

MS18.O03

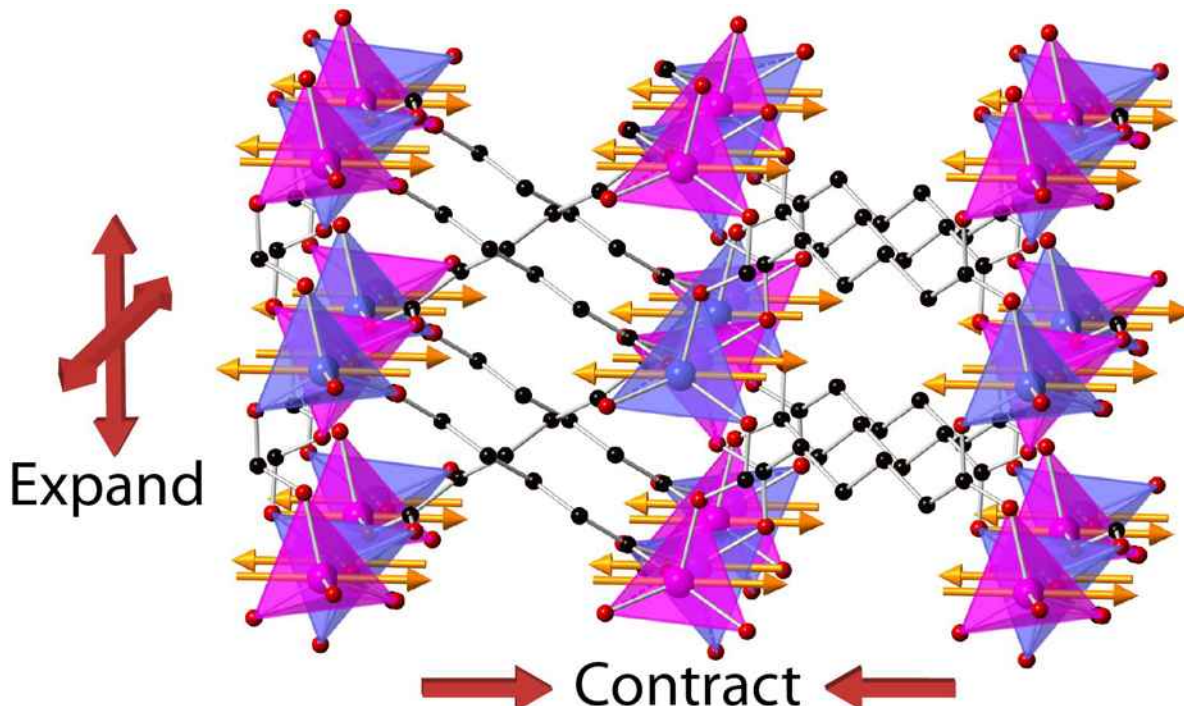
Magnetoelastic driven Negative Thermal Expansion in a Framework Antiferromagnet

P. Saines¹, P. Barton², M. Jura³, K. Knight³, A. Cheetham⁴

¹University of Oxford, Department of Chemistry, Oxford, United Kingdom, ²University of California Santa Barbara, Materials Research Laboratory, Santa Barbara, USA, ³ISIS Facility, Rutherford Appleton Laboratory, Harwell Oxford, United Kingdom, ⁴University of Cambridge, Department of Materials Science and Metallurgy, Cambridge, United Kingdom

Metal-organic frameworks (MOFs) have recently attracted great attention for their multiferroic, magnetocaloric and low dimensional magnetic order. These properties depend on the precise magnetic interactions in frameworks and a deeper understanding of the coupling between the lattice of these materials and their magnetic order is required to underpin the future developments of these promising compounds. Neutron diffraction is the ideal technique for such studies but its application to studies of the magnetic structure of MOFs has been limited to date due to challenges in solving the structure of these dilute yet complex magnetic compounds. We have recently examined the magnetic properties and structure of a new dicarboxylate framework, cobalt adipate, $\text{Co}(\text{C}_6\text{H}_8\text{O}_4)$, which adopts $P2_1/c$ monoclinic symmetry.[1] This compound has been found to order antiferromagnetically at low temperature and fits to neutron diffraction data have shown it adopts $Pb2_1/c$ magnetic symmetry. Its magnetic structure features sheets of Co cations coupled antiferromagnetically in two dimensions through carboxylate groups. The emergence of this order is accompanied by magnetoelastic coupling, which drives anisotropic negative thermal expansion along the a-axis at low temperature. This is the first evidence for such behaviour in a MOF and we find that both this behaviour and the spin orientation in this material are controlled by the presence of weak ferromagnetic dipole-dipole coupling between the layers of tetrahedral cobalt. Variable temperature high resolution synchrotron X-ray and neutron powder diffraction have also revealed that the monoclinic angle of Co adipate decreases on cooling, passing through a metrically orthorhombic phase without any indication of a phase transition. This unusual behaviour has been rationalised by examining the thermal expansion of the framework along its principal axis, highlighting the importance of such analysis in low symmetry materials.

[1] P. J. Saines, P. T. Barton, M. Jura, et al., *Mater. Horiz.*, 2014, In Press 10.1039/C4MH00009A



Keywords: Magnetic Structure, Metal-organic Framework, Magnetoelastic coupling