ESRF	**Experiment title:** Valence states of rare-earth ions and phase transitions in fulleride salts	**Experiment number**: CH-1702
Beamline: BM29	**Date of experiment**: from: 30 June 2004 to: 04 July 2004	**Date of report**: 1/9/2004
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Preliminary report:

The aim of the proposed research was to perform temperature-dependent X-ray absorption studies of the fullerides Ln_xC_{60} (Ln = Sm, Eu, Yb; x = 2.75) at the rare-earth *K*- and L_3-edges in order to study the valence states of the rare-earth elements by XANES and to extract their local geometric structure by EXAFS. The ESRF beamline BM29 was an optimal choice to perform this experiment, as the monochromator gives access to most of the energy ranges required (both in the transmission and in the fluorescence geometries) and the available cryostat enables to smoothly thermalise the samples in most of the temperature range required. As a consequence, in this series of measurements, we indeed managed to investigate all the foreseen samples. However, a variety of problems limited and in some cases seriously hampered the experiment, not allowing us to obtain unequivocal results.

Some limitations were anticipated from the start, such as the impossibility of studying the K-edge of Yb with the same monochromator crystals as those necessary for studying the L_3-edges and the difficulty in decreasing the temperature of the sample below 15 K. Another limiting aspect, which was foreseen was the necessity to work in the fluorescence mode due to the possible low transmission signal of the samples (finally, we were able to measure the samples in the transmission mode).

Nevertheless, the main drawback in performing optimally the experiment arose as a consequence of needing to use capillaries as sample-holders (which are standard type of sample environment in X-ray diffraction experiments). This was necessary in order to prevent direct contact of the highly air- and moisture- sensitive samples and there was no possible way to introduce the samples in the current cryostat set-up without exposing them to air. The first problem, which arose from this experimental configuration was that the obtained absorption signals were of low quality,

due to presence of glitches and a high noise/signal ratio, probably due to bad compensation between the incident and the transmitted beams through the curved surface of the glass capillaries. The other aspect that appears to have affected the measurements was poor thermalization of the samples especially during the heating cycle. This may have been caused by the small contact between the capillaries and the rest of the sample-holder as well as by the poor thermal conductivity of the capillary itself. The use of an appropriate sample-holder for air-sensitive pellets is deemed necessary for continuation of this research programme.

Besides all the technical difficulties, several spectra have been acquired and data analysis has been initiated. However, considering the short time since completion of the experiments (July 2004), analysis is still at an early stage and the current results inconclusive. We have concentrated our efforts on the L_3-edges since the XANES region is more sensitive to the valence changes and since attempts in performing K edge measurements did not result in acceptable quality spectra (probably again because of the effect of the capillaries on the transmitted signals). For the three samples investigated, the differences that can be observed by eye are subtle in both the XANES and in the EXAFS regions. The noise associated with the signals in some cases hampers a clear analysis of the temperature evolution. As an example, we present in Figs. 1 and 2 the evolution of the XANES and the Fourier Transform spectra of $Sm_{2.75}C_{60}$ between room temperature and 38 K. The XANES spectra seem to indicate a very slight decrease of the intensity of the Sm^{3+} peak occurring in this temperature range, while the FT spectra show a decrease of the intensity of the first peak, which may be attributed to an increased disorder of the sample.

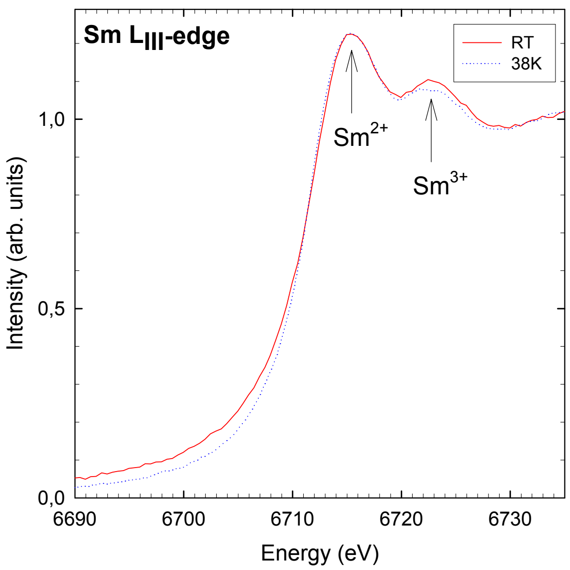

Fig. 1. XANES spectra of $Sm_{2.75}C_{60}$ at room temperature and 38 K.

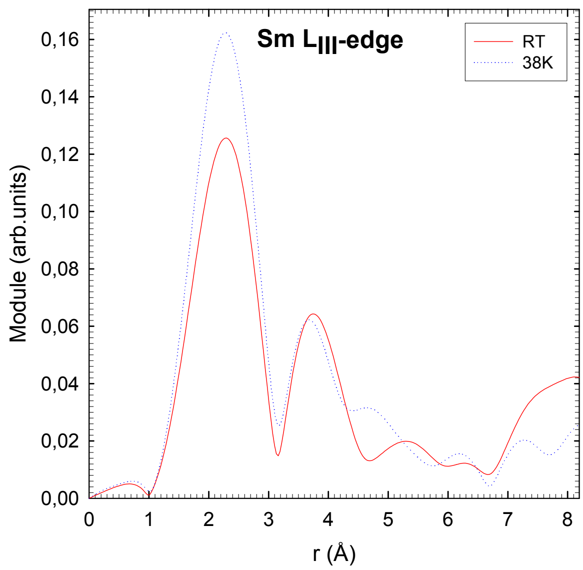

Fig. 2. Modulus of the FT of the EXAFS spectra of $Sm_{2.75}C_{60}$ at room temperature and 38 K.

While we are currently making progress in analysing the data already collected, a new series of measurements is being proposed in which we will attempt to remove the serious problems encountered with the sample holder and the thermalisation process. The implementation of a new cryostat chamber with an increased cooling power to reach temperatures down to 10 K should also allow us to access the temperature range in which the changes in rare-earth valence and local coordination geometry are especially pronounced.