Deuterium Site Occupancies in Ce$_2$Ni$_7$D$_4$ and Comparison with CeNi$_3$D$_{2.8}$

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Ce$_2$Ni$_7$ 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$_3$D$_{2.8}$ [1]). In spite of the structural differences their hydrogen equilibrium pressures at 50°C do not much differ: 0.2 bar for Ce$_2$Ni$_7$H$_x$ and 0.1 bar for CeNi$_3$H$_x$. In contrast to the hexagonal La$_2$Ni$_7$D$_{6.5}$ analogue [2] Ce$_2$Ni$_7$D$_4$ shows an orthorhombic distortion. A comparison with CeNi$_3$D$_{2.8}$ 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$_2$Ni$_7$D$_4$, ~30% for CeNi$_3$D$_{2.8}$), while their basal planes remain nearly unchanged. Both deuterides display 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.