

Bulk and key surface structures of hematite, magnetite, and goethite: A density functional theory study

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ABSTRACT

The iron oxides hematite, magnetite, and goethite were studied with density functional theory to establish a consistent set of structures for both the bulk mineral and key surfaces, characterize surface relaxation, and predict and test calculated scanning tunneling microscopy (STM) images. Spin-polarized, plane-wave pseudopotential calculations were carried out on recognized terminations of the hematite (0001) and goethite (010) surfaces and on two terminations of magnetite (111), derived from bulk structures optimized with the same simulation parameters. In the bulk, geometry optimizations having different spin configurations were compared, to find that even without an on-site Coulomb correction, the expected spin states were found to have lowest energy: antiferromagnetic in hematite and goethite and ferrimagnetic in magnetite. However, magnetite shows a conducting minority spin. All four surfaces showed structural relaxation consistent with previous work. The $\frac{1}{2}$ -monolayer termination (octahedral and tetrahedral Fe) of magnetite (111) underwent slightly more relaxation than the $\frac{1}{4}$ -monolayer termination, with consequently lower surface energy. A calculated STM image for $\frac{1}{4}$ -monolayer magnetite is compared to an observed image at positive bias and suggests that the tetrahedral Fe dominates the image. STM images are predicted for hematite and goethite to aid interpretation of future experimental work.

Keywords: Magnetite, hematite, goethite, surface, STM, electronic structure