| ESRF | **Experiment title:**<br>Precise determination of multipole contributions in XPS photoelectric cross section | **Experiment number**:<br>SI-1994 |
|---|---|---|
| **Beamline**:<br>ID32 | **Date of experiment**:<br>from: 4/12/2009 to: 15/12/2009 | **Date of report**:<br>16/4/2010 |
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## Report:

The aim of the experiment was to determine accurately multipole contributions to XPS photoelectric cross section in the normal-incidence X-ray standing wave (NIXSW) detection mode. As detailed in the proposal, the NIXSW is very sensitive to any non-dipolar effects in photoemission, especially if the emitted electrons detection direction is at 45 deg. with respect to the incident photon beam polarization. The way to determine the multipole contributions is to compare a multipole-insensitive XSW signal (X-ray fluorescence in our case) with the multipole-sensitive signal (XPS) originating from the same species that occupy the same crystallographic position in the sample structure. Any differences in the two XSW yields may be assigned to quadrupole or higher-order multipole effects. Such effects will vary for different core levels, depending on the emitting shell and/or its angular momentum and the kinetic energy.

We have chosen chlorine adlayer on Cu(001) as a model system because of the minimization of probability of secondary effects (i.e. elastic and inelastic scattering of photoelectrons on their way from the excited atom to the sample surface). Also, from theoretical predictions [1] chlorine is expected to have sizable non-dipolar effects, comparable to those of carbon [1] which are of high interest in the XSW user community.

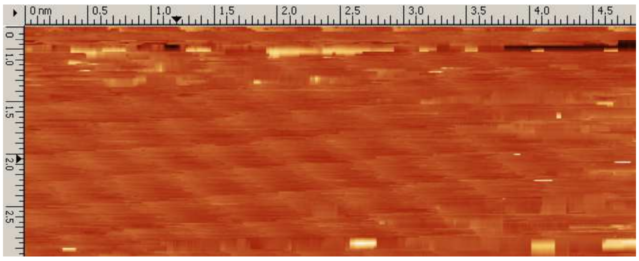

*Fig. 1*
*Atomic resolution STM image of the clean Cu(001) surface with 1x1 reconstruction. Images with about 40nm wide terraces is not shown.*

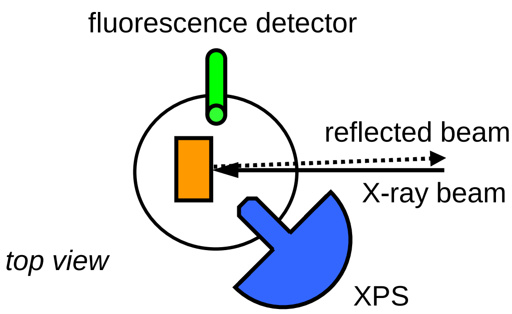


*Fig. 2*
*Schematic (top) view of the experimental setup showing that the simultanous XFS and XPS data acquisition in backscattering geometry is possible only for specular reflections.*

Prior to the experiment, a test cleaning and deposition experiment was performed in the small UHV system of Surface Characterization Laboratory (SCL) of ID32. A clean Cu(001) surface was prepared by sputter annealing, its quality checked by LEED and STM (see Fig. 1). The chlorine adsorbate layer was deposited using chlorine dispenser based on the solid-state electrolysis of AgCl [2] and the quality of the adlayer checked again by LEED. The same sample preparation/LEED characterization procedure was then used during the beamtime. During the beamtime, special care was given to the reproducibility of the results and to the effect of beam damage - two sample preparations were studied, the beam position on the sample was controlled (either kept constant or changed in order to record differences in yields). In a part of the experiment the sample has been cooled down to liquid nitrogen temperature for Debye-Waller factor estimation.

In fluorescence mode, two specular reflections [(002) at E = 3.432 keV and (004) at E = 6.862 keV] and four off-specular reflections [(111) – E = 2.979 keV, (222) – E = 5.958 keV, (113) – E = 5.710 keV and (220) – E = 4.872 keV] were measured in order to get the pure structural parameters of Cl adsorbed on Cu(001). Preliminary analysis of the data (see first panel in Fig. 3) shows rather high coherent fraction F suggesting high degree of order in the studied system. The fluorescence data will then be compared to photoemission yield in various XPS lines measured at the following Bragg reflections: (002) – E = 3.432 keV, (004) – E = .862 keV, (111) – E = 2.979 keV, (222) – E = 5.958 keV. A secondary monochromator was used in measurements (both XFS and XPS) for higher-order reflections such as (004) and (222). Because of geometrical restrictions (see the experimental layout on Fig. 2), the fluorescence and XPS yields could not be recorded simultaneously for the off-specular reflections. Although the simultaneous data acquisition on the specular reflection was possible, for intensity reasons this was not always done. Very often it proved necessary to detune the monochromator from the maximum of its reflectivity for a more efficient harmonics rejection.

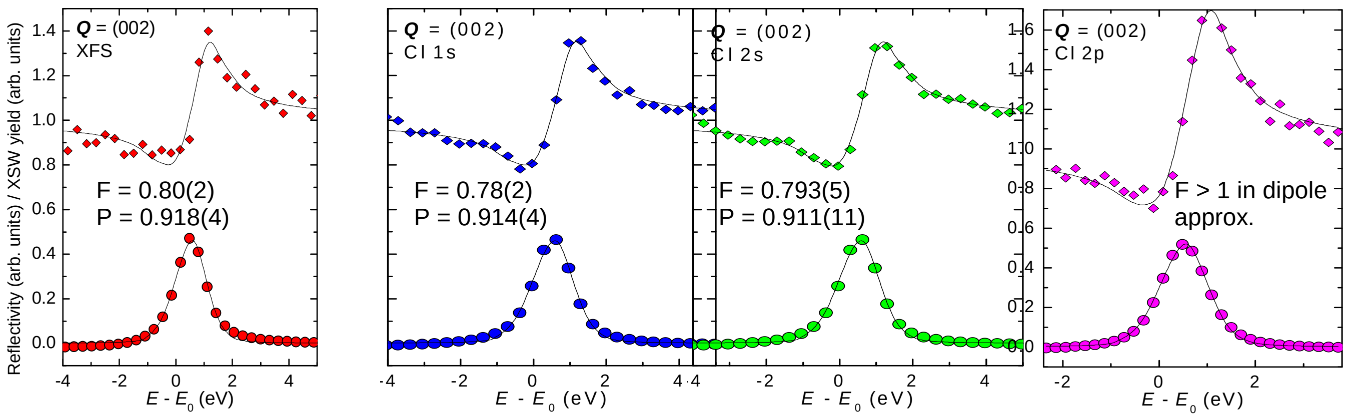


*Fig. 3*
*Preliminary data analysis showing reflectivity and XFS/XPS yield analysis in the dipolar approximation.*

Taking into account the large amount of data taken during the beamtime, the full data analysis is still underway. Fig. 3 shows only a preliminary analysis of one of the reflections: XFS yield gives comparable results to Cl 1s and Cl 2s XPS lines suggesting very weak non-dipolar effects on these orbitals. On the other hand, analysis of the Cl 2p data in the dipolar approximation yields $F > 1$ suggesting the multipolar effects to play an important role. Further conclusions will be drawn from the full analysis of the whole dataset.

## References:


[1] V.I. Nefedov, V.G. Yarzhemsky, I.S. Nefedova, M.B. Trzhaskovskaya and I.M. Band, J. Electron Spectrosc. Relat. Phenom. 107 (2000) 123. M.B. Trzhaskovskaya, V.I. Nefedov, V.G. Yarzhemsky, Atom. Data Nucl. Data Tables 77 (2001) 97.

[2] N.D. Spencer et al., J. Vac. Sci. Technol. A 1 (1983) 1554.