	Experiment title: Formic acid adsorption on Fe3O4(001) investigated by surface x-ray diffraction	**Experiment number**: CH4603
Beamline: ID03	**Date of experiment**: from: 6.7.2016 to: 12.7.2016	**Date of report**: 1.3.2017
Shifts: 18	**Local contact(s)**: CARLA Francesco	*Received at ESRF:*

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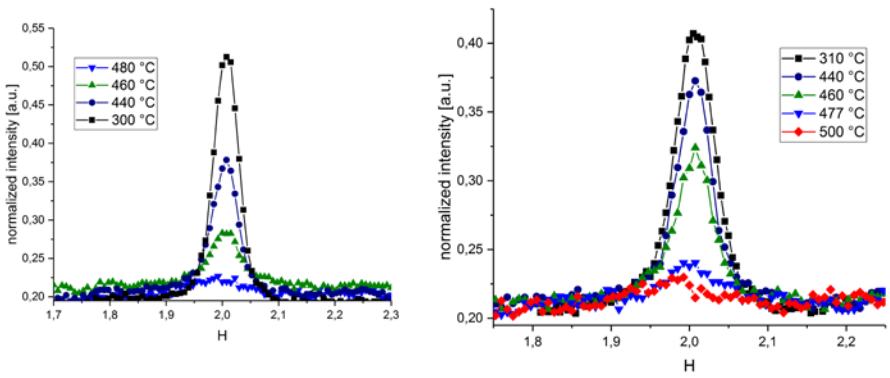
Report:

After successfully determining the structure of the clean (√2x √2)R45° reconstructed magnetite (001) surface based on a previous beamtime at ID03 [1], we wanted to adress the basic room temperature interaction mechanisms of formic acid with the (001) surface of magnetite, which lead to the lifting of the (√2x √2)R45° surface reconstruction [2]. In addition, we also wanted to investigate the reversible phase transition to a (1x1) bulklike-terminated surface [3] and determine its structure. All measurements were done under gracing incidence at a photon energy of 14 keV. Following a successful preparation of the (√2x √2)R45° reconstructed (001) surface of a natural magnetite single crystal by multiple sputter-anneal cycles (as confirmed by reference scans), a full reference dataset from the clean surface at room temperature was taken. This included 20 crystal truncation rods (10 symmetry independent) measured in static mode and 6 surface rods as well as the specular rod measured by performig rocking scans.



We then heated the sample in steps between 300 °C and 500 °C to probe the phase transition towards the unreconstructed surface. At each step, after reaching a stable temperature, we checked and corrected the alignment of the sample. Afterwards, we performed reference scans in

Figure 1:Scan through the (2,1) surface rod at l=1.6 for different sample temperatures while heating up (left) and cooling back down (right). The decrease in height and increase in width indicates a continuous phase change towards a (1x1) surface, that is reversible by cooling back down.

reciprocal h-direction through the (2,1) (shown in Figure 1) and (5,2) surface rods as well as rocking scans through the (2,2) crystal truncation rod. By doing this, we were able to follow the phase transition towards the

unreconstructed surface. A set of 15 (10 symmetry-independent) crystal truncation rods was measured at this temperature to probe the structure of this unreconstructed surface. Following this, the surface was cooled down in steps, again performing the same reference scans after reaching stable temperatures to probe the phase transition back to the (√2x √2)R45° reconstructed surface (also shown in Figure 1), and another small reference set of 3 crystal truncation rods was measured after cooling back down to room temperature.

Following this, we started adsorption of formic acid. In preparation for this, the surface was reprepared by sputtering and annealing, while the formic acid was cleaned by multiple freeze-pump-thaw cycles. Afterwards, formic acid was dosed on the surface at room temperature and a pressure around $1x10^{-9}$ mbar until a coverage of 10 L was reached, and we followed the lifting of the reconstruction by perfoming a scan along the reciprocal k-direction through the (2,1) surface rod and (2,2) crystal truncation rod in reciprocal at l=1.6 (shown in Figure 2). We observed the partial lifting of the surface reconstruction, and took a dataset of this surface containing the same 20 crystal truncation rods, 6 surface rods and the specular rod that we measured from the clean surface. After this, we dosed formic acid a second time to a total coverage of 50 L, lifting the reconstruction completely and following the process with the same reference scans. We took another dataset, again containing the same crystal truncation rods and the specular rod that were measured before. A comparision of the structure factors of the clean surface and after dosing formic acid obtained from these measurements is shown in Figure 3. We finally started to heat the formic acid covered surface up to a temperature of 120 °C, and checked for changes in the crystal structure on the (2,2)-rod as well as changes in the morphology of the surface by reflectivity.

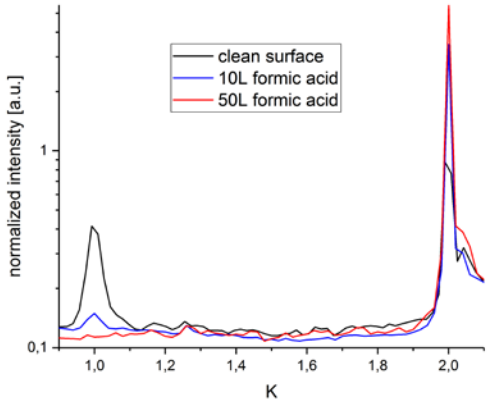


Figure 2: Scan through the (2,1) surface rod and (2,2) crystal truncation rod at l=1.6. The vanishing intensity on the surface rod shows the lifting of the reconstruction.

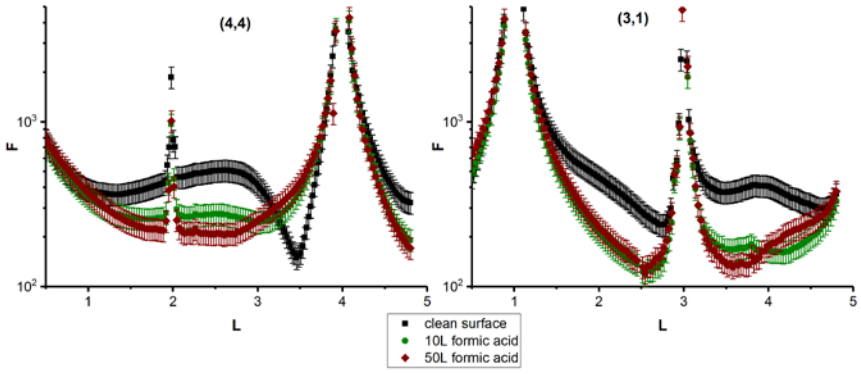


Figure 3: Crystal truncation rods before formic acid dosing, after dosing 10 L and after dosing 50 L formic acid on the surface.

Appart from a few beamdumps and problems with the hexapod of the diffractometer, the beamtime went smoothly without major problems. Based on the good quality of our data, we are confident that we will be able to determine the surface structures of both the unreconstructed surface at 500 °C and after dosing 50 L of formic acid as well as the partially reconstructed surface after dosing 10 L of formic acid.

References:

1. Arndt, B. *et al.* Surface Science Atomic structure and stability of magnetite Fe 3 O 4 (001): An X-ray view. *Surf. Sci.* **653,** 76–81 (2016).
2.Gamba, O. *et al.* Adsorption of Formic Acid on the Fe $_3$ O $_4$ (001) Surface. *J. Phys. Chem. C* **119,** 20459–20465 (2015).
3. Bartelt, N. C. *et al.* Order-disorder phase transition on the (100) surface of magnetite. *Phys. Rev. B* **88,** 235436 (2013).