Ab Initio Modeling of Transition-Metal Impurities in MgO

SERGEY V. LEVCHENKO, SEBASTIAN ALARCON VILLASECA, ALIAKSEI MAZHEIKA, MATTHIAS SCHEFFLER, Fritz-Haber-Institut der MPG, Berlin, DE — Fe- and Ni-doped MgO are promising materials for the catalytic conversion of methane and CO₂. However, theoretical studies of these materials are scarce. The self-interaction error (SIE) in approximate DFT leads to an incorrect description of the electron localization and hybridization between $d$ states of Ni or Fe and the oxide electronic bands. Replacing a fraction $\alpha$ of the (semi-)local exchange by the exact exchange reduces the SIE, but $\alpha$ remains a parameter depending on the target property. We explore the dependence of the formation energies of $\text{Ni}_\text{Mg}$ and $\text{Fe}_\text{Mg}$ substitutional defects in MgO on $\alpha$ in the Heyd-Scuseria-Ernzerhof hybrid functional (HSE), and compare the results to CCSD(T) embedded-cluster calculations. For $\text{Ni}_\text{Mg}$ defects HSE($\alpha = 0.3$) reproduces CCSD(T) formation energies and CO adsorption energies on $\text{Ni}_\text{Mg}$. However, $\alpha = 0.48$ is needed in the case of $\text{Fe}_\text{Mg}$. For both $\text{Ni}_\text{Mg}$ and $\text{Fe}_\text{Mg}$, $\alpha = 0.44$-0.50 satisfies best the exact DFT condition that the HOMO does not depend on occupation. Contrary to PBE and HSE06, HSE($\alpha \approx 0.5$) reproduces the experimentally observed $O_h \rightarrow D_{4h}$ (oblate) Jahn-Teller distortion for $\text{Fe}_\text{Mg}$.

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