European SYNCHROTRON RADIATION FACILITY

	Atomic structure and composition of a novel SPtSe Janus 2D Transition Metal Dichalcogenide layer in epitaxy on Pt(111).	Experiment number: 32-03-750
Beamline: BM32/INS	**Date of experiment**: from: 20/04/2021 to: 02/05/2021	**Date of report**: 13/07/2021
Shifts: 18	**Local contact(s)**: Lucio Martinelli (email: lucio.martinelli@esrf.fr) Xiaorong Weng (email: xiaorong.weng@esrf.fr)	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

RENAUD Gilles, Laboratory CEA Grenoble - IRIG Modélisation et Exploration des Matériaux MEM

WENG Xiaorong, Laboratory CEA-GRENOBLE IRIG/DEPHY/MEM

MARTINELLI Lucio, Laboratory CNRS Institut Neel

MARTY Alain, Laboratory CEA Grenoble - IRIG SPINTEC UMR8191

BONELL Frédéric, Laboratory CEA Grenoble - IRIG SPINTEC UMR8191

JAMET Matthieu, Laboratory CEA Grenoble - IRIG SPINTEC UMR8191

SANT Roberto, Laboratory ESRF

The first aim of this experiment was to reproduce *in situ* the formation (see exp. report 32-02_817 and Ref. [1]) of an SPtSe Janus transition metal dichalcogenide single layer by sulphurization under H_2S partial pressure of an initial $PtSe_2$ layer in epitaxy on Pt(111) (exp. report 32-03-741), with the help of the Grazing Incidence Multiple Anomalous Diffraction (GI-MAD) technique [2,3]. The second aim was to quantitatively determine the Janus atomic structure by a combination of Surface X-ray Diffraction (SXRD) and (GI-MAD).

During this run, we optimized the GI-MAD measurements around the Se K-edge at 12.658 keV, including the necessary XAS reference, on the initial $PtSe_2$/Pt(111) structure. GI-MAD was next supposed to be used to control the sulfurization process leading to an exact Janus SPtSe layer by substitution of the top Se layer atoms by S one, and then to determine its atomic structure. However, the measurements (described here) on the $PtSe_2$ layer took more time than expected, so that the sulfurization and related measurements on SPtSe could not be done. A new proposal will be submitted for that sake.

Upon synthesis of a single layer $PtSe_2$ by selenization of Pt(111) [1], a (3×3)$PtSe_2$/(4×4) Pt(111) coincidence lattice site superstructure forms. Its atomic structure was previously studied by SXRD [exp. report 32-03-741] and qualitatively published [1]. The complete quantitative 3D atomic structure determination will soon be submitted.

The Nano-MAD (Multiple Anomalous Diffraction for nano-structures [2,3]) program allows to decompose the total structure factor $|F_T\ (hkL)|$ into the contribution $|F_A|$ of the anomalous atoms (here Se) and the contribution $|F_N|$ from the non-anomalous atoms (Pt for $PtSe_2$; Pt and S for SPtSe), together with the phase difference according to : $|F_T|=|F_{Pt}+F_{Se}\exp(i(\varphi_{Se}-\varphi_{Pt}))|$. An experimental determination of the atomic anomalous factors $f'_{Se}(E)$ and $f''_{Se}(E)$ was first performed by fluorescence measurement of the X-ray absorption at the Se K edge under exactly the same experimental conditions as for the MAD ones, and then applying the Kramers-Kronig transform. The deduced Se anomalous scattering factors *in* $PtSe_2$ are shown in Fig. 1.

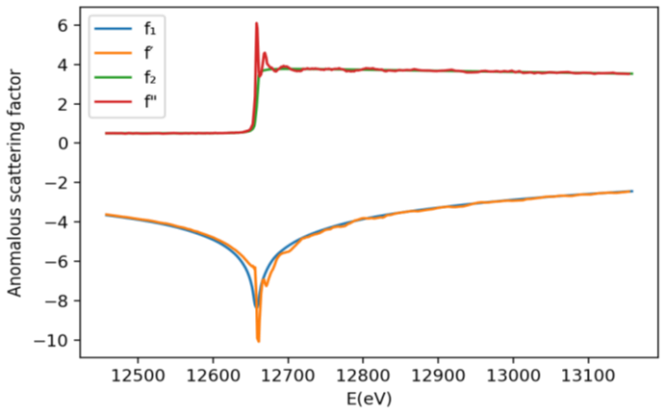

Fig.1: Anomalous scattering factors f'Se(E) and f''Se(E) as a function of energy near the Se K edge, deduced by the Diffkk program of the XAS LARCH [4] data analysis suite. The reference sample was made of 10 $PtSe_2$ single layer arranged in a way similar to the experimental SL $PtSe_2$. f_1 and f_2 are the theoretical values for single atoms.

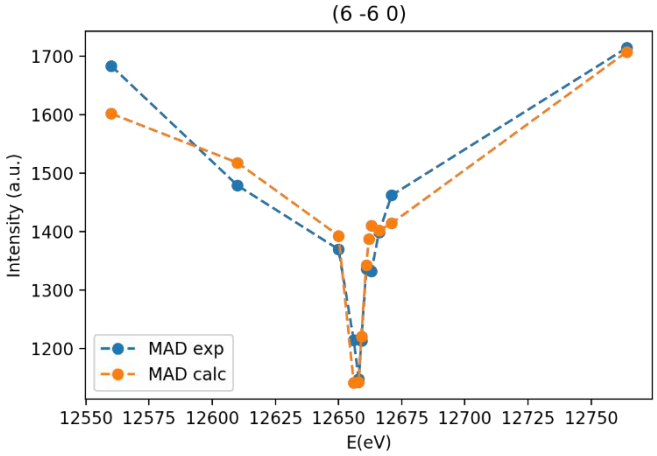

Fig. 2: Experimental and fitted intensity of the (6 -6 0) $PtSe_2$ Bragg reflection as a function of energy.

GI-MAD measurements consisted in measuring rods of scattering by the $PtSe_2$/Pt superlattice, for 12 different energies around the Se K-edge. This was performed for many rods of scattering from the $PtSe_2$ layer and the $PtSe_2$/Pt superstructure. The rod intensities vary with the X-ray energy, as shown in Fig. 2 and 3a for the (6 -6 *L*) $PtSe_2$ Bragg rod. The NanoMAD program performs a fit of all these data, providing $|F_{Se}|$ and $|F_{Pt}|$ (see e.g. Fig. 3b for the (6 -6 L) rod). Qualitatively, the GI-MAD analysis confirms the SXRD results that Se and Pt atoms both contribute significantly to the $PtSe_2$ Bragg rods, while the superstructure rods are largely dominated by the Pt contribution. As an example, the Se partial (6-6*L*) rod (Fig. 3b in red) displays an oscillatory behavior with a period in *L* ~1.5, which is typical of 2 Se layers separated by the c-axis of Pt(111) divided by 1.5, i.e. ~ 4.5 Å. This corresponds well to the expected separation between the 2 Se planes

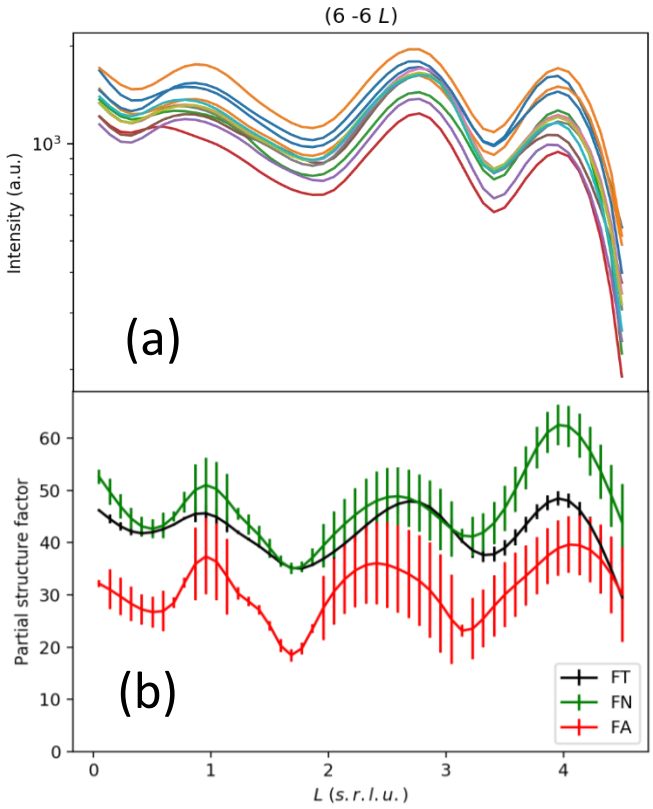

Fig.3: (a) (6 -6 L) rod integrated intensity for 12 different energies (see Fig. 2) around the Se-K edge, measured up to L=4.5 surface reciprocal lattice units (s.r.l.u.) (b) $|F_T|$, $|F_N|=|F_{Pt}|$ and $|F_A|=|F_{Se}|$ as a function of L, as deduced by Nano-MAD fit.

of $PtSe_2$. The complete GI-MAD analysis of the PtSe2 sample is almost finished, and a corresponding manuscript will soon be written.

The MAD measurements and analysis procedure have been optimized to be performed in less than half-an hour. This should allow, in a future experiment, to detect precisely the transition from $PtSe_2$ (a sandwich between 2 Se layers yielding the observed oscillatory $|F_{Se}|$ behavior) to the Janus SPtSe with exact stoichiometry. The presence of only one Se layer in this later should yield an almost perfectly flat Se contribution $|F_{Se}|$ as a function of *L*.

[1] Sant et al., *Synthesis of epitaxial monolayer Janus SPtSe*, npj 2D Materials and Applications (2020) 4:41 ; https://doi.org/10.1038/s41699-020-00175-z and R. Sant, PhD-Thesis, Univ. Gre. Alpes, 2019.
[2] V. Favre-Nicolin et al., Eur. Phys. J. Special Topics 208, 189–216 (2012)
[3] <http://sourceforge.net/projects/nanomad/>
[4] <https://xraypy.github.io/xraylarch/xafs.html