Phase stability of ZrH$_{1.5}$ - a DFT study

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Due to its low thermal neutron capture cross section and good corrosion resistance, zirconium-based alloys are commonly employed as fuel cladding material in the core of nuclear power reactors. While in service, the fuel cladding material is in contact with water, which promotes the oxidation of Zr. This process releases free hydrogen, of which a portion enters the alloy and gives rise to the formation of brittle hydrides. This can have a detrimental effect on the integrity and the longevity of the material. Among the zirconium dihydrides (ZrH$_x$, $1.5 \leq x \leq 2$), the face centered tetragonal ϵ ($c < a$) and the cubic fluorite-type δ phases are known to exist. The $\delta \rightarrow \epsilon$ phase transition is known to depend on the hydrogen concentration, where ϵ is preferred at high hydrogen concentrations and δ occurs at lower hydrogen content. At which concentration and under what conditions the transition occurs is not well established and there is much discrepancy among the experimental observations.

The purpose of this work is to investigate the thermal influence on the phase stability of ZrH$_{1.5}$ using quantum mechanical density functional theory (DFT). The free energy is studied for different temperatures based on the quasi-harmonic approximation using the phonon density of states and the electron density of states. All DFT simulations are performed using the QUANTUM-ESPRESSO package, which is a plane wave based DFT package. For the electron-ion interaction we have used ultrasoft pseudopotentials of the Vanderbilt type. For Zr a pseudopotential that considers 4d^{2}5s^2 valence electrons and the 4s^{2}4p^6 semi-core states in the valence band was used while only the 1s^1 electron is treated for H. The employed exchange correlation functional is that of Perdew, Burke and Ernzerhof (PBE) within the framework of the generalized gradient approximation.

We have evaluated the difference in free energy for the δ and ϵ phases for the temperature range 20-500 K in Fig. 1. The tetragonal structure has the lowest free energy for low temperatures. However, if the temperature is increased, at 229 K the δ phase becomes more stable. This implies that a phase transition occurs at that temperature and it explains why the cubic δ phase is observed experimentally at room temperature, despite the low formation energy of the tetragonal ϵ phase.
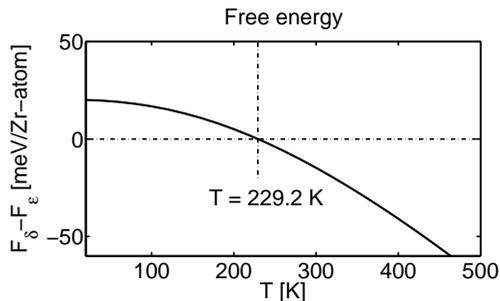

Figure 1: Difference in free energy for δ (cubic) and ϵ (tetragonal, $c < a$) hydrides for different temperatures. There is a phase transition at 229 K where the tetragonal phase transforms into cubic.