EUROPEAN SYNCHROTRON RADIATION FACILITY

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ESRF

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 using the **Electronic Report Submission Application:**

http://193.49.43.2:8080/smis/servlet/UserUtils?start

Reports supporting requests for additional beam time

Reports can now 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.

ESRF	**Experiment title: The structural origin of the ionic liquid gate voltage induced insulator to metal transition in thin vanadium oxide films**	**Experiment number**: HC-2621
Beamline: **ID03**	**Date of experiment**: from: 21/11/2016 to: 29/11/2016	**Date of report**:
Shifts: **18**	**Local contact(s)**: **Dr. Francesco Carla**	*Received at ESRF:*

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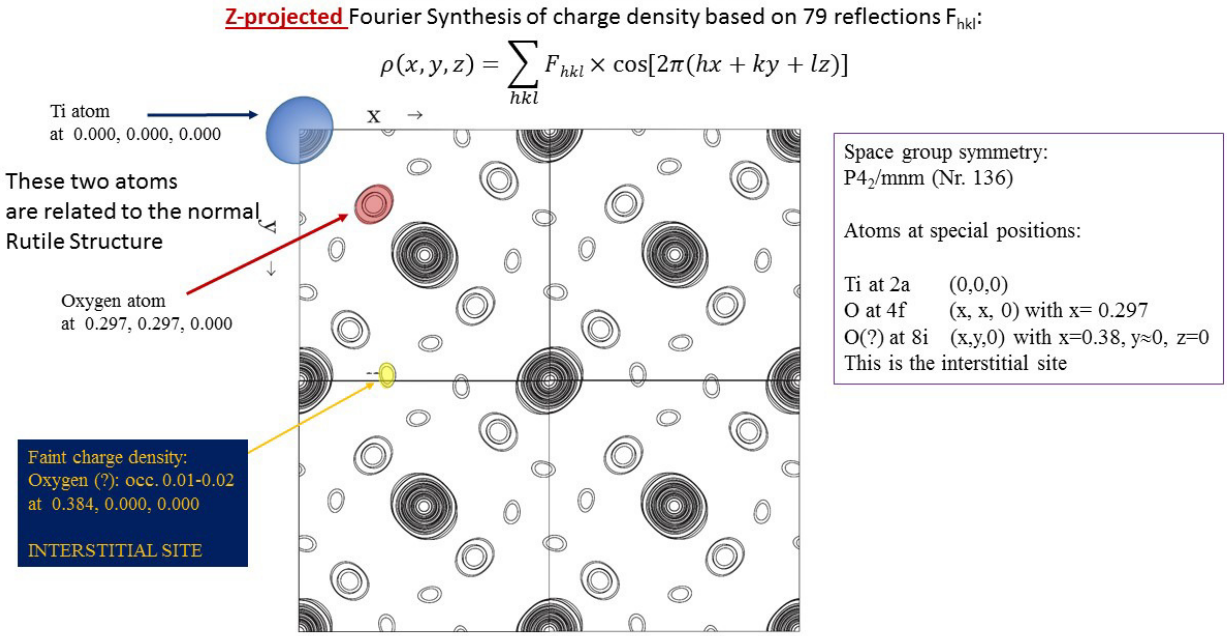
Report:

We have successfully carried out the proposed surface x-ray diffraction experiments to analyze the structure of thin (≈10 nm) VO_2 films grown on TiO_2. It has been observed that liquid gating of the film induces an insulator to metal transition which is accompanied by a structural phase transition from monoclinic to tetragonal symmetry and by an expansion of the c-lattice parameter by about 3% [1]. It is argued that for the liquid gating induced metallization of the film, the formation of oxygen defects plays a major role. [1,2].
In order to study in detail the effect of liquid gating and backgating on the VO_2 film structure we have carried out an extensive and precise collection of reflections after sample gating and after backgating, i.e. after bringing the film back to the insulating state in which the film structure becomes monoclinic.
For the gated sample we find that the film structure is purely tetragonal of rutile type. Monoclinic (superstructure) reflections were absent. Note, that the monoclinic (insulating) structure can be viewed as a (2x1x2) superstructure of the rutile structure type. In the following we shortly discuss the analysis of the gated sample for which 79 symmetry independent structure factor magnitudes ($|F_{hkl}|$) were collected.

Starting with the well known rutile structure the data could be fitted well by allowing the oxygen atom located at position 4f (xx0) of the space group $P4_2/mnm$ to vary. The only free positional parameter (x) in this structure was determined to x=0.297(1), which is a little larger than the value reported for the bulk [x=0.288(1)] [3]. In addition, we allowed for anisotropic displacement parameters (ADP's) for both, the V atom at site 2a (000) and the oxygen atom for which we typically find a considerable enhancement of the normal ADP's over the in-plane ones such as: $U^{11}=U^{22}=0.020(2)$ Å^2, $U^{33}=0.080(2)$ Å^2

for the V atom. Following the fit with an unweighted residuum of Ru in the 8% range we calculated the z-projected charge density which is shown in the figure below:



The charge density [ρ(x,y,z)] map of the projected structure shows four unit cells in which the strong peaks are related to the V atom at (000) and (½ ½ ½) as well as to the oxygen atom at (0.297, 0.297, 0.000) and the symmetrically equivalent ones.
In addition, the density map shows a faint charge density at an aysmmetric site at about (x,y,z)=(0.38, 0.00, 0.00). This comes unexpected at first, since this asymmetric site is unusual. Note that the calculation of ρ(x,y,z) is quasi model free since the rutile structure is well known and the signs of the 79 structure factors are thus calculated with 100% correctness. Note that owing to the centrosymmentry of the rutile structure the phase problem reduces to a determination of the signs of the structure factor magnitudes: ($F_{hkl}=\pm|F_{hkl}|$), i.e. the associated scattering phase is either 0 or π which facilitates the analysis.
The distance between the interstitial asymmetric site and the nearest V atom is equal to 1.76 Å, which is a bit shorter than the usual V-O distance in rutile type VO_2 (about 1.85 Å) which might be related to the reduced coordination number at this site. Thus the charge density might be attributed to low occupancy interstitial oxygen which also might be related to the unusal expansion of the c-lattice constant upon gating [1]. The data analysis is still in progress.
The monoclinic (backgated) sample was analyzed by using 225 independent reflections. The preliminary analysis shows that this structure -albeit monoclinic- is different from the bulk one reported in Ref.[3].

References:

[1] J. Jeong, N. Aetukuri, D. Passarello et al., PNAS 112, 1013 (2015)
[2] S. G. Altendorf, J. Jeong, D. Passarello, et al., Adv. Mater. 28, 5284 (2016)
[3] K. D. Rogers, Powder Diffraction 8, 240 (1993)