# Oxide surfaces and surfaces oxides - structural complexity and surprises revealed by LEED intensity analyses

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The surfaces of transition metal oxides are quite often not just bulk-like terminated but chemically and geometrically reconstructed. There can be vacancies within either the oxygen or cation lattice as well as site switches towards interstitial position. These processes are not restricted to the very surface but can also occur - even exclusively - within subsurface layers as e.g. in the cases of $Fe_3O_4$(100) [1] and CoO(111) [2] and by that remain largely hidden to imaging methods like STM. For ultra-thin oxide films grown on reactive substrates the situation further complicates by the competition of binding forces within the film and towards the substrate [3]. This may even lead to Moire-type films with a laterally modulated structure as found for a CoO(111)-type bilayer on Ir(100) [4]. Modification of the substrate interaction - here by a pseudomorphic buffer layer of metallic cobalt - leads instead to a CoO(100)-type layer with c(4×2)-ordered Co-vacancies. These interface-driven structures also determine the growth orientation for thicker films [5]. In the sub-monolayer regime there is a further competition between 2D-oxide island growth and 1D-nanostructure formation. On the plain Ir(100) surface for example, linear metal-oxide hybrid structures with $CoO_2$ and $CoO_3$ stoichiometry develop self-organised in threefold lateral distance, inducing a missing row substrate reconstruction below.

As demonstrated above, the structural solutions of nature for oxide surfaces and films are often complex and rather surprising, which makes the initial guess of the correct structure - the inevitable starting point of every structure determination - a demanding task. This is the more crucial the larger the surface unit cell becomes, since in such a case the contribution of one extra (or missing) atom alters the total wave field only moderately. This means that neglecting such an element in the model structure will also not lead to dramatic changes in the intensity spectra and so still seemingly plausible fits may result. As an example, LEED-IV analyses for the c(2×2)-reconstructed surface of $Fe_3O_4$(100) using models neglecting either the Fe vacancies or the interstitial ion still produce “best-fit” Pendry R-factors in the range 0.2 - 0.3, which are commonly called “acceptable fits”! As a consequence it has to be pointed out that trustworthy LEED fits in particular for complex structures have to be of significantly better quality ($R_P < 0.15$). To achieve this objective, large experimental and computational efforts are necessary: On the one hand, surface preparation has to be controlled and optimised preferably by local probes like STM in order to minimise structural defects and phase coexistence. On the other hand, also minute atomic relaxations have to be fitted and this can only be performed on the basis of huge data sets with large redundancy factors. And as a final proof, the derived structural parameters should be compared with those of a corresponding, fully relaxed total-energy calculation and coincide on a level below 0.1 Å.

## References

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