



## 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://www.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.

**Experiment title:**

Probing the Lifshitz transition of black-phosphorus at high-pressure

**Experiment number:**

HC-2348

**Beamline:**

ID12

**Date of experiment:**

from: 06/07/2016 to: 11/07/2016

**Date of report:**

19/07/2016

**Shifts:**

18

**Local contact(s):**

F. Wilhelm

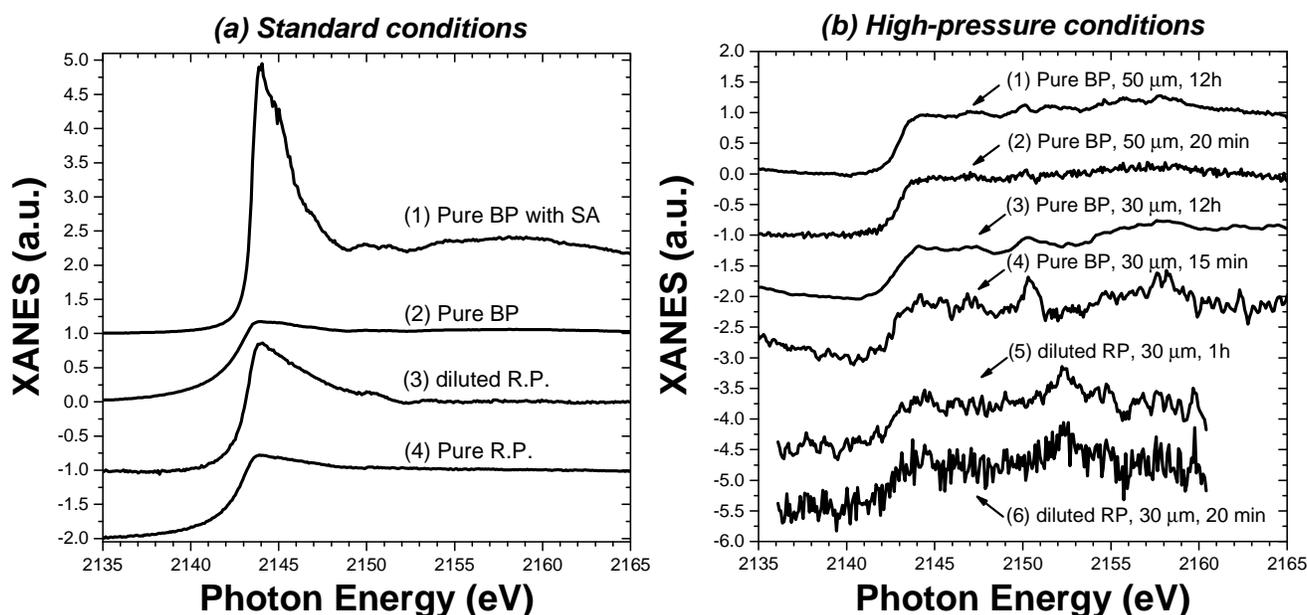
*Received at ESRF:***Names and affiliations of applicants** (\* indicates experimentalists):

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**Report:**

Black phosphorus shows rich and astonishing properties under pressure which remain however largely understudied as highlighted by the recent discovery of a new electronic transition at low temperatures.[1] The aim of the proposal HC-2348 was to measure XANES/XAFS at the phosphorus K-edge under pressure and as a function of the temperature. It should bring matchless information on the evolution of the phosphorus electronic structure as a function of the hydrostatic pressure and temperature, in particular sensitive to its  $3p$  states which are directly correlated to its semi-conductor properties.

Beside scientific questions, the proposal HC-2348 was also aiming at extending the energy range for which x-ray absorption experiments can be carried out under high-pressure. It should be recalled that this represents a major technical challenge. For instance, at the phosphorus K-edge, the lost in photon flux due to the high-pressure conditions can be estimated as follow: decrease by a factor 6 due to focalization with Be lenses, 0.08% of transmission of incoming light though a  $30\ \mu\text{m}$  diamond plate, and 0.06% of transmission of the fluorescence. At the end the signal can be anticipated to be to at least 1300 smaller than that taken in normal conditions.



**Figure.** X-ray absorption spectra measured in partial fluorescence mode at the Phosphorus K-edge. (a) in standard conditions (measurement time  $\sim 10$  min per spectrum). (b) in fully perforated diamond anvil cell with different windows thicknesses for black phosphorus (BP) and red phosphorus (RP).

The phosphorus K-edge XANES spectra are presented in the figures (a) and (b) here above, recorded in standard and high-pressure conditions, respectively. From these measurements the following remarks can be made:

- On pure BP crystal (a.2), the spectrum taken in standard conditions clearly shows the edge jump, but no additional spectral features can be distinguished. Self-absorption effects thus turn out to be quite dramatic. Self-absorption corrections can be carried out, cf. spectrum (a.1). The outcome is comparable to BP spectra measured in TEY mode, in particular in terms of intensity of the white line.[2] The correction however greatly amplifies the noise, so that a spectrum quality comparable to that of (a.2) is the minimum to have the possibility to address the scientific question.
- The BP spectra taken at 1.1 GPa in a DAC equipped with 50  $\mu\text{m}$  diamond window correspond to the curves (b.1) and (b.2). The edge jump is well noticeable on a single spectrum measurement. Averaging the data during about 12 h (80 times the standard conditions) leads to a significant improvement of the noise level. However, this latter remains too high to apply the self-absorption corrections. Comparing spectra (a.2) and spectra (b.1) to estimate the noise level indicates that an improvement by a factor 8 is still needed.
- BP XANES spectra have been measured in DAC equipped with 30  $\mu\text{m}$  diamond window, curves (b.3) and (b.4). The improvement in regards to curves (b.1) and (b.2) is less than a factor 2. On top of that, the highest pressure reachable by these windows is of the order of 3 GPa, so that the approach based on decreasing the window thickness cannot be pursued further for this project.
- Instead of trying to get spectral quality compatible with the use of self-absorption correction, another strategy has been to tackle the self-absorption effect itself. We dispersed and exfoliated BP flakes in a CHP liquid phase, as done for instance in [3]. However, even at concentration of about  $8 \text{ gL}^{-1}$ , the BP XANES spectra could not be satisfactorily measured in standard conditions (not shown).
- We also tried solid-solid dilution using graphite, PTFE,  $\text{SiO}_2$  or Al thin powders (particle  $< 5 \mu\text{m}$ ). Due to the difficulty to prepare (sub-)micrometric BP powder from the available crystals by ball-milling, we rather used red phosphorus powder as sample. As seen on curves (a.3) and (a.4) taken in standard conditions, the dilution allows to partially recover the white line intensity. Different dilution ratios were tested and an optimum of about 1:25 in PTFE was used to prepare a DAC with 30  $\mu\text{m}$  diamond window. One however immediately sees on the spectra taken in high-pressure conditions that the dilution strongly impairs the signal, curves (b.5) and (b.6). The noise level is significantly larger than on the bulk BP crystals, and the white line intensity does not show any significant improvements.

To sum up, measurements at the P K-edge under pressure have been made very challenging by strong re-absorption effects, so that the scientific question has not been addressed. The usual ways to limit such re-absorption turn out to be complex to implement in case of high-pressure conditions. It appears necessary to first demonstrate the possibility to measure the P K-edge spectrum at high-pressure in samples not suffering from re-absorption effect, for instance such as in intermetallic alloys containing phosphorus.

Regarding the use of ESRF beamtime for this project, it should be noted that some tests have been carried out on IHR or BLC time. 4 shifts were used during BLC-9415 for the BP measurements with 50  $\mu\text{m}$  window. 4 shifts were used during BLC-9519 for the BP measurements with 30  $\mu\text{m}$  window. 1 shift during BLC-9894 for BP dispersion. 1 shift during IH-HC-2910 for red P solid-solid dilution. 8 out of 18 shifts have been used for this project during HC-2348 (diluted red P under pressure). The remaining shifts of HC-2348 were used for various IHR purposes. At the end, a total of 18 shifts have been used for this project, preliminary tests included.

## References:

- [1] Z. J. Xiang *et al.*, Phys. Rev. Lett. 115, 186403 (2015) ; [2] A. Jürgensen, Phys. Scripta 115, 548 (2005) ; [3] D. Hanlon *et al.*, Nature Comm. 6, 8563 (2015).