ESRF	**First High-Pressure Exploration of the Fluorine-Nitrogen System**	**Experiment number**: CH-6640
Beamline: ID11	**Date of experiment**: from: June 23 2023 to: June 26 2023	**Date of report**: 31.07.2023
Shifts: 9	**Local contact(s)**: Jonathan Wright	*Received at ESRF:*

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Report:

Objectives

The aim of this proposal was to investigate the fluorine-nitrogen system up to 130 GPa in laser-heated diamond anvil cells (DACs) and observe the formation of the first pressure-formed polynitrogen cation. Previously employed successfully during preliminary experiments, CoF_3 was used as the fluorine reservoir and loaded along with molecular nitrogen (N_2). All samples were characterized by single-crystal X-ray diffraction (SCXRD). The goals were: *i*) the investigation of the fluorine-nitrogen system at pressures up to 130 GPa, *ii*) the synthesis of novel F_xN_y solids with polynitrogen cations as well as potential $Co_xN_yF_z$ solids, *iii*) the determination of their crystal structure by employing *in-situ* synchrotron SC-XRD and, *iv*) establishing the produced compounds' equation of state and find out if they are recoverable to atmospheric pressure.

Results

BX90-type DACs with culets of 250 to 120 μm were prepared. CoF_3 was loaded along with molecular nitrogen, acting as a reagent as well as a pressure transmitting medium. Pressures were measured based on the equation of state of gold;[1] a small Au chip having been placed inside the sample cavity. As planned, the samples were precompressed to pressures between 10 and 70 GPa and laser-heated to temperatures above 2000 K at our laboratory in CSEC (Edinburgh). These samples were brought to ID11 for single-crystal X-ray diffraction measurements of the synthesized phases.

Over the whole investigated pressure range, our preliminary analysis revealed only two phases besides the precursors: the previously found Co_2F_3 compound and a CoF_2 solid with the fluorite-type structure (PdF_2), both shown in Figure 1. Although the latter had not been detected during our preliminary measurements, it has

been reported by Barreda-Argüeso *et al*.[2] Interestingly, they only found PdF_2-type CoF_2 when compressing CoF_2 in non-hydrostatic conditions. This is a curious observation since laser-heating is thought to locally relieve strain in the heated and recrystallized crystals. In any case, the formation of CoF_2 is another strong indication that fluorine is being released from CoF_3 (*e.g.* $2CoF_3 \rightarrow 2CoF_2 + F_2$). High-precision maps of the samples' experimental chambers were performed, but, puzzlingly no sign of a N_xF_y, $Co_xF_yN_z$ or the known CF_4 solid[3] was observed. This seems to suggest that the released fluorine either forms a new phase that is amorphous or poorly crystalline, or that it might react with the Re gasket. A more in-depth data analysis will be necessary to get a better grasp of fluorine's behavior. Still, it appears that chemically insulating not only the diamonds, but the gasket as well, is a necessity. Moreover, perhaps that materials proven to be effective at containing fluorine, such as Teflon, would be good contenders as chemical insulators. After being unable to distinguish the desired phases, the DACs were decompressed and the equation of state of CoF_2 and Co_2F_3 obtained.

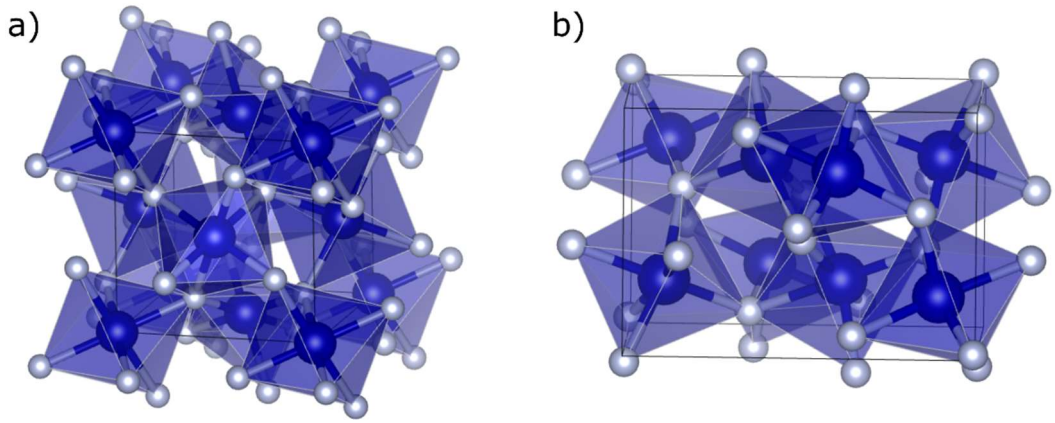

Figure 1: Crystal structure of a) PdF_2-type CoF_2 and b) Co_2F_3.

We would like to emphasize how well the ID11 beamline was working. In particular, a new procedure allowing to put on the center of rotation a submicron-sized single-crystal was developped and implemented by Jonathan Wright. The method uses the Friedel pairs of the desired single-crystal to perform the centering macro. We tested extensively this new approach, which proved to work remarkably well. This macro, currently nonexistant on any other beamline—whether at the ESRF or elsewhere—significantly increases our efficiency and a truly welcome addition.

References

1. Dewaele, A., Loubeyre, P. & Mezouar, M. Equations of state of six metals above 94 GPa. *Phys. Rev. B - Condens. Matter Mater. Phys.* **70**, 1–8 (2004).
2. Barreda-Argüeso, J. A. *et al.* Pressure-induced phase-transition sequence in CoF2: An experimental and first-principles study on the crystal, vibrational, and electronic properties. *Phys. Rev. B* **88**, 214108 (2013).
3. Laniel, D. *et al.* A reentrant phase transition and a novel polymorph revealed in high-pressure investigations of CF4 up to 46.5 GPa. *J. Chem. Phys.* **156**, 044503 (2022).