Contribution ID: **10** Type: **Oral**

Effects of orientational disorder on the dynamics of barocaloric adamantane

Monday, 12 September 2022 17:15 (25 minutes)

Weak van der Waals interactions that bind together organic molecules in the solid state lie at the heart of many highly relevant scientific problems, from soot formation in the atmosphere to polymorphism in pharmaceutical compounds. Nonetheless, the effects of these forces on the structure and (especially) dynamics of molecular materials are not yet fully understood.
Another application of van der Waals solids that has drawn recent attention is in environmentally-friendly solid-state cooling. These materials often undergo orientational order-disorder transitions with temperature and pressure, which can form the basis of a barocaloric cooling cycle. To optimise the cooling efficiency by crystal engineering, it is necessary to understand the atomic basis of these materials' functional behaviour.
Two recent developments – respectively in experiment and simulation – have finally allowed us to do this. Together, they provide an unrivalled insight into the atomic dynamics of these materials under working conditions. In this talk, I will highlight the impact of both these developments with the case study of adamantane, a paradigmatic close-packed van der Waals (or 'plastic') crystal.
First, the atomic dynamics under working conditions – that is, under pressures similar to those that would be needed in a working refrigerator – can now be studied in detail with neutron spectroscopy, due to the recent development of low-background, high-pressure gas cells. Pressure QENS and single-crystal INS experiments combine to provide a complete view of the pressure-induced phase transition in adamantane. Further insight can be drawn from calculation; however, the presence of disorder in adamantane's high-temperature phase complicates the calculation of vibrational modes. This brings us to the second development: a new theoretical framework for studying phonons in disordered systems, by mapping the vibrational modes of representative supercells onto the Brillouin zone of the disordered crystal. This reveals the disorder-induced broadening in different parts of the Brillouin zone, and a significant shift in the distribution of librational/translational modes between the two phases. Hence, combining experiment and modelling has allowed us to characterise in new detail the molecular dynamics of this orientationally disordered, barocaloric van der Waals material.

Primary author: Ms MEIJER, Bernet (Queen Mary University London)

Co-authors: PHILLIPS, Anthony; WALKER, Helen (ISIS Neutron and Muon Source); DEMMEL, Franz; Dr DIXEY, Richard (Queen Mary University of London); Dr PERRY, Robin (University College London)

Presenter: Ms MEIJER, Bernet (Queen Mary University London)

Session Classification: Session 1 : Materials Science 1