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Electronic Structure and Electric Field Gradients of HfV_2 and ZrV_2 Intermetallic Compounds – Pure, Doped with Tantalum and Cadmium, and Their Hydrides

Doctoral Dissertation

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Abstract

This doctoral dissertation consists of density functional theory based calculations, conducted with Wien2k computational code, which implements full-potential linearized augmented plane wave plus local orbital method. The dissertation is divided into two segments. First part addresses the local structure, electronic properties, and electric field gradients of pure and doped intermetallic compounds HfV_2 and ZrV_2. Three temperature modifications of HfV_2 – cubic, tetragonal and orthorhombic – and only one, cubic, modification of ZrV_2 were investigated. After the analysis of electronic structure and electric field gradients of pure intermetallic compounds, crystal lattices were doped with impurities tantalum or cadmium. Electric field gradients were calculated on the atomic site of the inserted probe-atoms, and results were compared with the existing experimental data from the time differential perturbed angular correlation and nuclear magnetic resonance measurements. This comparison enabled us to determine the lattice site occupied by impurities in every examined structure, exact space group, and crystallographic positions of hafnium and vanadium in the low-temperature orthorhombic modification of HfV_2. In addition, we have confirmed that the measured, nonzero electric field gradient in the tantalum-doped cubic HfV_2 structure originates from the displacement of tantalum from its equilibrium position in the cubic environment.

In the second part of the thesis, first principles calculations of the electronic structure, formation enthalpies, and electric field gradients in the cubic hydride HfV_2H_x are presented. In cubic, C15 Laves phases, hydrogen can occupy three possible interstitial positions: 96*g*, 32*e*, and 8b. To investigate the change in electronic structure before and after hydrogenation, and effects that hydrogen has on the unit cell, electric field gradients induced by this atom on the surrounding vanadium were calculated, and compared with the existing nuclear magnetic resonance measurements. By this comparison, distribution of hydrogen atoms in the crystal lattice, as well as the occupation of possible interstitials was studied. By calculating the formation enthalpies of every formed hydride, stability changes that occurred during the hydrogen insertion were investigated. In addition to this, origin of the electric field gradient on vanadium in HfV_2 hydrides was determined.