A Linear Response DFT + U(Fe) Study of the α-Fe_2O_3(0001) Surface

Xu Huang, Sai Kumar Ramadugu, and Sara E. Mason

Department of Chemistry, University of Iowa, Iowa City IA 52242

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Abstract

The surfaces of iron oxides are essential components to a wide range of environmental and technological processes such as contaminant adsorption and heterogeneous catalysis. However, even for the most stable and abundant iron oxides surface, hematite α-Fe_2O_3(0001), our understanding of the phase diagram is incomplete. DFT modeling using an $ab\ initio$ thermodynamics framework [1] has the potential to provide insight on the preferred surface structure as a function of T and p conditions, but these strongly correlated materials pose challenges to the methodology. Various predictions for the (0001) surface phase diagram have been summarized in the literature [2] and note that supposedly improved calculations using GGA + U actually lead to worsened stability predictions. Herein, we aim to identify methods for reliable theoretical predictions for the surface phase diagrams of strongly correlated materials by studying the α-Fe_2O_3(0001) surface. We focus on four terminations: -O3Fe, -O3Fe2, -Fe=O and -Fe2O3. Only the -O3Fe and -Fe2O3 terminations are reported experimentally, while GGA + U predicts the -Fe=O surface to be stable over a wide range of T and p_{O_2} conditions [3]. We use a linear response method to derive U values for chemically distinct Fe sites in each surface structure. We go on to show that this U(Fe) approach alone does not recover a realistic phase diagram. Further investigation shows that the hybridization between transition metal d- and oxygen p-orbital is strong enough to warrant an additional Coulomb correction, U^p, to balance their repulsion effects. Our results show that a U(Fe) + U^p approach does yield a reasonable α-Fe_2O_3(0001) phase diagram, as well as good predictions of the physical properties of hematite such as lattice constant, bulk modulus, and band gap. Finally, we demonstrate how the U(Fe) + U^p method impacts predictions for heterogeneous reactivity on the hematite surface.

References

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