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, Fe_3O_4 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 $Fe_3O_4(001)$ a $(\sqrt{2}x\sqrt{2})R45°$-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 $Fe_3O_4(001)$-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 Fe^{3+} which would fulfil 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 Fe^{2+} and Fe^{3+} 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 A. 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 $5x10^{-6}$ 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.

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