Dissolving Iron Oxide

Influence of correlation effects on structural and reactive properties of Hematite.

***M. Schüler, T. O. Wehling**, Institut für theoretische Physik/Bremen Center for Computational Material Science, Universität Bremen*

Kurzgefasst

- Iron oxide appears in many environmental and technological issues.
- Dissolution of oxides hosting strong electronic correlations is an outstanding computational problem: Hematite serves as model system.
- Ab-initio study of elementary dissolution processes.
- Combination of density functional theory and dynamical mean-field theory to cope with structural complexity and electronic correlations.

Understanding structural, reactive and thermodynamic properties of oxides containing strongly correlated electrons under environmental conditions is an outstanding problem. In cooperation with an experimental group (Prof. Lüttge, Uni Bremen), which performs large scale atomistic simulations and atom-scale microscopic structural analysis of dissolving surfaces in the lab, we study the model system Hematite. Hematite is the most stable iron oxide (Fe_2O_3) which has well defined surface facets making it handleable from the simulations point of view and therefore an ideal candidate for model studies.

Bulk hematite is studied intensively in the context of strong correlations, since density functional theory vastly underestimates magnetic moments of Fe and the spectral gap. Due to its environmental and technological importance, the surfaces of hematite are subject of many studies applying a multitude of density functional theory variants (e.g., hybrid functionals, DFT+U) which attempt to cure the underestimation of localization.

We will perform ab-initio simulations of elementary processes of dissolving Fe ions by calculating minimum energy path ways of ions leaving the surface from step and kink features of the surface (compare figure 1) which are known to be most important for desorption processes. An accurate description of the energetics of these elementary processes will serve as input for large scale kinetic Monte Carlo simulations done by our project partner.

We focus on the accurate and efficient description of correlation effects stemming from localized Fe d-electrons. We incorporate these correlation effects in a ab-initio density functional theory framework by using dynamical mean field theory (DMFT). It is well known that correlations are of paramount importance for accurately describing properties of Hematite in equilibrium. This will be even more important for studying non-equilibrium reaction pathways for dissolution processes due to the breaking of bonds.

For the density functional theory part we rely on the VASP package. To deal with correlation effects we use the dynamical mean-field theory with impurity solvers of different complexity. We use the computationally light-weight but more approximative exact diagonalization method implemented with MPI-parallelized ARPACK-ng [1]. As a benchmark for simple bulk and surface systems we choose the numerically exact but computationally costly continuous-time Quantum Monte Carlo method packaged in the triqs library [2].

For simulating kink and steps on the surface, we use super cells with several hundred atoms, which limits the choice of the impurity solver to exact diagonalization. Finding a pathway of Fe ions desorbing from the surface is a high-dimensional problem due to the structural complexity. We apply an approximation called nudged elastic band 3, which relies on defining a reaction pathway, which is fixed relative to a common coordinate system of a single Fe atom desorbing from the surface, while letting the surrounding atoms relax as a reaction to the distorted atom.

These calculations will enable us to characterize the elementary dissolution processes by their energy difference and involved energy barrier. These observables then define the dissolution kinetics of Hematite and our project partners can use these findings as an input for large scale kinetic Monte Carlo simulations 4.

WWW

http://www.itp.uni-bremen.de/ag-wehling/

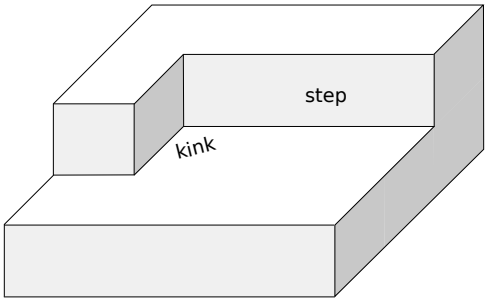

***Abbildung 1:** Sketch of surface features - a kink and a step - important for describing elementary desorption processes.*

Weitere Informationen

[1] https://github.com/Q-solvers/EDLib

[2] https://github.com/TRIQS/cthyb

[3] G. Mills, H. Jonsson, G. Schenter, *Surface Science* **324**, 305 (1995). doi:10.1016/0039-6028(94)00731-4

[4] B. Wehrli, *J. Colloid Interface Sci.* **132** 230 (1989) doi:10.1016/0021-9797(89)90232-4

Projektpartner

Working group of Prof. Andreas Lüttge der Uni Bremen, Graduate school Quantum mechanical materials modeling - QM^3