

Theoretical modelling of SFM contrast formation on the CeO₂ (111) surface

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The wide applications of cerium oxide have maintained general interest in studying its properties, particularly those of the most stable (111) surface. Scanning force microscopy (SFM) images[1,2] have demonstrated high quality atomic resolution on the surface. Unusually for an insulating material, study of Ceria surfaces with atomic force microscopes (AFMs) revealed a wealth of defects stable over a timespan of minutes, but clear interpretation remains absent, hindering efforts to study defects and reactions at the atomic scale.

Here, we use a multiscale simulation approach to investigate SFM contrast formation of this complex system. Using advanced first principles methods (LDA+U) [3], we establish a rigorous model of the surface and the most probable surface defects. This is then used as a reference for larger scale simulations using a combination of first principles and empirical methods. We study a variety of different oxide tips, including surface and ambient contaminants, and relate the resulting simulated images to experimental results. We show that water covered tips, or those with mobile oxygen defects may explain 'rare' images, but generally a more stable oxide model is required for standard contrast patterns.

We examined a variety of proposed surface defects – oxygen vacancies and interstitials, alkaline-earth metals as well as a variety of adsorbates, including molecular hydrogen. Potential defects were screened by calculating adsorption energies and surface diffusion barriers, which enabled us to determine which defects may have a sufficient site-occupancy time to be imaged by AFM and, hence, are candidates for the experimentally observed defects: These parameters are also fundamental in regards to the important ionic conduction properties and variable oxidation state of Ceria in catalytic systems.

Finally, we simulate the interaction of the most probable tip models with surface defects and adsorbates, and provide candidates to explain defect features seen in experiment.

[1] Y Namai, K Fukui, Y Iwasaw, J. Phys. Chem. B. **107**, 11666 (2003)

[2] S. Gritschneider, Y. Namai, Y. Iwasawa, M. Reichling, Nanotechnology, **16** S41 (2005)

[3] O. Begone, M. Alouani, P. Blochl, J. Hugel, Phys Rev B, **62**, 16392 (2000)