The structure of the (100) surface of magnetite: a combined approach by X-ray diffraction, LEED and DFT-calculations

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The surface structure and composition of magnetite, Fe₃O₄, is of fundamental interest and has significant consequences for its reactivity, its mechanical and magnetic properties. Magnetite is not only important in geology and mineralogy, but also attracts increasing attention as a potential material for spintronic devices [1] due to its half-metallic behaviour, coupled with a high Néel temperature of 858 K.

For Fe₃O₄(001) a (2x2)R45° reconstruction has been observed experimentally [2-7]. However, the surface structure and the stoichiometry have not been unambiguously solved so far and are subject of a controversial debate in the literature. Magnetite has the inverse spinel structure with a sequence two types of layers in [001] direction and two possible volume truncations. Both volume truncations of the Fe₃O₄(001)-surface are classified as polar of type 3 after the scheme of Tasker [8] and are considered to be unstable. The mostly favoured model up to now has been the termination with a half filled A-layer of Fe³⁺ which would fulfill the autocompensation rule with all anion-derived dangling bonds filled, and empty cation-derived bonds, respectively [9]. Recent STM results, however, indicate a termination with the B-layer (with mixed Fe²⁺ and Fe³⁺ in octahedral sites) [10]. In order to obtain a consistent result from different methods we have performed DFT calculations [11] and analysed the surface structure with X-ray diffraction and LEED. In order to explore the effect of oxygen on the stability of the surface we combined the DFT calculation with ab initio thermodynamics [12].

X-ray measurements were performed at the beam line DW12 at LURE/Orsay with a wave length of 0.826 Å. 220 symmetrically independent reflections were measured in 5 crystal truncation rods and 6 superstructure rods. The surface was cut from a naturally grown crystal by spark erosion and mechanically polished. In UHV the surface was prepared by standard methods, Ar⁺ ion bombardement and annealing up to 850 K for 1 h after which the crystal exhibited a c(2x2) LEED pattern. The LEED pattern and the I/V curves remained unchanged when annealing the crystal in oxygen atmosphere up to 5x10⁶ mbar, indicating that the formation of the superstructure does not sensitively depend on the preparation conditions. The cleanliness of the crystal was checked by EPMA, electron probe micro analysis, by which a small impurity of 0.014 at% Mn was found.

The DFT calculation resulted in a modified B-layer termination with a wave-like lateral and vertical distortion of the Fe and oxygen atoms in the top layers. This model is consistent with the x-ray results, the analysis of the LEED I/V measurements is not yet completed, results will be presented at the conference. The x-ray analysis tuned out to be not unambiguous and lead to a similar agreement for the half occupied A-layer termination. The present result shows that the combination of structure analysis methods with DFT calculations is the most fruitful approach to solve complex surface structures.
References

[10] G. Güntherodt et al., private communication