Deuterium site occupancies in $Ce_2Ni_7D_{\sim 4}$ and comparison with $CeNi_3D_{2.8}$

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Abstract

The deuterium atoms in both $Ce_2Ni_7D_{\sim 4}$ and $CeNi_3D_{2.8}$ occupy interstices in the $CeNi_2$ structural slabs only, while the interstices in the bulk of the $CeNi_5$ slabs remain empty. A considerable fraction of these deuterium atoms surround nickel in deformed tetrahedral configurations reminiscent of the $[NiH_4]^{4-}$ complexes found in complex metal hydrides, like Mg_2NiH_4 and $LaMg_2NiH_7$. The hydrogen equilibrium pressures of both systems are similar (0.1–0.2 bar at 50 °C). These findings not only provide further evidence for directional bonding effects in hydrides that are traditionally considered as "interstitial", but also suggest that the thermal stability of metal hydrides having composite crystal structures is correlated with metal-hydrogen bond formation/breaking in specific structural units.
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1. Introduction

Metal hydrides based on nickel-rich intermetallic compounds of composition R_2Ni_7 and RNi_3 (R, Rare earth) and their substitution derivatives are of renewed interest because their properties in rechargeable metal hydride batteries are superior to those of their congeners of composition RNi_5 [1]. In a previous paper we have reported structure data for the cerium-nickel deuteride $Ce_2Ni_7D_{\sim 4}$ [2]. Deuterium was found to occupy interstices in the $CeNi_2$ slabs only, while those in the bulk of the $CeNi_5$ slabs remain empty. Interestingly, a significant fraction of these deuterium atoms was bonded in tetrahedral configurations around nickel, similar to those in nickel based complex metal hydrides such as Mg_2NiH_4 and $LaMg_2NiH_7$ [3]. These site preferences cannot be explained by the interstitial concept usually applied to rationalize hydrogen atom distributions in such hydrides.

The purpose of this paper is to investigate the nickel atom environment in RNi_2 structure slabs of other hydrides and to compare the hydrogen equilibrium pressures of the corresponding metal-hydrogen systems. It will be shown that quite a few

compounds display tetrahedral D atom configurations around nickel in RNi_2 structure slabs, and that the hydrogen equilibrium pressures of the corresponding hydrides do not much differ.

2. Composite crystal structure, lattice distortion and hydrogen equilibrium pressure

The intermetallic compounds RNi_3 and R_2Ni_7 have closely related but significantly different crystal structures. Both are built up by $MgCu_2$-type and $CaCu_5$-type slabs that correspond to structural fragments of RNi_2 and RNi_5, respectively, and are stacked along the hexagonal axes. However, the slab thickness in these composite crystal structures differs. Ce_2Ni_7, for example, contains two sorts of alternating slabs, one consisting of double layers of $CeNi_5$ and the other of double layers of $CeNi_2$ [4]. $CeNi_3$ has the same building principle except that it contains single, instead of double, layers in the $CeNi_5$ slabs [5]. Both compounds react easily with hydrogen and form so-called "interstitial" hydrides. Those which have been structurally fully characterized are deuterides of composition $Ce_2Ni_7D_{4.1}$ [2] and $CeNi_3D_{2.8}$ [6]. A striking aspect of the corresponding hydrides is their hydrogen equilibrium pressures. For $CeNi_3H_{2.8}$ and $Ce_2Ni_7H_4$, these pressures were reported to be, respectively, 0.1 bar and 0.2 at 50 °C [7]. Such small differences are surprising

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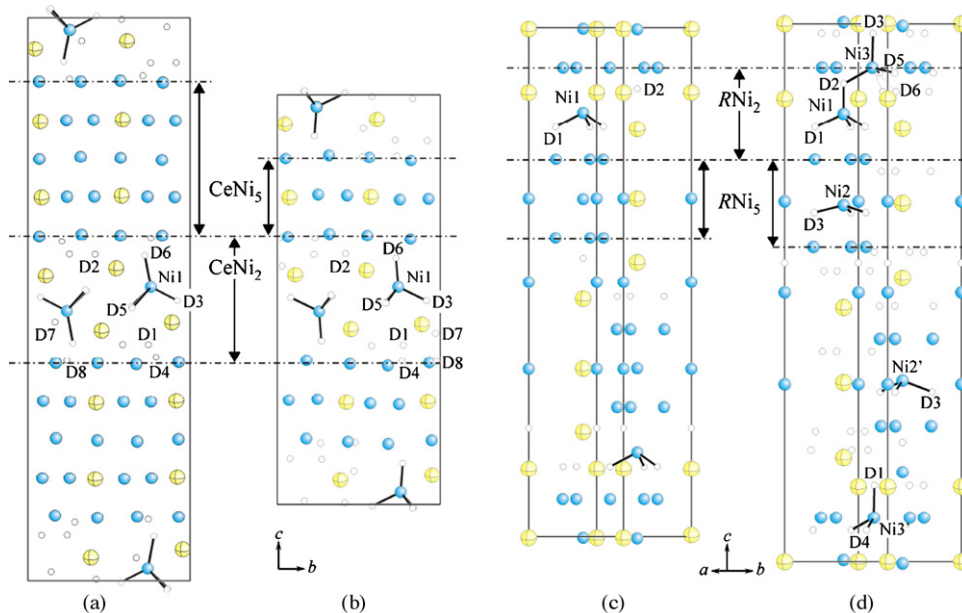
Fig. 1. Crystal structure of $Ce_2Ni_7D_4$ (a), $CeNi_3D_{2.8}$ (b), β_1–$HoNi_3D_{1.3}$ (c) and γ–$ErNi_3D_{3.8}$ (d). Ce: big ellipsoids (yellow), Ni: smaller spheres (blue), D: very small circles (white). Atom labels and Ni–D bonds (black lines) are shown for all D and Ni atoms participating in tetrahedral NiD_4 and pyramidal NiD_3 configurations. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of the article.)

in view of the significantly different chemical compositions and crystal structures involved.

Another striking aspect of these hydrides is their lattice expansion and lattice distortion. Both hydrides show anomalously large expansions along the hexagonal axes of the respective alloys ($\Delta c/c \sim 21\%$ for $Ce_2Ni_7D_4$, $\sim 30\%$ for $CeNi_3D_{2.8}$), while their basal planes remain nearly unchanged. Interestingly, the expansion of $Ce_2Ni_7D_4$ is similar to that of its lanthanum analogue $La_2Ni_7D_{6.5}$ ($\Delta c/c \sim 20\%$ [8]), therefore it is unlikely to be the result of a possible valence change of the lanthanide atoms. The fact that the expansion is very anisotropic is presumably due to the hydrogen-inactive $CeNi_5$ slabs in the structure that "block" its expansion in the basal plane. Furthermore, in contrast to the lanthanum system La_2Ni_7–H which appears to remain hexagonal ($La_2Ni_7D_{6.5}$: space group $P6_3/mmc$ [8]), the cerium system undergoes various degrees of orthorhombic lattice distortions, $\delta = (b/\sqrt{3} - a)/a$. Hydrogen pressures of ~ 30 bar, for example, stabilize a phase having a negative distortion ($\delta < 0$), while decreasing the pressure leads to another phase having a positive distortion ($\delta > 0$) [2]. Both phases are nearly isostructural, and have the same space group symmetry and nearly the same composition. The origin of these anisotropic expansion and lattice distortions cannot be explained by simple atomic size arguments.

3. Deuterium atom distribution and tetrahedral nickel coordination

In $Ce_2Ni_7D_4$ only 5 out of 11 Ni sites have D atoms among their nearest neighbors. As shown in Fig. 1, these D atoms are located in the $CeNi_2$ structural slabs only (or at the boundary between the $CeNi_2$ and $CeNi_5$ slabs), while the bulk of the $CeNi_5$ slabs remains empty. A significant fraction of these D

atoms ($\sim 50\%$ of the total D-content) surrounds nickel (Ni1) in fully occupied deformed tetrahedral configurations (D3, $2 \times D5$, D6) displaying Ni–D bond lengths and D–Ni–D bond angles in the ranges 1.56–1.89 Å and 77–128°, respectively. These configurations are presumably at the origin of the very strong and anisotropic expansion of the $CeNi_2$ slabs ($\sim 60\%$, as compared to $\sim 21\%$ average expansion of the structure along the stacking direction c), and the creation of new interstices in the $CeNi_2$ slab that are occupied by deuterium. Clearly, these hydrogen induced structural changes cannot be explained by the interstitial concept alone but suggest that the rigid nature of the tetrahedral H atom configurations around nickel plays a major role. In fact, these configurations are reminiscent of the tetrahedral $[NiH_4]^{4-}$ complexes found in complex transition metal hydrides such as Mg_2NiH_4 and $LaMg_2NiH_7$ (for a review see Ref. [9]). The latter derive both from stable intermetallic compounds (Mg_2Ni and $LaMg_2Ni$) that undergo reconstructions and/or distortions of their metal atom substructure due to the formation of such tetrahedral complexes. The $LaMg_2Ni$–H system is of particular interest due to its metal-insulator transition that accompanies the formation of the $[NiH_4]^{4-}$ complexes [3].

Similar H-site preferences are also observed for $CeNi_3H_{2.8}$. As shown in Fig. 1b, the D atoms in the deuteride are located in the $CeNi_2$ structural slabs (or at the boundary between the $CeNi_2$ and $CeNi_5$ slabs), while the bulk of the $CeNi_5$ slabs remains empty. As in $Ce_2Ni_7D_4$ a significant fraction of these D atoms ($\sim 50\%$ of the total D-content) surrounds nickel in deformed tetrahedral configurations with fully occupied D sites. The Ni–D bond lengths and D–Ni–D bond angles cover the ranges 1.50–1.65 Å and 91–122°, respectively. As $Ce_2Ni_7D_4$ the structure of $CeNi_3H_{2.8}$ is orthorhombically distorted compared to the structure of the parent alloy. A hydrogenation induced symmetry breaking due to the formation of Ni–H species also

occurs in the closely related holmium and erbium systems $HoNi_3$–H [10] and $ErNi_3$–H [11]. Their hydrogen/deuterium free structures are centrosymmetric and made up by rhombohedrally stacked RNi_2/RNi_5 slabs (R = Ho, Er). As shown in Fig. 1c, they form deuterium-poor non-centrosymmetric β_1-phases at low deuterium pressure, and their RNi_2 slabs contain ordered pyramidal D atom configurations around nickel. The shape and a rigid nature of these configurations are presumably responsible for the loss of the inversion symmetry. At high deuterium pressures evidence for the formation of tetrahedral NiD_4 configurations has been obtained at least for the $ErNi_3$–D_2 system [11]. As in the cerium compounds, the main structure expansion during deuteration occurs in the RNi_2 slabs and is directed along the c axis. Although the expansion is relatively small ($\Delta c/c \sim 14\%$), the structural changes are very similar to those observed in $Ce_2Ni_7D_4$ and $CeNi_3D_{2.8}$, especially at low D contents of ~ 1.3 D-atoms per RNi_3 unit. In the more D rich high-pressure γ-$ErNi_3D_{3.8}$ phase the tetrahedral NiD_4 configurations do not break the symmetry further, but order in a parallel orientation (Fig. 1d). Note that the tetrahedral NiD_4 configurations in $Ce_2Ni_7D_4$ and $CeNi_3D_{2.8}$ order in anti-parallel orientations (Fig. 1a and b). As to the RNi_5 slabs in this series they tend to become occupied by deuterium only at relatively high pressures, as shown by γ-$ErNi_3D_{3.8}$ (Fig. 1d).

Finally, it is worth mentioning that the symmetry and D atom distributions in the cobalt analogues differ significantly from those in the nickel analogues. The $ErCo_3$–D system, for example, is centrosymmetric and shows disordered octahedral rather than ordered tetrahedral D atom configurations around transition (T) metal [12]. Locally, however, the configurations around cobalt could be square-pyramidal such as those of the $[CoD_5]^{4-}$ complexes found in Mg_2CoD_5 [9]. This lends further support to the idea that the hydrogen atom distributions in these types of metal-hydrogen systems are governed by electronic factors rather than by atomic size effects, i.e. the T metals tend to form relatively rigid metal-hydrogen moieties whose geometry depends mainly on the nature of the T element and less on atomic size effects.

In conclusion, hydrogen in R_2Ni_7–H and RNi_3–H systems cannot simply be considered as a sphere which has a certain radius but is otherwise stereochemically inactive. It should be rather considered as a ligand capable of forming transition metal-hydrogen moieties that govern major structural changes during hydrogenation. In this context it is worth mentioning that the equilibrium pressures for the $CeNi_3$–H and Ce_2Ni_7–H systems (0.1–0.2 bar at 50 °C) and some other RNi_3–H and R_2Ni_7–H systems are very similar. Binary $LaNi_3$, $PrNi_3$ and $NdNi_3$, for example, readily absorb hydrogen at pressures below 1 bar at room temperature [13], while ternary $La_{1/3}Y_{2/3}Ni_3$ and $Ce_{1/3}Y_{2/3}Ni_3$ have hydrogen equilibrium pressures of 0.1–0.12 bar at 25 °C [14]. The La_2Ni_7–H system has an equilibrium pressure of 0.6 bar at 25 °C [15]. Whether or not the thermal stability of hydrides in such systems can be correlated with metal-hydrogen bond formation/breaking in specific structural units needs to be further investigated.

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