## EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

# **Experiment Report Form**



The double page inside this form is to be filled in by all users or groups of users who have **E** 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: <u>https://wwws.esrf.fr/misapps/SMISWebClient/protected/welcome.do</u>

#### **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, <u>you must submit a report on each of your previous measurement(s)</u>:

- 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 form 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**

- > 1<sup>st</sup> March Proposal Round 5<sup>th</sup> March
- > 10<sup>th</sup> September Proposal Round 13<sup>th</sup> 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 <u>each project</u> 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.

<b>ESRF</b>	<b>Experiment title:</b> Epitaxial monolayer CrCl <sub>3</sub> grown on Au(111)	<b>Experiment</b> <b>number</b> : IH-MA-98
Beamline:	Date of experiment:	Date of report:
ID32	from: 09/09/2020 to: 22/09/2020	16/10/2020
Shifts:	Local contact(s):	Received at ESRF:
	Nicholas Brookes	
Names and affiliations of applicants (* indicates experimentalists):		
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#### Introduction:

 $CrCl_3$  is an antiferromagnetic layered material whose single layer unit is intrinsically ferromagnetic with inplane aligned magnetic moment [1]. It represents a typical example of layer dependence in van der Waals (vdW) materials. However, almost all experimental proofs of single layer properties in  $CrCl_3$  come from exfoliated flakes, and only a very small amount of works describe few or single layer compounds prepared by epitaxial solid state methods [2]. Hereafter, we report the main results that we obtained from the preliminary characterizations of epitaxial ultra-thin films of  $CrCl_3$  grown on Au(111) substrate in our ultra-high vacuum (UHV) system.

### Growth methods:

We grew epitaxial  $CrCl_3$  by codeposition of Cr and Cl atoms on Au(111) single crystal substrate. Chromium is deposited from an e-beam evaporator source using highly pure (99.99%) Cr rods. Evaporation conditions have been found with the help of a quartz micro balance (QMB) mounted *in situ* in our UHV system and the effective deposited amount of Cr was calibrated by estimating the partial coverage in scanning tunnelling spectroscopy (STM) images. Chlorine is instead evaporated by applying resistive heat to a crucible containing anhydrous  $CrCl_3$  powder (99.99%). Halogens in fact cannot be supplied directly in UHV because the high vapor pressure of the pure elements is extremely polluting for a UHV chamber. Since halogen evaporation from metal halides is far preferable, we chose  $CrCl_3$  powder as Cl precursor, which avoid contaminations of the substrate with other metallic species different from chromium. The crucible can be filled under inert atmosphere inside a glove box, i.e. in N<sub>2</sub> gas, in order to reduce the sample exposure to moisture. We found that Cl evaporation temperature in our evaporator is 500°C. The deposition time was set in order to reach a total  $CrCl_3$  coverage lower than one monolayer and a stoichiometric ratio close to Cr:I=1:3. Substrate temperature varies between 180°C and 210°C. Hereafter we report the preliminary results gathered from  $CrCl_3$  growth attempts by two methods: 1) codeposition of Cr and Cl on Au(111) from the two different element sources described above and 2) by simple  $CrCl_3$  evaporation on the same substrate, without the use of Cr e-beam source.

#### 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 CrCl<sub>3</sub>. 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 CrCl<sub>3</sub> 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 CrCl<sub>3</sub> 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 CrCl<sub>3</sub> clusters reach and nucleate on the substrate. This observation is consistent with Ref[2]. In fact halogens atoms are expected to desorbs 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 CrCl<sub>3</sub> 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 CrCl<sub>3</sub> monolayer. More likely, our probes suggest the presence of multiple possible phases, that we may identify among CrCl<sub>3</sub>, CrCl<sub>2</sub>, 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 CrCl<sub>3</sub> phase must include: 1) low rate deposition to obtain sub monolayer coverages; 2) lower CrCl<sub>3</sub> evaporation temperature (favouring Cl atoms sublimation without Cr) to get rid of a second Cr source; 3) new depositions of CrCl<sub>3</sub> from CrCl<sub>3</sub> 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<sub>3</sub> evaporation (two different LEED instruments have been used to take (a) and (b) diffraction pattern images). c) STM (180x180)nm<sup>2</sup> image of the as grown material sfter codeposition; d) STM (40x40)nm2 image focusing on R-islands; e) STM (12x12)nm<sup>2</sup> image focusing on a T-island (moire pattern on the island and nearby is identical). f) STM (70x70)nm<sup>2</sup> image acquired after CrCl<sub>3</sub> evaporation on bare Au(111)



Fig 2: XAS and XMCD spectra acquired at Cr L<sub>2,3</sub> edge of the sample prepared by codeposition.