DFT+U STUDIES INCLUDING SPIN-ORBIT COUPLING – A CASE STUDY FOR F-ELECTRONS IN PRASEODYMIUM-DOPED CERIA

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Key Words: Ceria, DFT+U, polaron, spin-orbit coupling

The mixed ionic electronic conductor Ceria exhibits not only a high concentration of Anti-Frenkel defects with high mobility, resulting in ionic conductivity of oxygen ions, but also enables an additional electronic conduction mechanism in form of small polaron hopping between the f-states of the cations. This promotes the reversible exchange of oxygen with the surrounding atmosphere and thus the oxygen storage capacity of the binary oxide $CeO_{2-\delta}$. The material has been established as a model system to describe both ionic and electronic transport processes in bulk material to gain deeper insights into the characteristics of polaron hopping and defect-defect interactions in mixed conductors. By introducing the redox active lanthanide Praseodymium to the Ceria host lattice, both electronic and ionic conductivities are increased in temperature and oxygen partial pressure regions where pure Ceria lacks of good performance. The redox properties of Pr-ions, shifting the equilibrium from Pr^{4+} to Pr^{3+} and forming oxygen vacancies, is key to understand the additional contribution to the total electrical conductivity and the enhanced catalytic activity. So far in literature, only the effect of Pr^{3+}-ions in the Ceria host lattice has been investigated by means of density functional theory. To complement these investigations with the impact of Pr-ions in both oxidation states, density functional theory was applied, including a Hubbard-U correction for electronic correlation in the f-states of both cations in $Ce_{1-x}Pr_xO_{2-\delta}$. A systematic study of spin polarization, antiferromagnetic coupling and spin-orbit interaction of the unpaired 4f-electrons was performed to investigate the influence of magnetic interactions on the description of localized polarons. The preferred localization of the excess electrons on Pr- rather than Ce-ions as well as the defect formation and configuration is discussed by analyzing the resulting energy levels and densities of states of the investigated ideal and defective super cells.