# O 26 Oxide und Isolatoren I

Zeit: Samstag 15:00–17:00 Raum: TU EB202

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**Jahn-Teller stabilization of a "polar" metal oxide surface: $Fe_3O_4$(001)** — •Rossitza Pentcheva, Wolfgang Moritz, and Matthias Scheffler — Section Crystallography, Dept. of Earth and Environmental Sciences, LMU München

We present a systematic investigation of the composition, structure and properties of the $Fe_3O_4$(001)-surface based on density-functional theory (DFT). Using *ab initio atomistic thermodynamics* [1] we predict that a "polar" termination is the lowest energy configuration over the entire range of accessible oxygen pressures. The stabilization of the surface involves a fundamentally different mechanism, which has not been considered so far: While most of the previous studies proposed an ordering of surface vacancies as the origin of the experimentally observed $(\sqrt{2}\times\sqrt{2})R45°$-reconstruction, here it is explained as a Jahn-Teller distortion of the surface atoms forming a *wave-like* pattern along the [110]-direction. Both x-ray diffraction (XRD) [2] and low energy electron diffraction (LEED-I/V) analyses support the theoretically predicted model. Calculated STM images and surface core level shifts are compared to available experimental data. The predicted halfmetal-to-metal transition from bulk to the surface is relevant in view of future applications (*e.g.* in spintronic devices). [1] K. Reuter and M. Scheffler, Phys. Rev. B 65, 035406, (2002). [2] R. Pentcheva, F. Wendler, N. Jedrecy, H.L. Meyerheim, W. Moritz, and M. Scheffler, submitted to Phys. Rev. Lett.

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**Theoretical Study of the $Fe_3O_4$(111) Surface Structure and Physical Properties** — •Aleksey Kuznetsov, Martin Friák, and Matthias Scheffler — Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany

The $Fe_3O_4$(111) surface has been studied intensively since several years due to its potential application in spintronics (Yu. S. Dedkov et al., Phys. Rev. B 65 (2002) 064417). The unreconstructed surface can expose six possible terminations, but only three of them have been clearly resolved experimentally (e.g. N. Berdunov et al., Phys. Rev. B 70 (2004) 085404). Moreover, self-consistent band structure calculations of the $Fe_3O_4$(111) surface are still lacking.

We present the results for the different surface terminations, in particular addressing the stability, electronic structures, and magnetic properties. Employing ab initio atomistic thermodynamics we identified the most stable surface termination. All calculations were performed using density-functional theory together with the all-electron full-potential linearized augmented plane-wave method as implemented in the WIEN2k code.

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**DFT-Rechnungen zur Adsorption und Dissoziation von Wasser auf Fe3O4(111)** — •Wolfgang Ranke[1], Maria E. Grillo[2] und Carsten Menke[2] — [1]Fritz-Haber-Institut der MPG, Faradayweg 4-6, 14195 Berlin — [2]Accelrys GmbH, Inselkammerstr. 1, 82008 Unterhaching

Die Fe3O4(111)-Oberfläche ist regulär mit 1/4 ML Eisen über einer vollen Sauerstofflage terminiert. Die anfängliche Adsorption von Wasser verläuft ungewöhnlich, nämlich dissoziativ [1,2] und ohne Aktivierungsschwelle [1]. DFT-Rechnungen zeigen, dass die Dissoziation über einen molekular auf Fe gebundenen Zwischenzustand erfolgt. Die OH-Gruppe bleibt auf diesem Platz während das abgespaltene H-Atom über zwei konkurrierende Wege zum übernächsten O-Platz gelangt, wo es eine strukturell unterschiedliche zweite OH-Gruppe bildet, in voller Übereinstimmung mit IRAS-Messungen [2]. Nach Sättigung dieser gamma-Spezies adsorbiert weiteres Wasser (beta-Spezies) molekular über Wasserstoffbrücken zu den beiden OH-Gruppen. Deren Bindungen zum Substrat bleiben erhalten sodass die gebildeten Aggregate nicht einem konventionellen Wasser-Dimer entsprechen. Die mögliche Rolle einer solchen Anordnung für die Aktivierung von Wasser in katalytischen Prozessen wird diskutiert. [1] Y. Joseph et. al., J. Phys. Chem. B 104 (2000) 3224. [2] U. Leist et al., Phys. Chem. Chem. Phys. 5 (2003) 2435.

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**Interaction of atomic hydrogen with FeO(111), Fe3O4(111) and alpha-Fe2O3(0001-biphase) surfaces** — •Wolfgang Ranke[1], Weixin Huang[2], and Robert Schlögl[1] — [1]Fritz-Haber-Institut der MPG, Faradayweg 4-6, 14195 Berlin — [2]Now at: Dept of Chem. Phys., Univ. of Science and Technology of China, Hefei 230026, P.R.China

Hematite Fe2O3 is used as catalyst in the dehydrogenation of ethylbenzene to styrene. The formed hydrogen reduces the oxide but little is known about the the mechanism. Therefore, the interaction with molecular and atomic hydrogen and its desorption was studied on epitaxial iron oxide films of different phases using LEED, XPS and TDS. Room temperature exposure to atomic H causes partial disordering. Both OH groups and reduced (but not yet metallic) iron appear in XPS. FeO domains react very quickly and TDS shows only water desorption explaining the observed reduction. Fe2O3 domains react more slowly. Even at RT, Fe3O4 domains are formed. TDS shows desorption of both H2O and H2. Upon flashing, reduced iron and OH remain but the oxide reorders and separates into Fe2O3 and Fe3O4. Oxidation restores the original surface. The implications for the behavior of the catalyst will be discussed.

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**Pt surface structure in presence of an oxygen atmosphere** — •Timo Jacob and Matthias Scheffler — Fritz-Haber-Institut der MPG, Berlin, Germany

Nowadays Platinum is used to catalyze a whole variety of different reactions. Expecially for electrocatalytic processes (such as in fuel cells) Pt is still one of the most sufficient materials providing a high rate for oxygen reduction at the cathode. However, this reaction occurs in a multicomponent environment and under conditions of finite temperature, pressure, and electrode potential ($p = 1\,\mathrm{bar}$, $T = 80 - 100\,\mathrm{C}$, $\phi \neq 0\,\mathrm{V}$). Thus, the model of an pure and perfect Pt(111) surface, which is often used to study this reaction, is clearly incomplete.

Therefore, to study the cathode reaction mechanism our first investigations aim on the realistic Pt(111) surface structure, which then will be the basis of further studies. Using density functional theory (DFT) in combination with a modified *ab inito* atomistic thermodynamics (capable to treat the electrode potential), we started with the $V = 0$ case and calculated the corresponding $p/T$-phase diagram, which led to interesting surface-oxide structures.

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**A Combined In-situ SXRD and HRCLS study of the Oxidation of Ag(111)** — •Alexander Reicho[1], Andreas Stierle[1], Ioan Costina[1], Helmut Dosch[1], Edvin Lundgren[2], Johan Gustafson[2], and Jesper Andersen[2] — [1]Max-Planck-Institute for Metals Research, Heisenbergstr. 3, 70569 Stuttgart, Germany — [2]Department of Synchrotron Radiation Research, Lund University, Box 118, S-22100, Sweden

Silver is used as catalyst for the epoxidation of ethylene and during the partial oxidation of methanol to formaldehyde. The formation of an oxygen induced p(4x4) reconstruction of the Ag(111) surface was reported, which was made responsible for the catalytic activity of Ag. We will present an in-situ surface x-ray diffraction study on the interaction of oxygen with the Ag(111) surface from UHV up to 2 bar, which will shed new light on the previously proposed structural model of the p(4x4) reconstruction and the stability diagram of the Ag(111)/O-system, which can be compared with theoretical studies. In addition High Resolution Core Level Spectroscopy was applied to get information about the binding geometry of the oxygen atoms. In the presentation several structural models of the p(4x4) reconstruction will be discussed.

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**In-situ investigations of $Ga_2O_3$ stability on the CoGa(100) surface** — •Alina Vlad[1], A. Stierle[1], I. Costina[1], P. Nolte[1], M. Delheusy[1], H. Dosch[1], E. Lundgren[2] und J. Andersen[2] — [1]Max-Planck Institut für Metallforschung, Heisenbergstraße 1, 70569 Stuttgart — [2]Department of Synchrotron Radiation Research, Institute of Physics, University of Lund, Box 118, SE-221 00 Lund, Sweden

The oxidation behavior of metallic alloy surfaces is of interest for fundamental studies, as well as for numerous applications in a variety of different fields such as heterogeneous catalysis, high temperature resistant coatings, microelectronics and gas sensors. As an example, the stability diagram of gallium oxide on CoGa(100) surface was determined. Surface X-ray Diffraction and High Resolution Core Level Spectroscopy experiments were performed at different temperatures in an oxygen partial pressure range up to 1 bar, following under which conditions the surface oxide starts to transforms into a bulk oxide. It was observed that at T < 350$^o$C, the formation of the bulk oxide is kinetically hindered, the surface gallium oxide layer being stable even at 1 bar oxygen. Oxidation at 650$^o$C and $2 \cdot 10^{-2}$ mbar oxygen leads to the formation of a smooth and well-ordered epitaxial bulk $Ga_2O_3$, whereas at temperatures higher than 750$^o$C the formation of the bulk oxide is accompanied by substrate faceting.

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**Reaction Kinetics on Oxide Supported Metal Nanoparticles: On the Role of Surface Oxygen, Subsurface Oxygen and Surface Oxides** — •Tobias Schalow, Mathias Laurin, Swetlana Schauermann, Björn Brandt, Jörg Libuda, and Hans-Joachim Freund — Fritz-Haber-Institut der MPG, Faradayweg 4-6, 14195 Berlin, Germany

The nature and formation of different oxygen species on iron-oxide supported Pd nanoparticles and their influence on catalytic reactions are investigated on well-defined supported model catalysts by combining molecular beam methods and various surface science techniques. IR reflection absorption spectroscopy of adsorbed CO is employed as a sensitive probe in order to identify the different adsorption sites on the metal particles and the support.

Remarkable differences are observed in comparison with previous studies on single crystal surfaces. For example it is found that the interaction with oxygen strongly depends on the particle size, involving e.g. reaction conditions under which the nanoparticle surface becomes only partially covered by surface-oxides. Moreover, the onset of surface-oxide formation is shown to be directly related to morphological transformations of the nanoparticles.