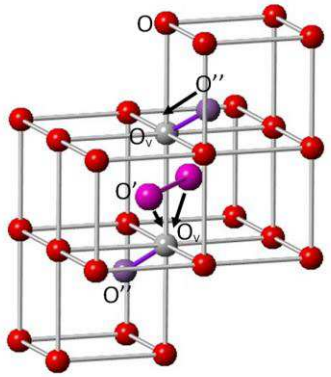
Dynamics of oxygen defect cluster and spatial and temporal correlation with 5f electron in uraninite (UO_{2+x})

JIANWEI WANG [1]

[1] Department of Geology and Geophysicsy, Louisiana State University, Baton Rouge, LA, United States. jianwei@lsu.edu

Determination of the local configuration of interacting defects in a crystalline, periodic solid is problematic because such defects typically only have a local order but not long-range periodicity. Uranium dioxide, the primary fuel for fission reactors, exists in hyperstoichiometric form, UO_{2+x}. Those excess oxygen atoms occur as interstitial defects, and these defects are not random but rather partially ordered. The widely-accepted model to date, the Willis 2:2:2 defect cluster based on neutron diffraction, cannot be reconciled with the first-principles molecular dynamics simulations present here. We demonstrate that the Willis cluster is a fair representation of avarge structure of the numerical ratio of different interstitial O atoms; however, the model does not represent the actual local configuration. The simulations show that the average structure of UO_{2+x} involves a combination of defect structures including split di-interstitial, di-interstitial, mono-interstitial, and the Willis cluster, and the latter is revealed to be a transition state that provides for the fast diffusion of the defect cluster. The 5f electrons, and U^{5+} species are partially delocalized and coupled with the lattice dyanmcis, but decoupled with locations of excess oxygen atoms. The results provide new insights in differentiating the average structure from the local configuration of defects in a solid and the transport properties of UO_{2+x} [1].



Configuration of Willis 2:2:2 defect cluster with the arrows showing its instability. The O_v is oxygen vacancy, O' and O" are oxygen interstitials in [110] and [111] directions.

[1] Wang, J., Ewing, R.C. and Becker, U. (2014) Average structure and local configuration of excess oxygen in UO_{2+x}. Scientific Reports 4, 4216.