# Chemistry-dependent magnetic properties at the FeNi oxide-metal interface
## Supplementary Information

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# I. OXIDATION OF $\mathbf{Fe_{0.7}Ni_{0.3}}$

## A. LEEM-IV characterization

Fig. 1 shows the electron reflectivity curves for the bcc and fcc regions as a function of $O_2$ exposure during the oxidation of the $Fe_{0.7}Ni_{0.3}$ thin film. At the very early stages of oxidation (8.4 L dose) the reflectivity in the bcc region changes drammatically, whereas the changes in the fcc curve are less evident. At 18.6 L, both regions show entirely different LEEM IV curves as compared to the curves from the respective oxygen-free regions. Consistent with the LEED data, at 1240 L, both regions transform into a uniform FeO(111) layer, as evident from the easily recognizable LEEM IV fingerprint.[1,2] At the oxygen dose of 1700 L an additional heterogeneity appears within both the fcc and bcc phases with slightly different IV curves. We attribute this to the onset of $Fe_3O_4(111)$ island formation consistent with the weak (2 × 2) pattern observed in LEED.

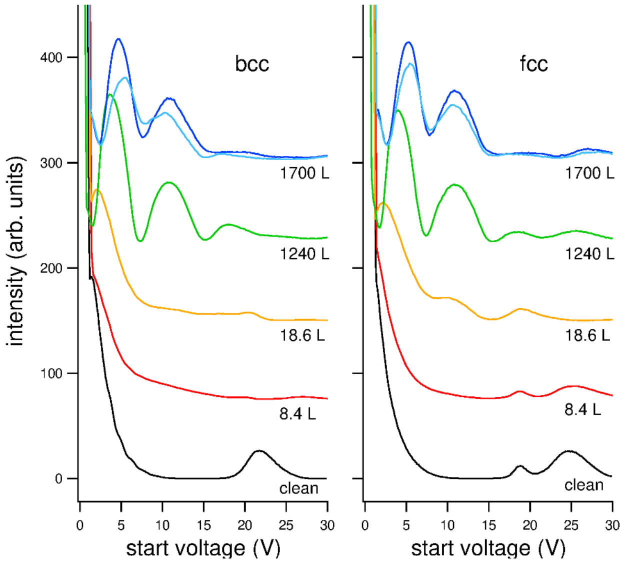

FIG. 1: LEEM IV curves from the bcc and fcc regions of the phase separated Fe-Ni surface as a function of oxygen dose. At the highest dose shown (1700 L), surface appears heterogeneous at a length scale below 100 nm, and two distinct regions can be resolved both within the bcc and the fcc regions.

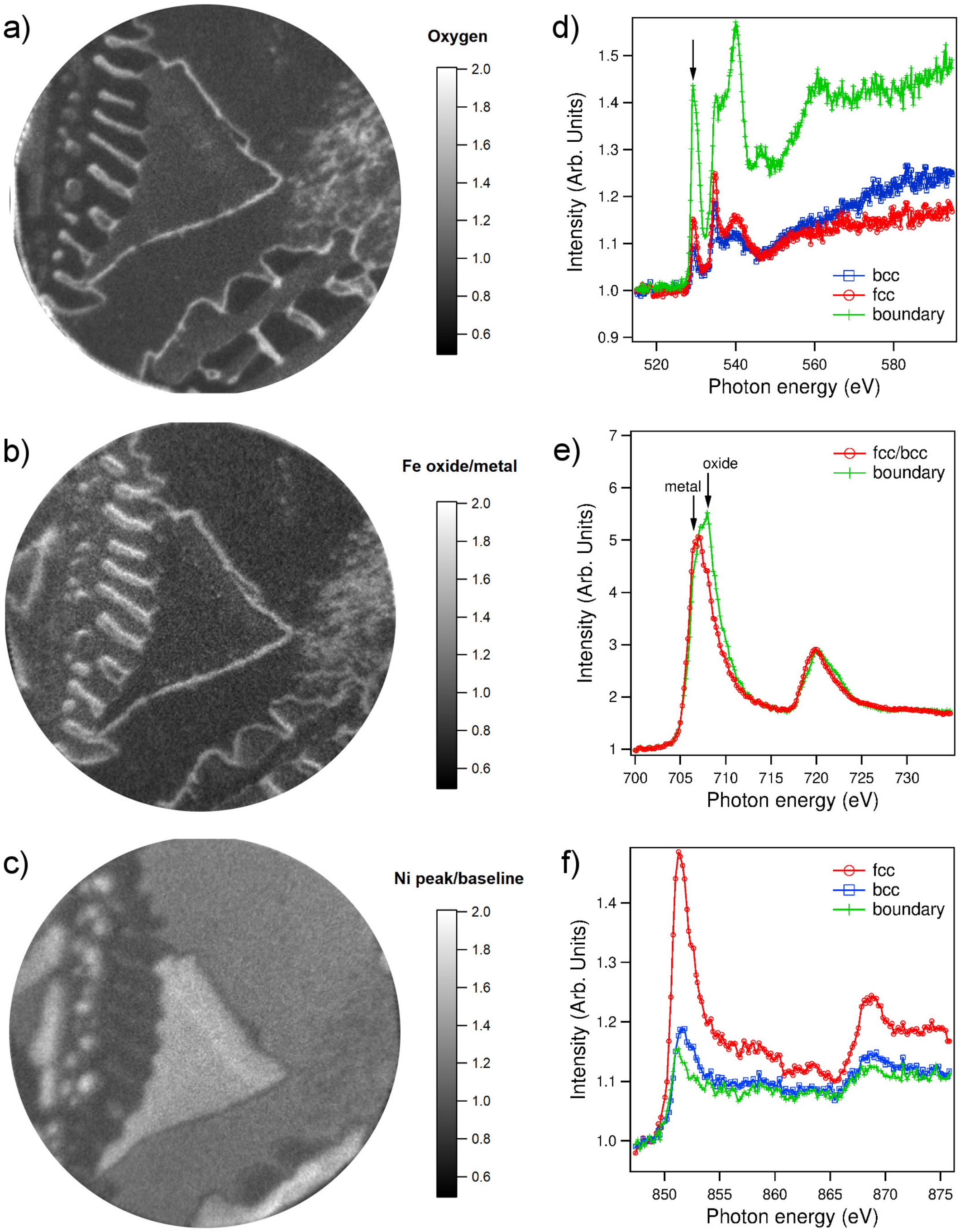

FIG. 2: XAS images and spectra from the Fe-Ni alloy film at the O K, Fe L and Ni L edges, after exposing the sample to 1250 L of oxygen. a) O K-edge XAS-PEEM, b) ratio between the images acquired at the "oxide" and "metal" peaks at the Fe $L_3$ edge, c) Ni $L_3$-edge XAS-PEEM. d) O $K$-edge, e) Fe $L$- edge, f) Ni $L$- edge XAS spectra are shown on the right column.

### B. Reactivity of the fcc-bcc phase boundary

Fig. 2 shows the spatially resolved XAS measurements at the O K (Fig. 2a,d), Fe $L_{2,3}$ (Fig. 2b,e) and Ni $L_{2,3}$ (Fig. 2c,f) edges after exposure to 1250 L of $O_2$. The fcc-bcc phase boundary has a different chemical contrast in laterally resolved images, arising from the higher amount of oxygen and oxidized Fe at the border, as compared to the rest of the surface. The specific features in both XAS spectra indicate the formation of $Fe_3O_4$ at the fcc-bcc phase boundary well before the rest of the surface.

## II. $Fe_3O_4$/bcc(FeNi) FERROMAGNETIC COUPLING

The coupling between the $Fe_3O_4$ and bcc(110) Fe-Ni film underneath is not easy to determine using XMCD-PEEM, due to the small irregular magnetic domains. Nevertheless, a careful analysis of the XMCD contrast as a function of photon energy at the Fe $L_3$ edge (in Fig. 3) reveals the general tendency. In all three panels, the horizontally-elongated region on the top of the images correspond to a dewetted area with no magnetic contrast. Fig. 3a, taken at a photon energy (708.0 eV) at the metallic Fe peak as well as the $Fe^{2+}$ $O_h$ peak of $Fe_3O_4$, shows dark contrast in most of the bcc region. In Fig. 3b, which is taken at 709.1 eV at the $Fe^{3+}$ $T_h$ peak, the XMCD nearly disappears. In Fig. 3c at the $Fe^{3+}$ $O_h$ peak, the dark contrast reappears. In short, the XMCD signal in Fig. 3a and Fig. 3c has the same sign, which is an indication that the magnetization within the metallic alloy underneath is aligned in the same direction as the majority axis of the oxide above.

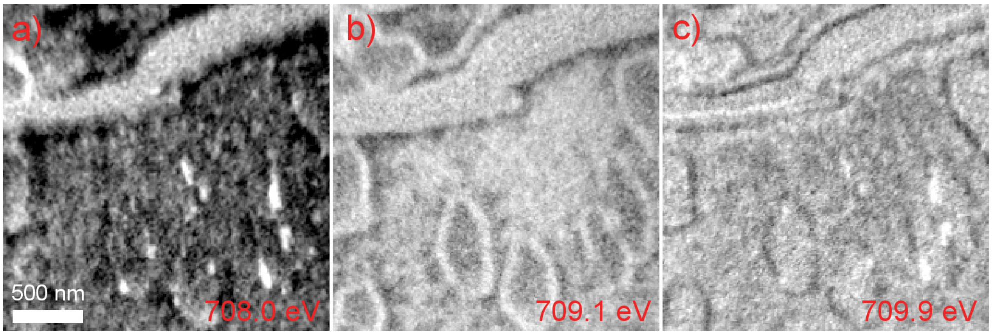

FIG. 3: XMCD images at the Fe $L_3$-edge for a phase separated $Fe_{0.70}Ni_{0.30}$ film exposed to 1750 L of molecular oxygen.

## III. OXIDATION OF $\mathbf{Fe_{0.5}Ni_{0.5}}$ THIN FILM AND MAGNETIC PROPERTIES

A homogeneous thin film having the same structure (fcc) and stoichiometry ($Fe_{0.5}Ni_{0.5}$) was prepared to mimic the oxidation of the fcc crystallites. We oxidized the sample (T = 200-250 °C; $1\times10^{-6}$ mbar $O_2$) stepwise, consistently to what was done for the $Fe_{0.7}Ni_{0.3}$ thin film. These measurements confirm the general trend found for the mixed bcc-fcc case; the higher Ni concentration the slower the oxidation. In particular, we find that the exposure of 3000 L is not sufficient to form a superficial $Fe_3O_4$. The outcomes of the spectroscopic and structural data are contradictory with each other, and do not allow the assessment of the superficial oxide phase. On one hand, the LEED of the surface (Fig. 5c) shows a (1x1) reconstruction typical for FeO(111) (Fig. 4b), on the other, the XAS (Fig. 4d) and CEMS measurements (see Table I and Fig. 4) suggest the presence of an oxide with higher oxidation level. The low $B_{hf}$ value for such non-specific oxide components in the CEMS spectrum points toward a non-ferromagnetic phase. More than half of the Fe remains in the metallic state. We note that the exposure to 10500 L was necessary to observe a weak (2x2) reconstruction in LEED (see for instance Figure 4c) .

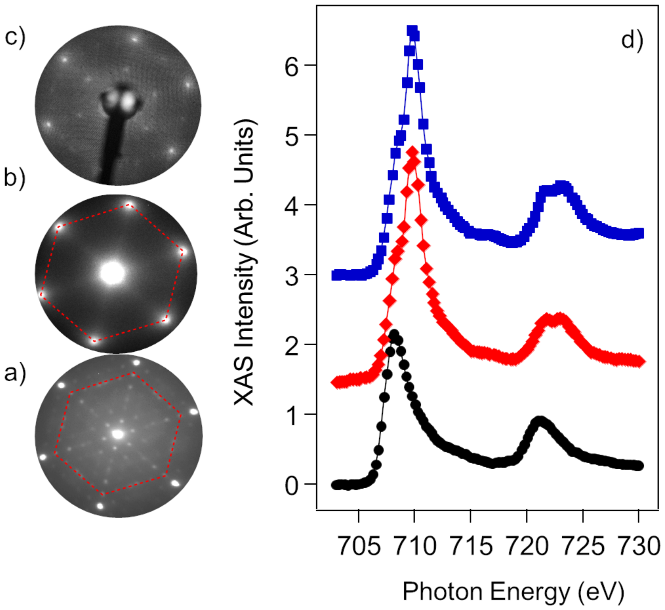

FIG. 4: On the left, LEED pattern of the $Fe_{0.5}Ni_{0.5}$ film as prepared (a) and after exposure to 3000 L (b) and 10500 L (c) ($E_k = 45$eV); the red hexagon indicates the positions of the FeO(111) main diffraction spots. d) corresponding XAS spectra at the Fe $L_{2,3}$ edge for samples exposed to the same $O_2$ dose.

| | IS [mm/s] | $<B_{hf}>$ [T] | Relative Intensity % |
|---|---|---|---|
| metallic | 0.04 | 29.6 | 53.8 |
| Non-specific oxide | 0.35 | 9.5 | 46.3 |

TABLE I: Mössbauer hyperfine parameters of the $Fe_{0.50}Ni_{0.50}$ film after exposure to 3750 L $O_2$ at 250°C, with an intermediate annealing step to 350°C after 750 L dose.

The variation of the XPS core level intensity ration ($I_{Fe}^{XPS}/I_{Ni}^{XPS}$) (Figure 6) and XAS ( Figure 4d) measurement demonstrate that the oxidation causes the segregation of Fe the surface of the film. Based on both the XPS and the CEMS measurements, we find that the amount of Fe segregated to the surface layer and the degree of oxidation are lower in the homogeneous $Fe_{0.5}Ni_{0.5}$ film when compared to that of the fcc islands having the same stoichiometry and structure.

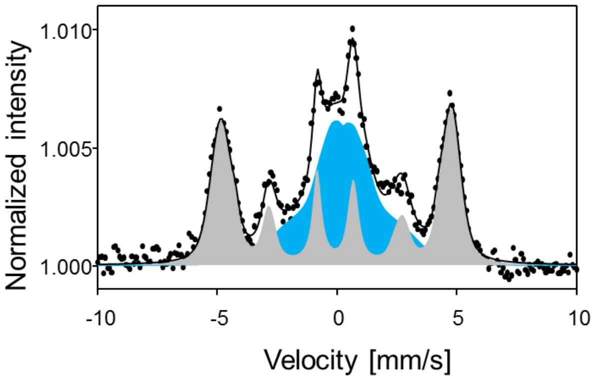

FIG. 5: CEMS spectrum of the $Fe_{0.5}Ni_{0.5}$ film after exposure 3750 L $O_2$. The spectral components are color-coded: light gray – metallic FeNi, blue – non-specific oxide component.

The magnetic coupling between the top most oxide and the metallic layer was investigated using XMCD-PEEM at each oxidation step. At both oxidation stages (3000 L and 10500 L $O_2$ exposure) we find FM coupling between Fe and Ni in the alloy, along the W(1-10) direction, as demonstrated by the XMCD-images a and c in Figure 7 at the $Fe^{met}$ and $Ni^{met}$ peaks. In the XMCD-Images acquired at the $Fe^{oxide}$ there is no magnetic contrast (images b and d in Figure 7), demonstrating that the oxide layer is not magnetic.

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[1] M. Monti, B. Santos, A. Mascaraque, O. Rodríguez de la Fuente, M. A. Niño, T. O. Menteş, A. Locatelli, K. F. McCarty, J. F. Marco, and J. de la Figuera, The Journal of Physical Chemistry C **116**, 11539 (2012).

[2] M. Monti, B. Santos, A. Mascaraque, O. Rodríguez de la Fuente, M. A. Niño, T. O. Menteş, A. Locatelli, K. F. McCarty, J. F. Marco, and J. de la Figuera, Phys. Rev. B **85**, 020404 (2012).

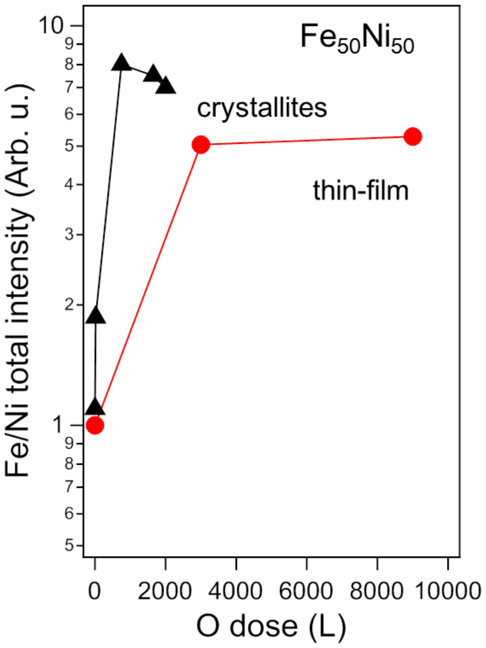

FIG. 6: Comparison of the Evolution of the Fe 3*p* and Ni 3*p* core level intensity ration as function of $O_2$ exposure between the crystallite and their thin-film counterpart. The plot shows that Fe surface segregation is smaller in the thin film case, leading to a thinner surface Fe-oxide layer. (hv = 250 eV).

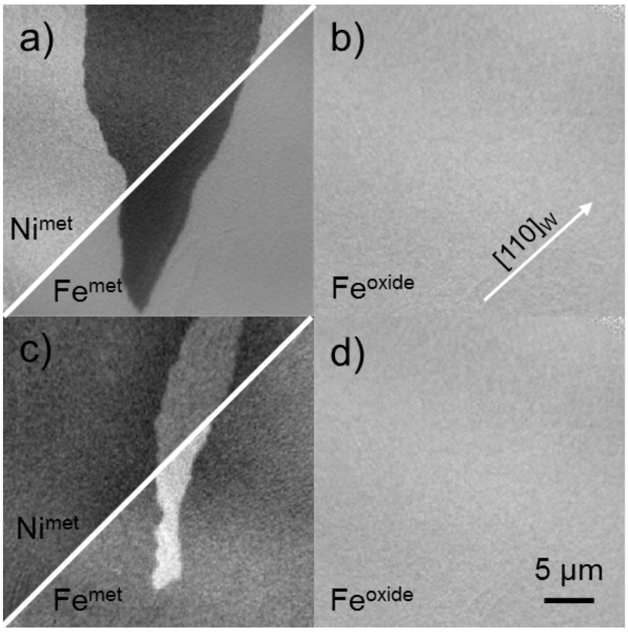

FIG. 7: XMCD-PEEM images at the Fe $L_3$- edge (metal and oxide components) and Ni $L_3$- edge for the $Fe_{0.5}Ni_{0.5}$ thin film after 3000 L (a,b) and 10500 (c,d) $O_2$ exposure. The FM coupling of the FeNi layer is evident from the superposition of the corresponding XMCD images. The oxide layer does not show any magnetic contrast. The incoming photon beam directions, oriented as the $[110]_W$ crystalline axes of the substrate is shown in the Fig. 7b as an arrow.