ESRF	**Experiment title:** Structure–property relationships in multiferroic metal–organic frameworks at high pressure	**Experiment number**: MA-2569
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Report:

Recent research carried out on dense metal–organic frameworks (MOFs) has shown a wealth of interesting physical properties, such as ferroelectricity [1,2], magnetic ordering [2,3], ferroelasticity [4] and multiferroicity [1,5,6]. The great chemical and structural diversity of MOFs, as well as its numerous host-guest interactions, can allow the tuning of ferroic parameters [7] and the coupling between them. So far, these properties have been investigated using variation of temperature. Our approach is to investigate the dense MOFs using variable pressure because the larger structural distortions that can be achieved with pressure compared to temperature will enable a greater variety of structural configurations—with potentially enhanced electric and magnetic properties—to be investigated.

At ID09 we performed variable pressure single-crystal X-ray diffraction experiments on known low-temperature electrically and magnetically ordered $[NH_4][Fe(HCOO)_3]$ and $[NH_4][Ni(HCOO)_3]$ [2], and multiferroic $[(CH_3)_2NH_2][Fe(HCOO)_3]$ compounds [6]. All crystals were loaded using neon gas as the pressure-transmitting medium. In the case of the $[NH_4][M(HCOO)_3]$ compounds, upon pressurisation, there was sufficient pore accessible volume to allow the incorporation of neon gas into the framework structure [Fig. 1]. In order to study the empty $[NH_4][M(HCOO)_3]$ compounds, a cell with a $[NH_4][Ni(HCOO)_3]$ crystal was loaded at the ESRF with argon as the pressure-transmitting medium. The larger size of the argon inhibitted its entry within the framework, and moreover gave rise to a reversible phase transition ~1.3 GPa to a monoclinic phase. This high-pressure phase transition is associated with large nickel formate distortions, which causes the off-centering of the ammonium cation, thus creating a net electric dipole [Fig. 1]. This mechanism of polarisation is different to what is observed in cooling for the other members of the $[NH_4][M(HCOO)_3]$ family, where polarisation is observed from ammonium displacements arising from the reduction in its vibrational motion at low temperature. Whereas the electric polarisation which arises with pressure originates from a strong distortion in the metal formate framework which causes a displacement in the ammonium cation. This mechanism may have interesting impacts on the magnetic properties as the metal-metal distances are reducing to a much greater extent than is observed with cooling.

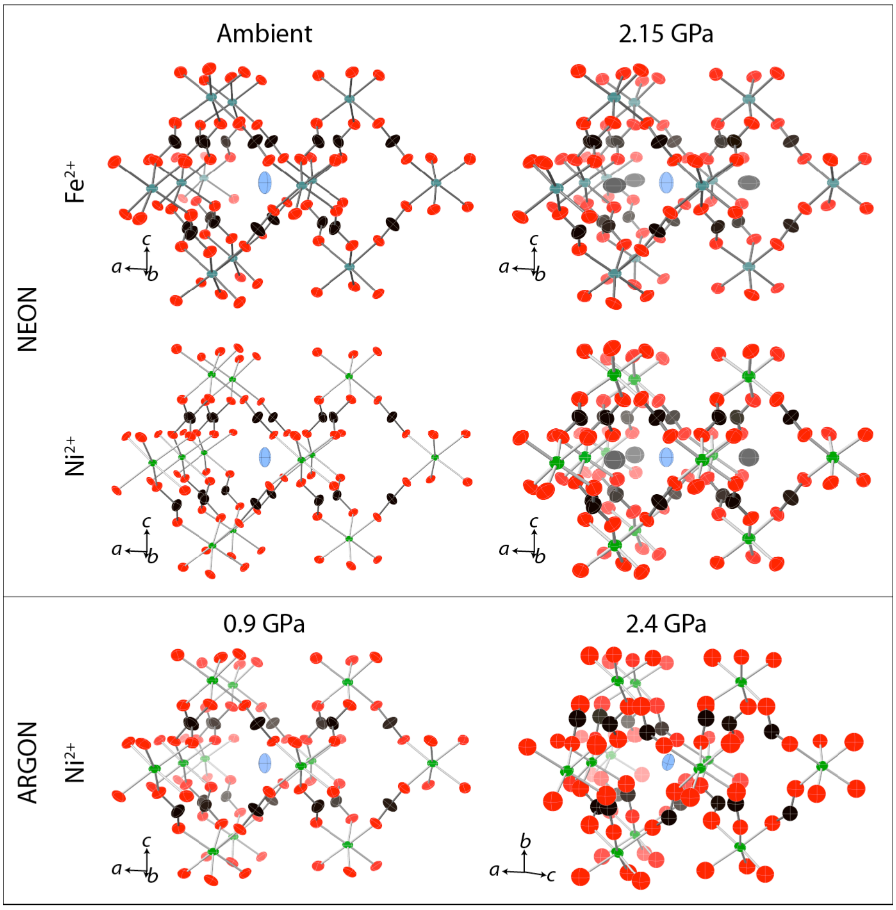

Figure 1

Selected refined crystal structures of $[NH_4][M(HCOO)_3]$, where M^{2+} = Ni or Fe, with neon or argon used as the pressure-transmitting medium. The colours represent the type of atoms, where red is O, blue is N, black is C, grey is Ne, teal is Fe and green is Ni. Hydrogen atoms have been ommitted for clarity.

Due to time restrictions, only large ω-step diffraction images were collected on the $[NH_4][Fe(HCOO)_3]$ compound in argon. From this diffraction as well as inhouse high-pressure Raman spectroscopy we observe a similar phase transition occuring (0.44 GPa) in $[NH_4][Fe(HCOO)_3]$ as was determined in $[NH_4][Ni(HCOO)_3]$, in addition to observing another phase transtion at higher pressures (2.05 GPa).

As we have observed in the $[NH_4][M(HCOO)_3]$ compounds, the density of the structure is important for the onset of metal formate framework distortion with pressure: in particular, the incorporation of neon inhibits metal formate distortions up to the pressure range studied of 3-4 GPa. Thus the presence of a bulkier cation in the framework pores, as is found in $[(CH_3)_2NH_2][Fe(HCOO)_3]$, stabilises the iron formate framework to higher pressures (~7 GPa), after which a phase transition is observed. The structure solution of this high-pressure phase is in progress.

References:

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