ESRF	**Experiment title:** Pressure evolution of the rare earth valence state in Sm and Eu fullerides	**Experiment number**: HC3043
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Report:

The objective of the current proposal was to determine the effect of external pressure on the valence state of Sm and Eu cations in rare earth fullerides with nominal stoichiometry $RE_{2.75}C_{60}$.

We performed XANES measurements on the Sm and Eu L_3-edges under high pressure conditions. Given their air and moisture sensitivity, the powder samples were loaded in high pressure diamond anvil cells (DACs) inside a glovebox. In order to avoid Bragg reflections from the diamonds of the DACs we used nanodiamonds and to reduce the absorption of the diamonds at this low energy range, we used one partially perforated nanodiamond on one of the culets. A fluorinert mixture of FC70-FC77 was used as pressure transmitting medium. XANES spectra of Sm_2O_3 (Eu_2O_3) and SmI_2 (EuS) were recorded during the experiment and used as references for the 3+ and 2+ valence states of the rare earth cations, respectively. We have measured XANES spectra of both fullerides up to 8-9 GPa. A detailed evaluation and interpretation of the obtained XANES data is ongoing. Therefore, in this report we only include preliminary conclusions.

The XANES spectra of $Eu_{2.75}C_{60}$ recorded under normal conditions and those of the reference samples is given in Fig.1. The comparison shows that while the valence of Eu in $Eu_{2.75}C_{60}$ is very close to 2+, there is also a small 3+ component, confirming the mixed valency in this rare-earth fulleride already at normal conditions. This is in accordance with indications from our earlier Raman measurements.

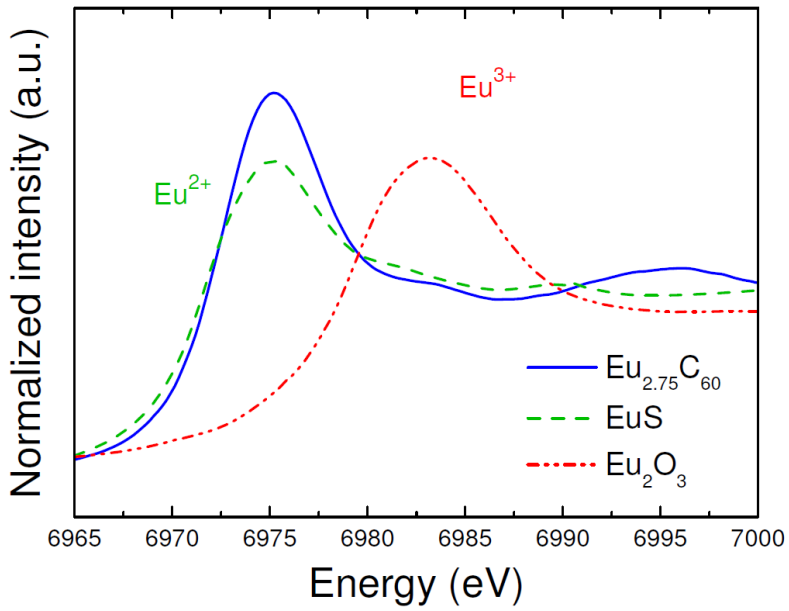

Fig. 1: XANES spectra of $Eu_{2.75}C_{60}$ on the Eu L_3-edge recorded at ambient pressure conditions. Divalent and trivalent europium in Eu_2O_3 and EuS, respectively, are overlayed for a direct comparison.

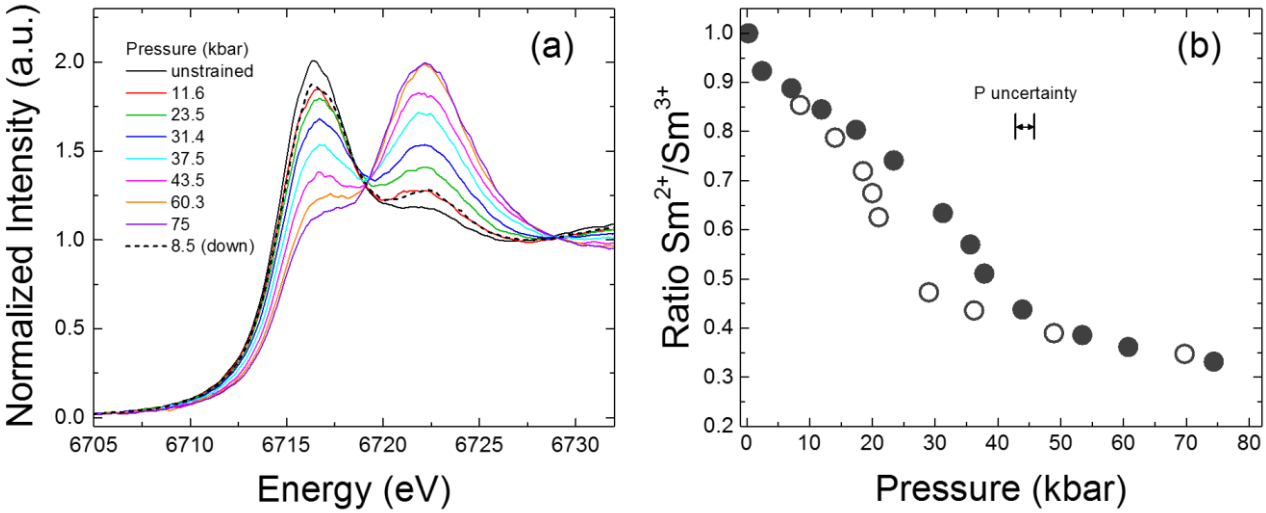

Fig. 2: (a) Pressure dependent XANES spectra of $Sm_{2.75}C_{60}$ on the Sm L_3-edge. (b) Pressure dependence of the intensity ratio of the Sm^{2+} and Sm^{3+} peak features.

A mixed valency at ambient conditions was also observed for $Sm_{2.75}C_{60}$ (black solid line in Fig.2). The high pressure evolution of the XANES spectra and the normalized ratio of the intensities of the Sm 2+ and 3+ features is also given in Fig.2. The XANES data clearly show a monotonic increase (decrease) of the Sm 3+ (2+) feature under hydrostatic compression, and therefore indicate a possible pressure-induced change in the average rare earth valence in $Sm_{2.75}C_{60}$. The preliminary analysis of their relative intensities demonstrates an abrupt decrease of the intensity ratio in the pressure range ~25-45 kbar. The XANES measurements performed upon pressure decrease demonstrate a substantial hysteresis (Fig.3). A similar abrupt lattice collapse and a hysteretic behaviour were observed in an earlier X-ray diffraction study on the same sample [1].

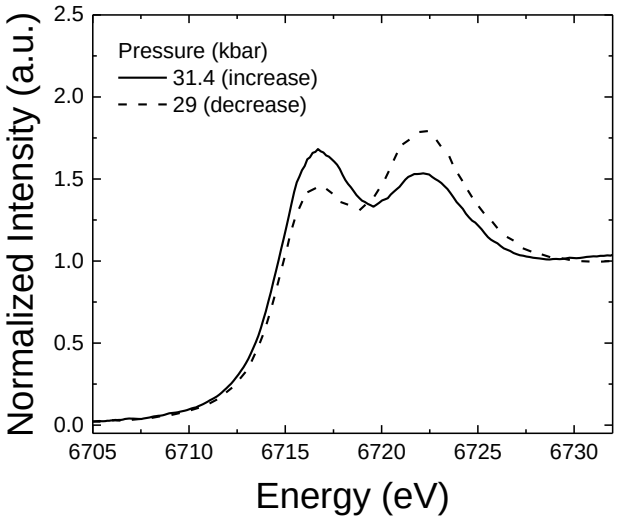

Fig. 3: XANES spectra of $Sm_{2.75}C_{60}$ on the Sm L_3-edge recorded upon pressure increase (31.4 kbar - solid line) and decrease (29 kbar – dashed line).

[1] Arvanitidis J. et al., Dalton Trans. 3144 (2004)