a massive flux concentrated on a small sample area (maximum 1x1 cm^2). Currently on LET, experiments in gas pressure cells (pressures up to ~10 kbar) with sample volumes of ~1 cm^3 are considered feasible. With MUSHROOM, the factor-of-20 increase in flux will enable experiments on sample volumes of ~50 mm^3 and less – compatible with Paris-Edinburgh cells currently in use on PEARL.

References

[1] E O R Beake, *et. al.,* Orientational Disorder in Adamantane and Adamantanecarboxylic Acid, *ChemPhysChem* **18**, 459 (2017) https://doi.org/10.1002/cphc.201601219

[2] G J Halder, *et al.,* Pressure-Induced Sequential Orbital Reorientation in a Magnetic Framework Material, *Angewandte Chemie* **50**, 419 (2011) https://doi.org/10.1002/anie.201003380