ESRF	**Experiment title:** Structural properties of hyperexpanded high-T_c fullerides at high pressure	**Experiment number**: HS 4474
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Report:

The superconducting transition temperatures, T_c, of the face-centred cubic (fcc) A_3C_{60} (A= alkali metal) fullerides increase monotonically with the inter-C_{60} separation, which is in turn controlled by the sizes of the A^+ cation intercalants. Recently, we reported pressure-induced bulk superconductivity at 35 K in the most highly expanded member of the fcc family, Cs_3C_{60} and at 38 K in its bcc-structured A15 polymorph. The existence of two structural packings of the same electronically active unit (C_{60}^{3-}) reveals that T_c scales universally in a structure-independent dome-like relationship with proximity to the Mott metal-insulator transition, which is governed by the role of electron correlations characteristic of high temperature superconducting materials beyond fullerides.

The aim of our current studies is to explore how the superconductivity and magnetism of C_{60}^{3-} systems can be controlled physically (externally applied pressure) and chemically (substitution of the intercalated alkali ions). We have been focusing on the $Cs_{3-x}Rb_xC_{60}$ ($0 \leq x \leq 1$) fcc family and its structural and electronic characterisation, both at ambient and elevated P, as we traverse the metal-Mott insulator transition. The temperature responses of the unit cell volume at ambient P and the magnetic susceptibility of the $Cs_{3-x}Rb_xC_{60}$ systems show well-defined anomalies (volume jump and maximum in $\chi(T)$, respectively) at temperatures which vary smoothly as we approach the MI transition boundary by varying x. These changes can be identified as signatures of the MIT induced by thermal expansion and allow the possibility of studying the electronic phase diagram in unprecedented detail. In the present experiment, we carried out detailed pressure-dependent structural studies at low and ambient T of selected members of the fcc-structured $Cs_{3-x}Rb_xC_{60}$ ($0 \leq x \leq 1$) family.

Synchrotron X-ray diffraction experiments at 20 K and at room temperature as a function of P were performed for $Cs_{2.5}Rb_{0.5}C_{60}$ and Cs_2RbC_{60} samples on beamline ID27. The powder samples were loaded in helium-gas-driven membrane diamond anvil cells (MDAC), which were equipped with stainless steel gaskets and placed inside a closed-cycle helium refrigerator. The diameter of the diamond culet was 600 μm and each sample was introduced in a hole made in the gasket 60 μm deep and 330 μm in diameter. The MDACs were loaded with helium using a high-pressure gas loading system. The applied pressure was increased at 20 K and at room temperature by controlling the He gas pressure on the MDAC diaphragm without dismounting the cell from the cryostat, and was measured with the ruby fluorescence method. The diffraction patterns (λ = 0.3738 Å) were collected using a flat image plate detector (MAR345, 345 mm diameter and 0.100 mm pixel size). Maximum pressures for the $Cs_{2.5}Rb_{0.5}C_{60}$ and Cs_2RbC_{60} experiments at 20 K were 10.2 and 22.6 GPa, respectively; $Cs_{2.5}Rb_{0.5}C_{60}$ was also easured at RT to 14.7 GPa. Masking of the strong Bragg reflections of the diamond anvil and integration of the two-dimensional diffraction images were performed with the Fit2D software. Data analysis of the resulting one-dimensional diffraction profiles is being performed with the GSAS suite of Rietveld programs.

Fig. 1 shows the extracted pressure dependence of the unit cell volume of $Cs_{2.5}Rb_{0.5}C_{60}$ at RT −for this composition, ambient P data show that the Mott insulator-to-metal transition occurs at ~100 K; further cooling leads to the appearance of superconductivity with T_c~ 30 K. The low P data shown in the inset of Fig. 1 provide a first evidence of a volume anomaly at ~0.3 GPa. This is more clearly evident in Fig. 2 where a well-defined change in slope is seen at ~0.3 GPa when the normalised stress, $F = P/[3f(1+2f)^{2.5}]$ is plotted as a function of Eulerian strain, $f = [(V/V_0)^{-2/3}-1]/2$. The room temperature unit cell volume (~3100 $Å^3$) at the critical pressure, P_c is comparable to that at which the MIT occurs at 100 K at ambient P confirming the same electronic origin (t_{1u} orbital overlap of neighbouring fulleride units that controls the bandwidth,W) for the observed lattice response as a function of both physical and chemical pressure.

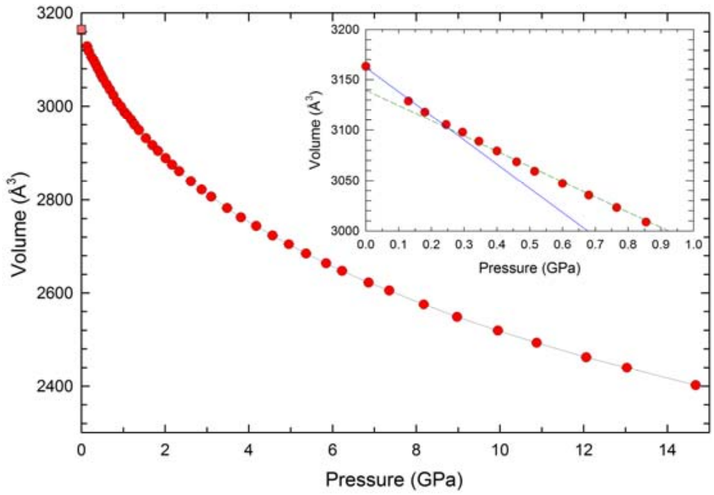

Fig. 1. Pressure dependence of the unit cell volume of fcc $Cs_{2.5}Rb_{0.5}C_{60}$ at room temperatue. *Inset*: expanded view of the low pressure region showing the existence of a lattice anomaly near ~0.3 GPa.

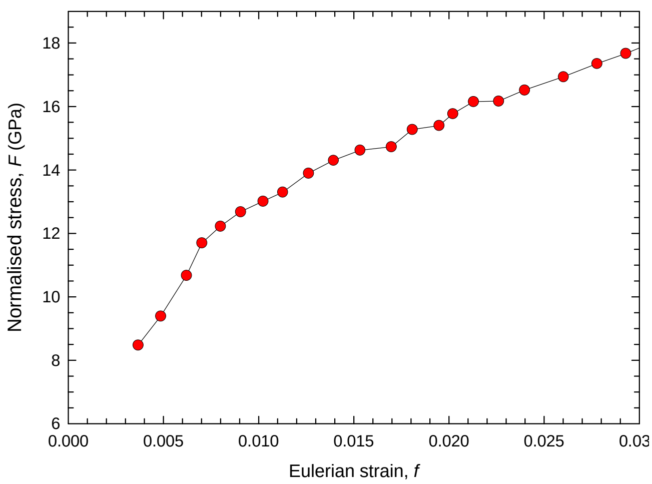

Figure 2. Normalized stress function, F versus Eulerian strain, f for $Cs_{2.5}Rb_{0.5}C_{60}$ at RT.