First principles calculations on the influence of defects on the electronic structure of copper-hexacyanoferrate

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Copper hexacyanoferrate (Cu-HCF), a Prussian blue analog (PBA), has an open channel structure which has the ability to sequester radioactive cesium from nuclear waste. For computational convenience, perfect Cu-HCF structures are generally analyzed. However, in reality, Cu-HCF often displays a defected structures, incorporating $Fe(CN)_6$ vacancies and water molecules. These defects can have notable influence on electronic structures of Cu-HCF using Density Functional Theory (DFT). Here, we determine the electronic structure of defective Cu-HCF and analyze the thermodynamics of cesium sequestration. Specifically, DFT is used to analyze perfect Cu-HCF structure, Cu-HCF with one $Fe(CN)_6$ vacancy, one water molecule and one cesium ions in its structure. GGA-PBE functional is used in all calculations and DFT+U is applied. The preliminary results show that the Fermi level of defective structure decreases by 0.7eV relative to the undefected system. Incorporation of Cs, is found to increase the structural stability by connecting cyanide group and metal ions (Cu ions and Fe ions).

Keywords: Cu-HCF, Cesium sequestration, Density functional theory, DFT+U, Density of states, Thermodynamics