

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>

Deadlines for submission of Experimental Reports

Experimental reports must be submitted within the period of 3 months after the end of the experiment.

Experiment Report supporting a new proposal (“relevant report”)

If you are submitting a proposal for a new project, or to continue a project for which you have previously been allocated beam time, you must submit a report on each of your previous measurement(s):

- even on those carried out close to the proposal submission deadline (it can be a “*preliminary report*”),
- even for experiments whose scientific area is different from the scientific area of the new proposal,
- carried out on CRG beamlines.

You must then register the report(s) as “relevant report(s)” in the new application form for beam time.

Deadlines for submitting a report supporting a new proposal

- 1st March Proposal Round - **5th March**
- 10th September Proposal Round - **13th September**

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.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report in English.
- include the experiment number 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.

Characterization of a Cr chloride prepared by codeposition of Cr and Cl

We prepared a sample by codeposition of Cr and Cl on Au(111). The low energy electron diffraction (LEED) is characterized by an array of intense spots arranged in hexagonal symmetry (fig 1a). At 59eV the Au substrate first-order reflections are expected in the positions marked by yellow circles. Overlayer spots (pink circles) are aligned along the substrate high symmetry directions and show a periodicity that is indicative of a 6x6 reconstruction (approximately 1.7nm large supercell). From Auger electron spectroscopy (AES) data we estimated that the deposited amount of chlorine is five times that of chromium, exceeding the 1:3 stoichiometric ratio expected in CrCl₃. Owing to that, we expect that the excess chlorine might be adsorbed on the bare gold surface. The STM images (fig 1c-e) show instead a variety of structures lying on the surface: several tens of nanometer large triangular (T) islands exhibiting a moiré pattern are surrounded by rectangular (R) stripes on top of which we do not notice any intensity modulation. Both the type of islands don't overcome the 2 Å apparent height. The same moiré as on the T-islands is observed instead on the surface nearby, whereas the characteristic Au herringbone reconstruction has not been found anywhere, accordingly with LEED. The size of the moiré superperiodicity is about 8.5 Å, half of that estimated by LEED. These values do not correspond neither to the $p(\sqrt{3} \times \sqrt{3})R30^\circ$ reconstruction reported for 0.33ML Cl/Au(111) [3] nor to CrCl₃ lattice parameters found in literature, i.e. 5.9Å [1]. Synchrotron X-ray absorption spectroscopy (XAS) measured at Cr edge (576eV) reveals a broad but structured profile, which hides multiplet features more consistent with hybridized rather than metallic chromium states (fig 2, left). However, X-ray circular magnetic dichroism (XMCD) signal is very weak or totally absent in some areas of the sample (fig 2, right), both when the beam is normal to the surface and when it is more grazing, and the sample does not seem to be ferromagnetic.

Simple CrCl₃ evaporation on Au(111)

When we evaporate CrCl₃ without depositing metallic Cr in parallel from the e-beam source, AES shows that both Cr and Cl are present on the gold substrate. We deduce that CrCl₃ clusters reach and nucleate on the substrate. This observation is consistent with Ref[2]. In fact halogens atoms are expected to desorb from the metal halides when they are annealed at few hundreds degrees temperature, whereas metal-chlorine sublimation might be favored at higher temperatures (however, our QMB does not detect evaporated species below 480°C evaporation temperature, while AES measurements on Au(111) exclude traces of chlorine at 330°C). The corresponding LEED pattern is shown in fig 1b. Two domains are identified, 30° rotated the one respect to the other, both having a periodicity 2.5 times larger than Au(111), i.e. 7.2Å, namely one angstrom above typical CrCl₃ lattice parameter. STM images in this case show irregular shape islands, 4-5Å high, without moiré pattern, homogeneously distributed on the surface but with negligible overall coverage. Annealing at 400°C restores a clean herringbone reconstructed Au surface. No XAS and XMCD measurements have been measured for this sample.

Conclusions

Experiments demonstrate the formation of extended ordered 2D structures on the Au(111) surface upon growth by codeposition of Cr and Cl. However, not all the results are converging at moment towards CrCl₃ monolayer. More likely, our probes suggest the presence of multiple possible phases, that we may identify among CrCl₃, CrCl₂, pure Cr, adsorbed Cl, as we know from the literature. The STM moiré features might be corresponding either to adsorbed Cl layer or to a full monolayer Cr chloride, on top of which other species have nucleated and grown, i.e. R and T islands. Overall, the sample does not show ferromagnetism. Next steps to follow in order to achieve a single CrCl₃ phase must include: 1) low rate deposition to obtain sub monolayer coverages; 2) lower CrCl₃ evaporation temperature (favouring Cl atoms sublimation without Cr) to get rid of a second Cr source; 3) new depositions of CrCl₃ from CrCl₃ source without the use of the Cr e-beam source, followed by XAS and XMCD investigations.

References

1. Cai et al., *Nano letters* (2019)
2. Bedoya-Pinto et al., *arXiv preprint arXiv:2006.07605* (2020).
3. Gao et al., *J. Am. Chem. Soc.* (2008)

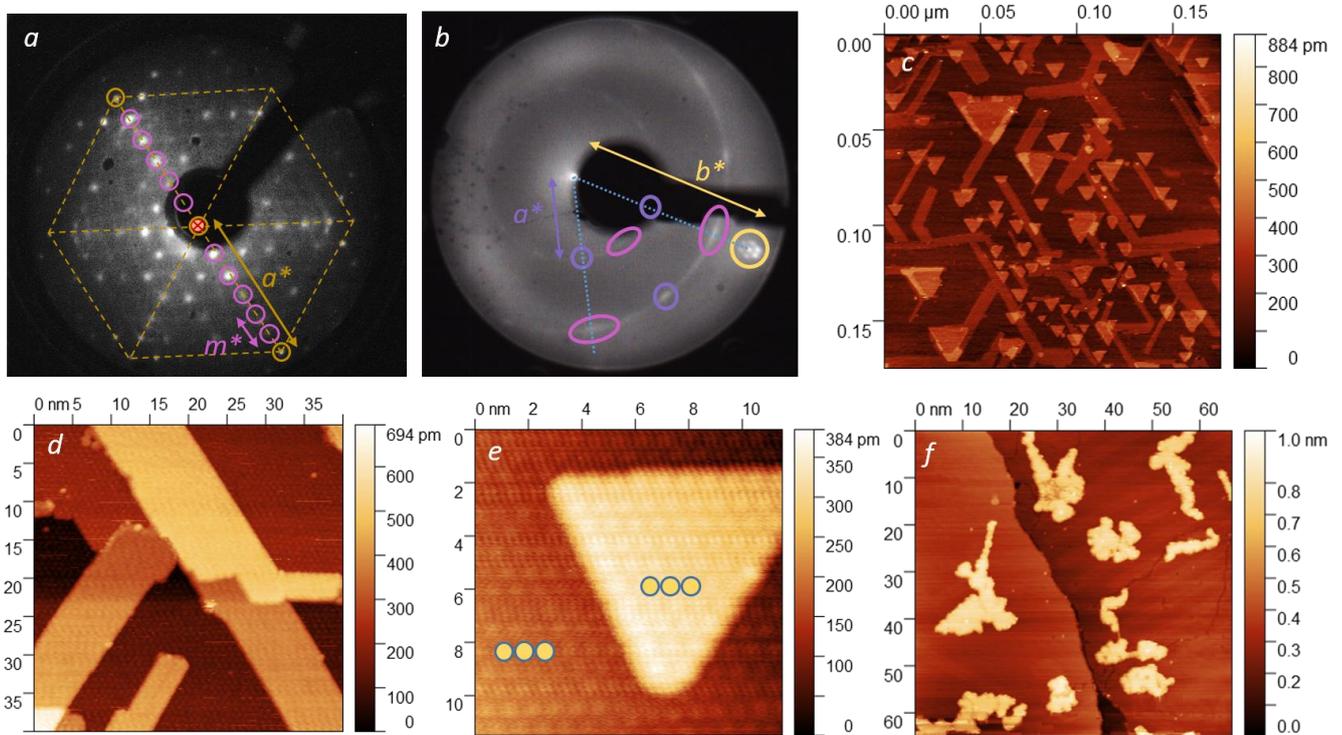


Fig 1: a) LEED image at 63eV acquired after codeposition. b) LEED image at 63eV acquired after CrCl_3 evaporation (two different LEED instruments have been used to take (a) and (b) diffraction pattern images). c) STM (180×180) nm^2 image of the as grown material after codeposition; d) STM (40×40) nm^2 image focusing on R-islands; e) STM (12×12) nm^2 image focusing on a T-island (moiré pattern on the island and nearby is identical). f) STM (70×70) nm^2 image acquired after CrCl_3 evaporation on bare Au(111)

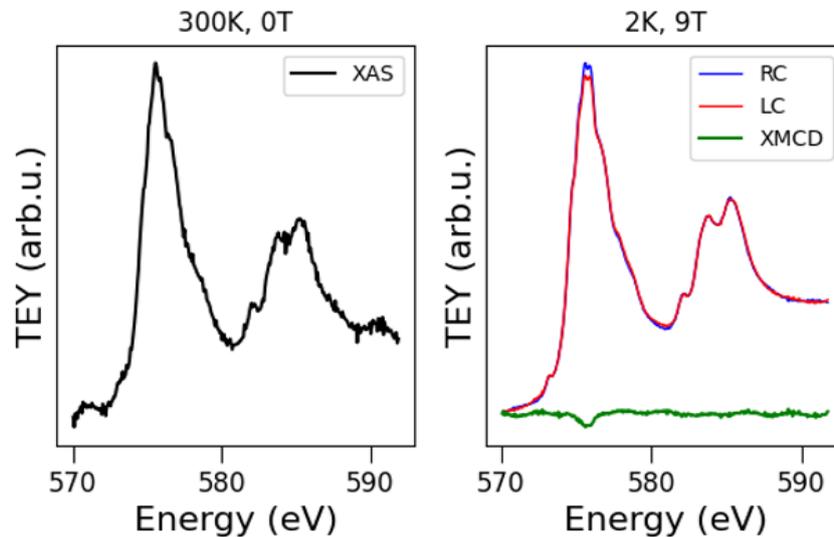


Fig 2: XAS and XMCD spectra acquired at Cr $L_{2,3}$ edge of the sample prepared by codeposition.