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ESRF

# Experiment Report Form

**The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF**.

Once completed, the report should be submitted electronically to the User Office via the User Portal:

*https://wwws.esrf.fr/misapps/SMISWebClient/protected/welcome.do*

***Reports supporting requests for additional beam time***

Reports can be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

***Reports on experiments relating to long term projects***

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

***Published papers***

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

## Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

## Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

| ESRF | **Experiment title:**<br>Electron-phonon coupling in superconducting $CaC_6$ studied at the Ca L-edge with RIXS | **Experiment number**:<br>HC-3326 |
|---|---|---|
| **Beamline**: | **Date of experiment**:<br>from: 2nd October 2017 to: 4th October 2017 | **Date of report**:<br>20th October 2017 |
| **Shifts:** | **Local contact(s)**:<br>Nick Brookes | *Received at ESRF:* |


**Names and affiliations of applicants** (* indicates experimentalists):

Dr Andrew Walters* (Diamond Light Source)

Mr Mohammed K. Bin Subhan* (University College London)

Mr Mitch Watts* (University College London)

Dr Chris Howard (University College London)

Dr Mark Dean (Brookhaven National Laboratory)


## Report:

The aim of the experiment was to study multi-phonon scattering at the Ca L-edge in $CaC_6$, which superconducts below 11.5 K. Ca-derived states at the Fermi surface are known to couple to high-energy (~90 meV) C-derived phonons, and recently RIXS has been shown to be sensitive to electron-phonon coupling.

The beamline and spectrometer gave an overall energy resolution of about 25 meV at the Ca L-edge using an exit slit opening of 40 μm. This resolution should be more than sufficient to see the phonons of interest (~90 meV): in principle a resolution of around 50 meV would also work. In order to try to enhance the incident flux at the expense of the energy resolution, we tried to open the exit slit from 40 μm to 60 μm. Unexpectedly this caused a two peak structure in the energy resolution function, so we remained at 40 μm.

We looked at 3 different $CaC_6$ samples over the 2 days of beamtime. The 1st and 3rd samples were made from the same starting graphite material, a natural flake graphite originating from Madagascar, which typically contains 1 or 2 different crystallites, misoriented from each other within the graphite plane (in-plane). The 2nd sample was made from HOPG (highly-oriented pyrolytic graphite), which is completely disordered in-plane.

The XAS (measured using total electron yield) from the 1st and 3rd $CaC_6$ samples both initially gave two broad peak features at the Ca $L_3$ and $L_2$ edges, as shown in the black line in Figure 1. We attempted to measure XAS via fluoresence using the CCD detector mounted on the sample vessel, but we saw no signal. We found that in all samples the XAS degraded significantly in time, and that the beam also caused the sample to degrade. We inferred that degradation was occuring due to the appearance of additional pre-peak structures on the primary 2 peaks (see the green line on Figure 1). These pre-edge features are typically observed in insulating Ca-containing compounds, including in CaO. All XAS measured on the 2nd sample (made from HOPG) contained these 2 pre-peaks, suggesting that this sample had already been exposed to air or water. We hypothesise that the disordered nature of HOPG could easily lead to microscopic fissures in the crystal that could allow air to rapidly react with the sample during sample introduction into the load lock. Moreover, any existing weakness in the structure would then be a natural location for the cleave to occur.

The 1st sample was cooled to approximately 30 K, but after 10 hours we found that from the XAS measurements most of the sample had dramatically degraded, apart from the part of the sample that had been

illuminated. This behaviour is likely to be due to water condensing on the sample (as the cryostat is effectively acting as a cryopump). The illuminated part of the sample was protected due to beam heating. As a result all measurements on the 2nd and 3rd samples were performed at room temperature.

We observed a very broad inelastic feature in the Ca L-edge RIXS data measured on the 1st and 3rd $CaC_6$ samples, but this feature was not the same in those two cases (see Figure 2). At the present time we cannot explain why these two datasets are not consistent with one another. Both were measured at approximately the same position in reciprocal space, and we have no reason to doubt the quality of either $CaC_6$ sample. Both of the datasets shown in Figure 2 were measured for between 4 and 5 hours.

We measured on the 3rd sample for approximately 36 hours. During that time we were constantly monitoring the XAS signal from the sample, and we were always able to find a part of the sample that gave a 'good' XAS spectrum (two broad peaks with minimal pre-peak structure: see the black line on Figure 1). However in the last 12 hours of beamtime we observed no inelastic signal on this 3rd sample. The XAS measurements are primarily sensitive to the surface of the sample, so it is difficult to understand how the surface could stay the same while the 'bulk' that we are sensitive in the RIXS process could degrade. One explanation could be that one of the byproducts of the $CaC_6$ sample degradation is metallic (e.g. calcium metal), and so observing metallic XAS is not necessarily a good measure of the sample quality. Unfortunately there does not appear to be any published data on elemental Ca at the Ca L-edge to help us understand this behaviour further.

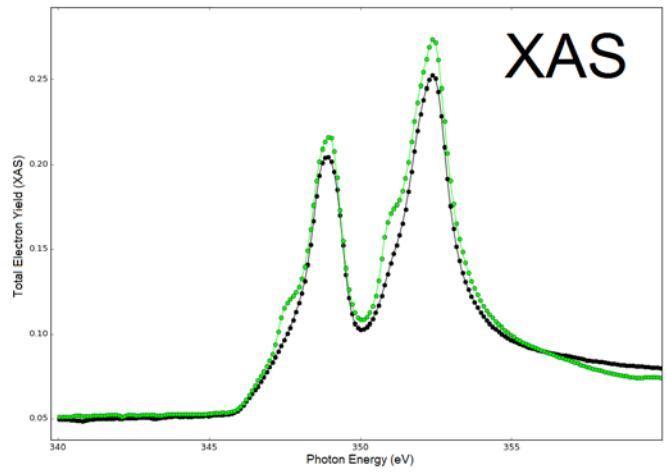


**Figure 1:** Ca L-edge XAS data from the 3rd $CaC_6$ sample. The black line shows pristine $CaC_6$ XAS data, while the green line shows a XAS scan done at the same position after that position was illuminated with beam for 1 hour.

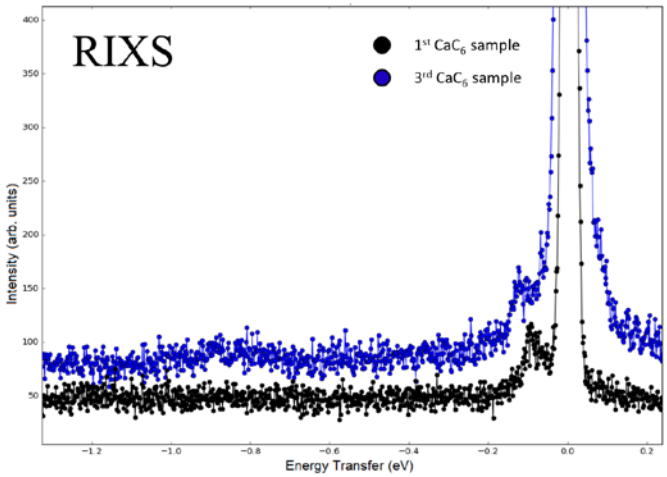


**Figure 2:** Ca $L_3$-edge RIXS spectra from two different $CaC_6$ samples. In both samples a broad inelastic feature is observed, but the energy of the feature is different in the two cases (~80 meV in the 1st sample and ~120 meV in the 2nd sample).

On the basis of this preliminary study, we request another 6 shifts of beamtime to assess the feasibility of this experiment further. In preparation for these 6 shifts we will prepare a new batch of $CaC_6$ samples from single-crystal graphite samples that will be prealigned with a lab x-ray source prior to our arrival at the ESRF. This would enable us to straightforwardly monitor the (00L) Bragg peaks from the $CaC_6$ samples to monitor the quality of the samples over time independently of the XAS measurements.

We also request that the beamline performs the following two tasks prior to these 6 shifts of beamtime:

1. A full bake-out of the sample chamber to reduce the amount of water in the vacuum space. This should radically increase the effective lifetime of the sample in the sample chamber. It would be interesting to explore whether the cryostat could be used as a cryopump while ensuring the sample is thermally isolated but still electrically connected to the sample mount (e.g. by mounting the sample on a plate of manganin). This would also reduce the amount of water adsorption onto the sample surface.
2. More x-ray commissioning at the Ca L-edge to understand better the origin of the two peak structure in the energy resolution function when increasing the size of the exit slit. The observed RIXS signal is very weak, so any increase in photon flux on the sample would be very helpful of course.