Bulk and (001) surface Fe_3O_4: electronic properties and water adsorption

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Magnetite exhibits an interesting phase transition, called Verwey transition, at the critical temperature T_V of about 120 K. [1] Though numerous efforts have been devoted to the understanding of this interesting transition, up to now, it is still under debate whether a charge ordering and a band gap exist in magnetite above T_V. Besides the interesting Verwey transition, magnetite also shows wide applications in catalysis [2-4], spintronic devices [5], magnetic resonance imaging (MRI) and drug delivering [6]. In these applications, surfaces and their interaction with water play an important role. Here, we systematically investigate the electronic properties of cubic magnetite bulk and (001) surface using different methods based on density functional theory: DFT+U and hybrid functionals. The water adsorption thermodynamics on Fe_3O_4(001) surface was studied by hybrid functional calculations. Our results show that, for bulk magnetite, upon release of symmetry constraints on the electron density but not on the geometry, charge disproportionation (Fe^{2+}/Fe^{3+}) is observed, resulting in a band gap of around 0.2 eV at the Fermi level. This implies that the Verwey transition is probably a semiconductor-to-semiconductor transition and that the conductivity mechanism above T_V is small polaron hopping. The (001) surface shows a band gap (about 0.6 eV) larger than that in the bulk. A mixed adsorption mode of water is favorable on Fe_3O_4(001) surfaces at a high coverage, indicating that the cooperative effects between adjacent water molecules is important in the dissociation reaction. Our results give a clear understanding of the electronic structure of magnetite bulk [7] and (001) surface [8], as well as the water adsorption behavior on the (001) surface, which is fundamental for Fe_3O_4 nanomaterials' applications.

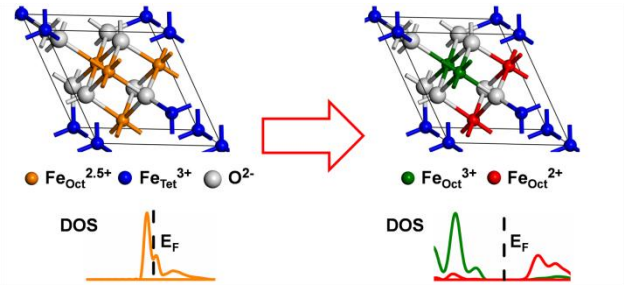

Figure 1. Symmetry breaking on the electron density induces a band gap in cubic magnetite.

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