Oxygen crystallographic positions in thin films by non-destructive Resonant Elastic X-ray Scattering

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Supporting information

S1. Simulation Parameters

Spectra simulations have been carried out in the range [-50, + 250] around the absorption edge. A 0.2 step has been chosen for the [- 50, + 50] part (more sensitive) and a 0.5 step for the [+ 50, + 250] part.

The calculus radius was 5 Å, which seemed a good choice when compared to the system's lattice parameter (around 8 Å). Larger values showed almost no difference in terms of spectrum shape but heavily increased the simulation time. Lower radius values, however, led to significant changes in the spectra.

Atomic coordinates were fixed for the cations, which occupy fixed special positions. The theoretical lattice parameter value was chosen for the simulations. Repeating the process with the value found through S-XRD led to practically no change in the final result.

S2. Noise adding and error calculation

In order to generate the Pseudo-Experimental Spectra (p-ES), Gauss-centred random noise was added to the Theoretical Spectra in the energy range that was simulated $[E_{min}, E_{max}]$, as indicated in **Equation S1**.

$$I_{p-ES}(E_j) = I_{TS}(E_j) + S_j \cdot \varphi \quad \forall E_j \in [E_{min}, E_{max}] \#(S1)$$

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S: Gass-centred randomizer. $S \in \mathbb{R}$, $[-1,1]$

φ: noise amplitude. $\varphi \in \mathbb{R}$

The S parameter is randomly generated for every noise-adding operation, whereas φ is defined in terms of how important the noise is desired to be. Working with φ can be tedious if we want to compare the noise of p-ES to actual experimental data, so a noise-to-signal ratio (NTS%) has been defined as shown in **Equation S2**. It consists of the relative difference between the (pseudo)experimental intensity at an energy value, and the intensity calculated through a linear regression taking the two closest intensity values. Differences are squared so that they don't nullify.

$$NTS = \frac{1}{n}\sum_{j}^{E_n}\left(1 - \frac{1}{I_{PES}(E_j)}\left(I_{PES}(E_{j-1}) + \frac{I_{PES}(E_{j+1}) - I_{PES}(E_{j-1})}{E_{j+1} - E_{j-1}} \cdot (E_j - E_{j-1})\right)\right)^2 \#(S2)$$

n: number of E_j energy values that are considered for the calculation.

This NTS formula can be applied to both pseudo-experimental and purely experimental spectra. If we simulate p-ES at different φ and calculate their NTS, we observe NTS increases linearly with the noise amplitude – as shown in **Figure S1**. Since 044 is more intense than 333 – see **Figure 1**, NTS values are naturally smaller for 044.

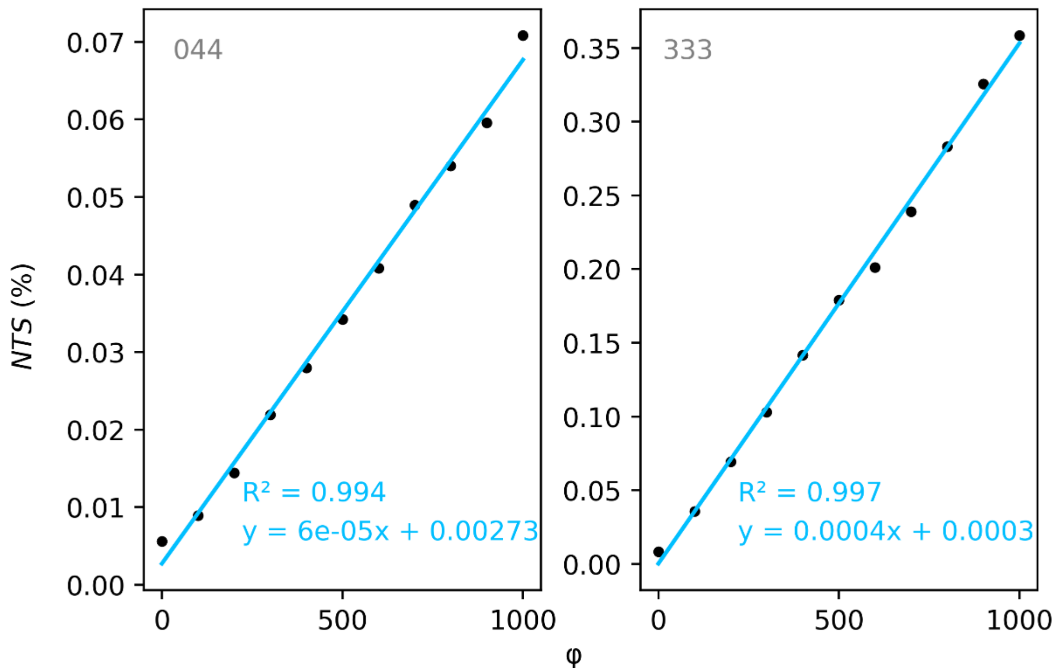

Figure S1 NTS vs. φ for the 044 and 333 reflections around the Fe K-edge. Values have been multiplied x100 to be presented as a percentage

The NTS formula – Equation S2 has been applied to experimental data, giving values of $NTS(\%) \approx$ 0.05, 0.07 for the 044 and 333 reflections, respectively. In terms of our simulations, this would correspond to the following φ values in the noise generation process: $\varphi_{044} \approx 730$ and $\varphi_{333} \approx 200$. Rounding-ups have been performed pessimistically above so that the calculated error is not underestimated.

The estimated φ values have been to generate the PSE and, using Equation 2 and Equation 3, to calculate the difference (X^2) between them and the TS. The minimum finding of X^2 led to the graph shown in **Figure 3**. Initial values have been imposed for the oxygen position (x_0 = 0.250) and the energy shift (E_0 = 0 eV) and the whole process (noise generation, X^2 calculation and minima finding) has been repeated 10 000 times.

Figure S2 shows a distribution of the $[x_i, E_i]$ sets which were found after the described process. Energy shifts have also been randomized with a normal function. A Gaussian fit has been carried out on the data distribution, giving a value of: x = 0.2500(2) for the position of oxygen atoms. Errors have been calculated as twice the value standard deviation (2σ), leading to a 95% of certitude in the given results.

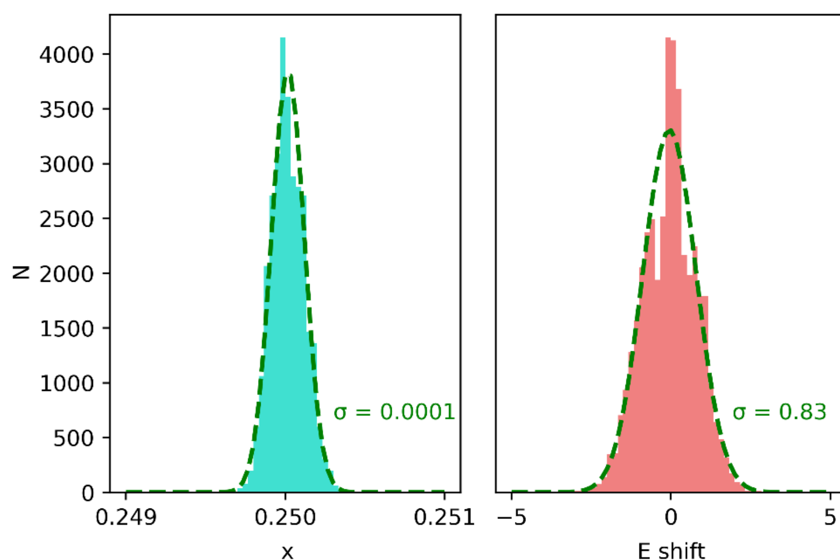

Figure S2 Results of minima found after refinement on the p-ES generated

Since p-ES were generated using the NTS of actual experimental data, it will be assumed that the error in the determination of experimental $[x_i, E_i]$ is the same of that found through the presented methods.

S3. Thin film characterization

Reflectometry measurements were performed on the thin film. The reflectometry curve has been fitted, as shown in **Figure S3**, giving a thickness of 24.76(6) nm, a density of 4.15(2) g cm^{-3} and a surface roughness of 0.598(1) nm.

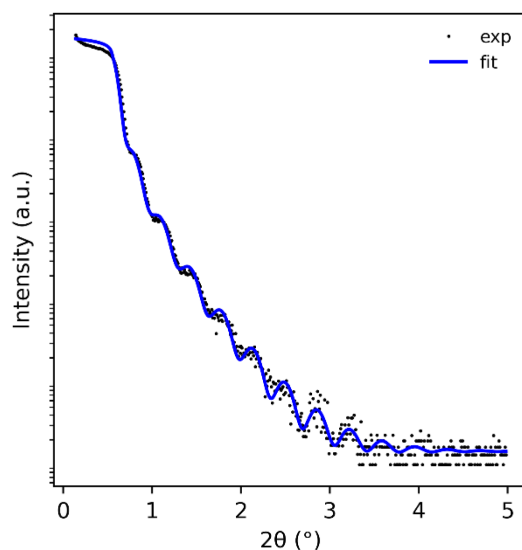

Figure S3 Reflectivity measurements on the 25 nm MgO//FVO thin film. Experimental data and fit

X-Ray Diffraction measurements (XRD) were performed in theA θ-2θ mode and showed the absence of spurious phases as well as a a good crystallinity (Laue oscillations) – **see Figure S4**. The fitting of the peak's position and the oscillations gave a lattice parameter of a = 8.434(7) Å and a thickness of 24.7(1) nm, which is consistent with the reflectometry results.

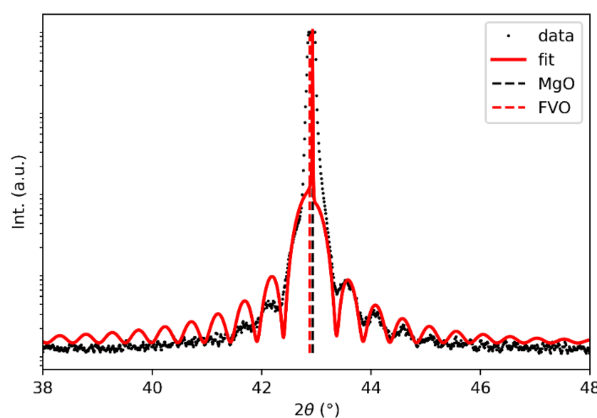

Figure S4 θ-2θ XRD scan for the MgO//FVO 25 nm film

Reciprocal Space Mapping (RSM)experiments were carried out around the $60\bar{2}$ reflection (**Figure S4**), active for FVO but not for MgO. The low lattice mismatch (0.4 %) made it almost impossible to scan a node which is active for both FVO and MgO, since the substrate would completely eclipse the film's signal.

The RSM intensity was fitted with a Gaussian function ($R^2 = 0.77$), giving an intensity maximum for $q_z = -0.2369(2)$ Å^{-1} and $q_x = 0.7089(1)$ Å^{-1}. This means an out-of-plane lattice parameters of c = 8.441(7) Å, consistent with the θ-2θ measurements. The in-plane lattice parameter was found to be a = b = 8.463(3) Å.

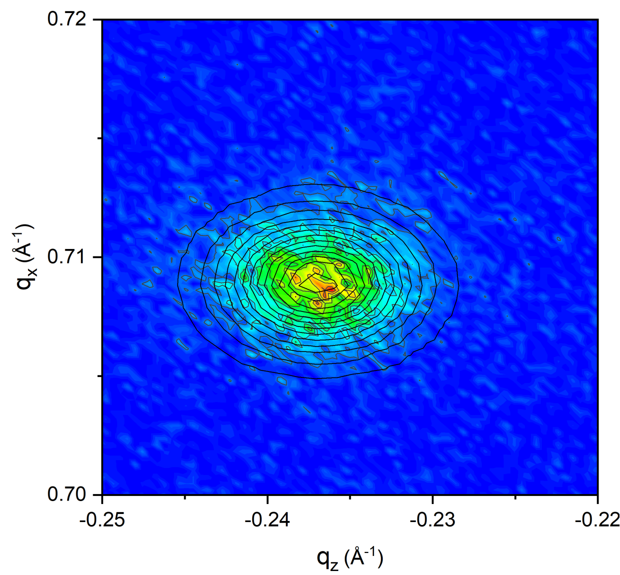

Figure S5 RSM around the $60\bar{2}$ reflection for the MgO//FVO thin film. The contour corresponds to the Gaussian fit which allowed us to obtained the peak's maximum