**Supplementary Material**

**Surface core hole electron energy loss fine structure in MgO: experiment and theory**

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**(1) *Statistical significance of edge onset ‘shoulder’ in surface EELS spectra***

The O K-EELS spectra in Figure 4a (main text) reveal extra intensity at the edge onset in the form of a weak ‘shoulder’. The signal-to-noise ratio of the ‘shoulder’ was calculated using the following procedure. After normalising the intensity of the main peak at ~537 eV the ‘bulk’ spectrum in Figure 4a was subtracted from the surface EELS spectrum. The resulting residual intensity is a measure of the differences in EELS edge shape between surface and bulk. If the ‘shoulder’ has good signal-to-noise it should therefore appear as a distinct peak in the residual intensity plot. Residual intensities for the left and right face surface EELS spectra in Figure 4a are shown in Figure S1 below.

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| **(a)** | **(b)** |
| **Figure S1:** Residual intensity plots for the (a) left and (b) right face surface EELS spectra in Figure 4a (see main text). |

A distinct peak is only observed in Figure S1b, which is also at the right energy for the ‘shoulder’ in Figure 4a. The noise in Figure S1b is defined as the average value of the absolute intensities within 525-530 eV and 535-540 eV energy windows. The former is a pre-edge energy window, while the latter overlaps with the intensity normalisation region. Therefore, the intensity within these energy windows should ideally be zero, and any non-zero intensity can be attributed to noise. Using this methodology, the signal-to-noise ratio for the peak in Figure S1b is estimated to be ~6.

**(2) *Reproducibility of surface EELS spectra***

EELS analysis was also carried out on other MgO cubes to establish the reproducibility of the surface EELS O K-edge. Figures S2a and S2b show STEM bright and dark-field images of one such MgO cube suspended over vacuum. An O K-edge line spectrum image was acquired across the middle of the cube, as indicated by the horizontal line in Figure S2b. The simultaneously acquired dark-field intensity profile is shown in Figure S2c. The scan direction was from right to left, i.e. towards the edge of the holey carbon film. Although the spectrum image region was defined entirely within vacuum, due to drift the measurement included part of the holey carbon film. This is evident from the anomalous increase in dark-field intensity in the 0-20 nm region in Figure S2c.

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| **(c)** | **(d)** |
| **Figure S2:** STEM (a) bight and (b) dark-field images of a MgO cube. (c) shows the dark-field intensity acquired simultaneously with the O K-edge line spectrum image. ‘Bulk’ and surface EELS spectra extracted from the spectrum image are shown superimposed in (d). Individual spectra are vertically shifted for clarity. |

O K-EELS spectra from the ‘bulk’ and free surfaces of the MgO cube were extracted from the line spectrum image and are shown superimposed in Figure S2d. Figure S2c was used to define ‘bulk’ and free surface regions. The EELS spectrum for the right cube face shows extra intensity at the edge onset in the form of a ‘shoulder’ (arrowed feature in Figure S2d), consistent with Figure 4a (main text). The ‘shoulder’ is however less clear for the left cube face, presumably due to this surface being more affected by the spatial drift during spectrum image acquisition.