Deuterium Site Occupancies in $Ce_2Ni_7D_4$ and Comparison with $CeNi_3D_{2.8}$

Y. Filinchuk
Laboratory of Crystallography, University of Geneva, Switzerland;
Current: SNBL at ESRF, Grenoble, France

K. Yvon
Laboratory of Crystallography, University of Geneva, Switzerland

Ce_2Ni_7 and $CeNi_3$ have closely related but distinctly different crystal structures in which $CaCu_5$-type and $MgZn_2$-type slabs alternate along the hexagonal axes. Both compounds react easily with hydrogen and form so-called "interstitial" hydrides of which one has been structurally characterized ($CeNi_3D_{2.8}$ [1]). In spite of the structural differences their hydrogen equilibrium pressures at 50°C do not much differ: 0.2 bar for $Ce_2Ni_7H_x$ and 0.1 bar for $CeNi_3H_x$. In contrast to the hexagonal $La_2Ni_7D_{6.5}$ analogue [2] $Ce_2Ni_7D_4$ shows an orthorhombic distortion. A comparison with $CeNi_3D_{2.8}$ shows that in both compounds deuterium enters only the $MgZn_2$-type slabs, resulting in an anomalous expansions along the hexagonal axes (~21% for $Ce_2Ni_7D_4$, ~30% for $CeNi_3D_{2.8}$), while their basal planes remain nearly unchanged. Both deuterides dispay Ni atoms having deformed tetrahedral D atom configurations: Ni-D bond lengths and D-Ni-D bond angles range 1.52-1.95 Å and 74-127°, respectively. These findings not only provide further evidence for directional bonding effects in hydrides that are traditionally considered as "interstitial" [3], but also suggest that the thermal stability of metal hydrides having composite crystal structures can be correlated with metal-hydrogen bond formation/breaking in specific structural units.

[1] V. A. Yartys et al., J. Alloys Compd. 356-357 (2003) 109.
[2] V. A. Yartys et al., J. Alloys Compd. 408-412 (2006) 273.
[3] Y. E. Filinchuk et al., J. Alloys Compd. 413 (2006) 106.