First principles study of noble gas impurities and defects in UO2

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There is a strong need to better understand the mechanisms of nuclear fuel swelling in uranium dioxide (UO_2) due to formation of fission product gases. Noble gases have little solubility in UO_2 and prefer to coalesce, forming gaseous bubbles. Using density functional theory (DFT+U) calculations, we have explored the energetics of noble gases (He, Ne, Ar, Kr, Xe) in UO_2, Schottky defects in UO_2, and the interaction between these defects. We find: (i) The noble gas atoms show a strong size dependence of the incorporation energy, with the energy of the larger impurities (such as Xe) showing the larger incorporation energies. (ii) The energetics of the Schottky defect in three different geometries shows that the preferred geometry is not simply driven by electrostatic effects. (iii) The energetics of each of the noble gas atoms incorporated in Schottky defects show a strong favorable binding, due to strain relief. (iv) For Ar, Kr, and Xe, the binding energy of a noble gas impurity with the Schottky defect is larger than the energy required to form a Schottky defect, thereby providing an energetic pathway for the "spontaneous" formation of these defects. (v) From our calculations, we have constructed a simple model of the critical number of noble gas atoms required to form a bubble.

When performing DFT calculations, we use the "+U" methodology to achieve the correct insulating behavior for UO_2. DFT+U is not guaranteed to converge to the global energy minimum for UO_2: it can also converge to metastable orbital occupations. We propose a systematic method for finding a low energy orbital occupation for the DFT+U calculation.