

DFT+U modeling of oxygen point defects in uranium dioxide: imposing and monitoring occupation matrices

Boris Dorado¹, Michel Freyss¹, Gérald Jomard² and Marjorie Bertolus¹

¹ CEA, DEN, DEC, Centre de Cadarache, 13108 Saint Paul Lez Durance Cedex, France
e-mail: boris.dorado@cea.fr

² CEA, DAM, DIF, F-91297 Arpajon, France

Despite the numerous *ab initio* studies performed on uranium dioxide, the accurate description of this system remains challenging. Uranium dioxide UO₂ attracts much interest due to its technological value as the standard nuclear fuel for pressurized water reactors. Within the Density Functional Theory (DFT) formalism, the strong correlations between the 5*f* electrons of uranium require a particular care in their description. Several approximations of the DFT were thus developed during the last decade in order to improve the treatment of these electrons, such as hybrid functionals, the self-interaction correction or the DFT+U formalism. The DFT+U approximation has been widely used to investigate the structural and electronic properties of UO₂, as well as the stability and the behavior of point defects which are created during in-pile irradiation. Numerous discrepancies, however, are observed between the formation energies of point defects obtained by the different groups using the DFT+U method. It has been shown lately on cerium,¹ as well as on plutonium oxides,² that finding the ground state of a system in the DFT+U formalism is difficult because of the existence of numerous energy minima (metastable states).^{3,4} In a previous work,⁵ we showed that in order to get as close as possible to the ground state, it is necessary to impose initial occupation matrices and monitor them, as well as to break the crystal symmetry.

In the present study, we report our results regarding the stability of UO_{2+x}. In order to ensure that calculations reach states with the lowest possible energy, we have switched off all symmetries in the supercells and imposed and monitored occupation matrices during the calculations. These are to our knowledge the first DFT+U calculations of point defects using this method developed on perfect crystals. The results prove that an accurate modeling of the defective and perfect supercells is required to get reliable point defect formation energies. We also show that imposing and monitoring the occupation matrices is an efficient and reliable method to get as close to the ground state as possible. However, this method becomes intractable for large defective supercells. The number of possible initial states increases dramatically, and finding appropriate initial electronic occupations would require a very thorough *a priori* knowledge of the underlying physics of the defective system. We therefore describe an alternative way to reach states with the lowest total energies. Finally, we report the formation energies of the oxygen single interstitial and vacancy obtained, and interpret our results in the light of available experimental observations.

References

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