

Theoretical investigation of hydrides based on CuAl₂-type materials.

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The intermetallic compounds Zr₂Fe, Zr₂Co, Zr₂Ni and Th₂Al with CuAl₂-type structure are known to form stable hydrides. Zr₂M (M = Fe, Co) form saturated deuterides (Zr₂MD₅) with essentially the same structure as the Zr₂M host, but the symmetry is changed from *I4/mcm* to *P4/ncc* with an ordered occupation of D in 16 of 32 Zr₃M tetrahedral intersites of structure¹. In contrast, Th₂AlH₄ and Zr₂NiH_{4.74} are formed without any change in the symmetry of the parent structure. Zr based hydrides obey the 2 Å rule, but Th₂AlH₄ does not. It is interesting to note that *c/a* of Zr₂Fe and Zr₂Co decreases on hydrogenation but for Th₂Al the ratio increases from 0.7695 to 0.8543. In Th₂AlH₄ and Zr₂FeH₅ the experimentally observed volume expansion during the hydrogenation is highly anisotropic. There are no theoretical studies available for these materials. As studies on the nature of the chemical bonding in hydrides and nonhydrides often provide better understanding about the effect of hydrogenation on anisotropy and symmetry changes, we have studied the electronic structure, bonding and cohesive properties of Th₂Al and Th₂AlH₄ using the accurate full-potential linearized-augmented-plane –wave (FP-LAPW) method.

Powder neutron diffraction (PND) studies have given two different H-H separations in Th₂AlH₄. Bergsma *et al.* report 1.79 Å, while a recent high resolution PND study³ gave a separation (1.97) closer to the expected 2.1 Å. So far no theoretical attempt has been made to solve this discrepancy. We have made structural optimizations by force minimization as well as total energy minimization calculations and found an H-H shortest separation for 1.94 Å is in good agreement with the latter experimental value. Owing to the anisotropy of the bonding nature the calculated interatomic H-H distance is different along *a* and *c*. Our calculation predicts strong covalent bonding between the hydrogens along *a* and repulsive interaction along *c* (where the next calculated shortest separation is 2.34 Å). This is the main cause of the anisotropy in the volume expansion during hydrogenation. The repulsed H is directly bonded to Th, hence H-Th-H form like dumb-bell shaped units. Our charge density and crystal orbital Hamiltonian population analyses revealed that the Th-H bond is stronger than the H-H bonds and other localized bonds in this structure. The formation of strongly bonded ThH₂ sub units in the Th₂AlH₄ structures makes repulsive interaction between the H atoms smaller and this is the precise reason why the 2 Å rule is violated. We also found a correlation between the changes in *c* and the structural stability of these phases, when *c/a* < 0.825 the symmetry changes from *I4/mcm* to *P4/ncc* on hydrogenation, whereas when *c/a* > 0.825 the crystal symmetry is not affected.

References

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