

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: Resonant Surface X-ray Scattering Study of the Effect of Charge Transfer on the Structure at the Electrochemical Interface

Experiment number:
28-01-906

Beamline: BM28	Date of experiment: from: 1 Sept 2010 to: 7 Sept 2010	Date of report: <i>Received at ESRF:</i>
Shifts: 18	Local contact(s): Paul Thompson	

Names and affiliations of applicants (* indicates experimentalists):

Christopher Lucas* – University of Liverpool
Naomi Wong* – University of Liverpool
Michael Darlington* – University of Liverpool
Yvonne Gruender* - University of Kiel

Report:

An unsolved and crucial question in electrochemistry is the issue of charge transfer between the metal electrode and the adsorbate as this defines the nature of the bonding. There have been few experimental electrochemical studies due to the complexity of the electrochemical environment which makes the surface inaccessible to most probes of charge transfer. Surface x-ray resonant diffraction (SXRRD) is one of the few techniques that may be applicable for probing the charge distribution at the electrochemical interface.

On Cu(100), Br and Cl form ordered $c(2 \times 2)$ adlayers that have been observed in both ultra-high vacuum (UHV) [1] and electrochemical studies [2-3] (a schematic of the structure is shown in **Figure 1**).

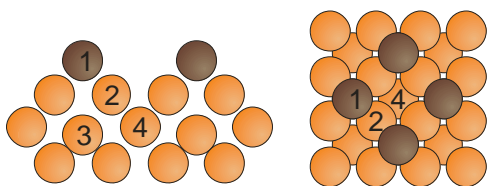


Figure 1: Structural model of the $c(2 \times 2)$ adlayer on Cu(001).

SXRD analysis of Cu(001)- $c(2 \times 2)$ -Cl (formed in a defined potential range in HCl) showed a corrugation in the second atomic copper layer which is opposite in phase to the corrugation observed for Cu(100)-Cl under UHV conditions. This reveals the importance of charge screening by the solvent molecules and the major influence of the electrochemical double layer on the charge distribution at the interface. The $c(2 \times 2)$ adlayer is a simple structure (the adlayer forms a square structure with a coverage of 0.5 halide atoms per surface Cu atom) and this makes the system an ideal candidate to investigate the suitability of resonant surface x-ray scattering experiments to probe the charge transfer and nature of the chemical bonding *in-situ*.

Measurements through the Cu K-edge at the anti-Bragg position of a Cu crystal truncation rod (CTR) for both Br and Cl are shown in **Figure 2**. In both cases the edge shifts to higher energy values compared to the Cu bulk value indicating stronger bound core electrons. In a simple qualitative interpretation this implies that the surface Cu atoms are positively charged. Interestingly, measurements through the Cu K edge at the superstructure rod, showed no near-edge shifts indicating that the atoms in the second Cu layer (atoms 2 in **Figure 1**) do not contribute to the charge transfer. **Figure 3** shows the intensity measured through the Br K

edge at (0 1 0.2), which probes the chemical character of the Br adatoms. A shift of the edge to lower energies at this position indicates that the Br K-electrons are less tightly bound and therefore negatively charged. The data shown in **Figures 2 and 3** are representative of a comprehensive data set and this is currently under analysis.

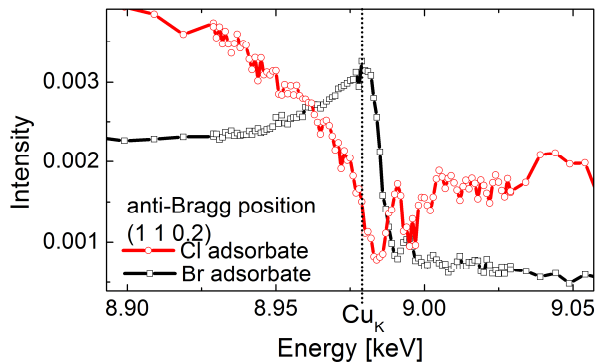


Figure 2: Intensity at the anti-Bragg position of a Cu CTR, (1 1 0.2), as the energy is scanned through the Cu K edge, for both Br and Cl adsorbates.

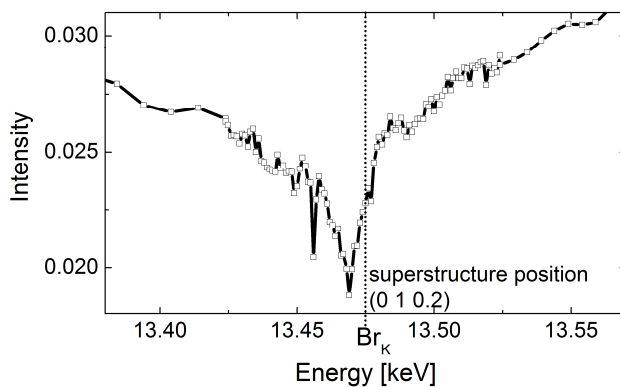


Figure 3: Intensity at the superstructure position, (0 1 0.2), as the energy is scanned through the Br K edge, for the Br-c(2x2) system.

- [1] Y. Gründer et al., *Phys. Rev. B* 81, 174114 (2010)
- [2] H. C. N. Tolentino et al., *Surf. Sci.* 601, 2962 (2007)
- [3] M. Saracino et al., *Phys. Rev. B* 79, 115448-11 (2009)