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NOTES

Reduction of Hydrogen Solubility by Alloying RNi_5 Systems with Al*

$LaNi_5$ has been extensively studied because of its ability to absorb and release large quantities of hydrogen (*1*). As a practical hydrogen storage material it suffers from high cost and weight. To correct these deficiencies ternaries with Al partially replacing Ni, e.g., $LaNi_4Al$, are being thoroughly investigated (*2–4*). $LaNi_5$ absorbs hydrogen at room temperature at about 5 MPa to form $LaNi_5H_{6.9}$ (*5*), whereas the system in which 20% of the Ni atoms are replaced by Al absorbs hydrogen to a much smaller extent (*2*), $LaNi_4AlH_{4.3}$. At the same time the plateau pressure decreases sharply from about 0.2 MPa for $LaNi_5$ to $<10^{-4}$ MPa for the Al-containing system. The purpose of this note is to offer an explanation for these rather striking changes.

Lundin *et al.* have shown (*6*) that the plateau pressure is inversely related to the size of the interstitial hole in which the hydrogen is situated in the lattice. The reduced plateau pressure for hydrogenated RNi_4Al compared to that of RNi_5 appears to be a simple consequence of the enlargement in the lattice when Ni is replaced by Al. This substitution produces an increase (*2*) in the unit cell size by about 5%. A lower hydrogen vapor pressure is expected. Lundin *et al.* find that an enlargement in tetrahedral hole size by 4% in the RNi_5 series lowers the free energy by about 10 kJ per mole of H. Thus, with the lattice enlargement produced by replacement of Ni with Al a reduction of pressure by some four orders of magnitude is expected, and this is borne out by experiment (*2*).

The reduction in hydrogen-escaping tendency when RNi_4Al is formed from RNi_5 implies greater stability for the hydride of the former material. This in turn would suggest, on the basis of superficial analysis, that the hydrogen capacity for the ternary material should be greater; the stabler hydride system would take on more hydrogen. This is not observed. It is thus clear that the reduction in capacity is a more subtle effect than the reduction in plateau pressure.

The structure of hydrided $LaNi_5$ has recently been determined (*7–9*). Essential features of the structure are represented in Fig. 1. Shown there are slices through the unit cell perpendicular to the *c* axis and at $Z = 0$ and $\frac{1}{2}$. Hydrogen (actually deuterium) occupies completely the octahedral sites at $Z = 0$ (2 La and 4 Ni neighbors). It statistically occupies the tetrahedral sites at $Z = \frac{1}{2}$ (2 La and 2 Ni near neighbors). There are twice as many tetrahedral sites as there are hydrogen atoms to fill them. The tetrahedral sites at $Z = \frac{1}{4}$ and $\frac{3}{4}$, which have only Ni near neighbors, are unoccupied. Actually, the hydrogen in the occupied sites is slightly displaced from the ideal tetrahedral or octahedral site, but these displacements are small and unimportant for the present consideration, and will be ignored.

There is strong chemical affinity between hydrogen and a rare earth, *R*. This is evident from the fact that the hydrides RH_3 are strongly exothermally formed from the ele-

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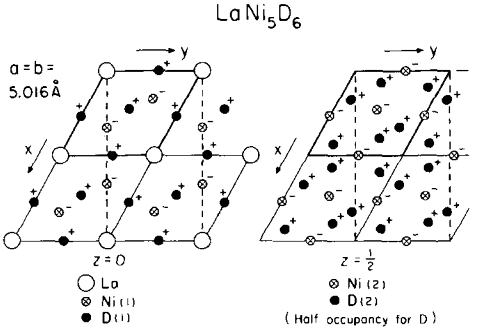

FIG. 1. Atomic arrangement in $LaNi_5D_6$ at the $Z = 0$ and $Z = \frac{1}{2}$ planes. The plusses and minuses indicate small displacements of atoms in the Z direction.

ments (*10*). Bonding in these hydrides comes close to being ionic. The hydrogen 1*s* electron is contained in a band composed of antibonding orbitals (*11*) that are lowered in energy below the conduction band of the host metal by the Madelung interaction. Thus to a first approximation the R–H bond can be considered ionic (*12*). It is proposed that this bonding is carried over into the hydrogenated RNi_5 and RNi_4Al systems. In these cases, in contrast with RH_3, the systems are conducting and a screened coulomb potential is involved. Accordingly, nearest-neighbor R–H interactions will be by far the strongest.

Ni also bonds to hydrogen. It forms a nickel hydride. Moreover, on the surface of $LaNi_5$, which consists of $La(OH)_3$ and Ni (*13*), H_2/D_2 exchange occurs at a very rapid rate (*14*). This involves cleaving the hydrogen and deuterium bonds, and this is accomplished because of the moderately strong (compared with the R–H bond strength) Ni–H interaction. Thus when H is in the octahedral or tetrahedral site it is bonded to its six or four near neighbors, two of which are R. It is proposed that when Ni is replaced by Al, the sites immediately adjacent become very energetically unfavorable for hydrogen, so unfavorable that they are not populated. With that simple idea the decrease in hydrogen capacity of RNi_4Al compared to RNi_5 can be readily understood. By counting the number of sites which are rendered ineffective it is possible to establish the hydrogen capacity of the RNi_4Al systems.

Achard *et al.* (*15*) and Mendelsohn *et al.* (*16*) have shown that in the $LaNi_{5-x}Al_x$ system Al substitutes randomly for Ni at the 3*g* position, i.e., at the planes lying at $Z = \frac{1}{2}$ in Fig. 1. Consider a volume element shown by the dashed lines in Fig. 1. It contains $R_2Ni_{10}H_{12}$ with hydrogen distributed equally between octahedral and tetrahedral sites. For RNi_4Al we assume that this volume will contain two Al atoms. These will incapacitate two octahedral sites. As regards the tetrahedral sites there are two possibilities. The two Al atoms may be adjacent to one another in the host lattice or not. If the former is true, they will eliminate three tetrahedral sites; if the latter, four sites will be eliminated.

The 2 Al atoms can be introduced 30 ways. The number of nonadjacent complexions is 18. Thus on the average 7.2 sites $[=2 \times (0.6 \times 4 + 0.4 \times 3)]$ will be eliminated, or 3.6 atoms, since the sites are only half occupied statistically. Accordingly, the total atoms "expelled" on passing from hydrogenated $LaNi_5$ to $LaNi_4Al$ is 5.6. Hence, from the known capacity of the binary system $LaNi_5H_{6.9}$ one expects for the ternary $LaNi_4AlH_{4.1}$. Experimentally, one observes $LaNi_4AlH_{4.3}$, in excellent agreement with the estimated values.

Good capacity data for other RNi_5 systems are unavailable because of the large pressures entailed. It is to be expected that they would be similar to that of $LaNi_5$, and hence the RNi_4Al systems would have a H/RNi_4Al ratio the same for all values of R. The average value for this ratio for the six systems with R = La, Ce, Pr, Nd, Sm, and Gd is (*2*) 3.8 whereas the value computed from the present model is, as noted in the preceding paragraph, 4.1. The model therefore seems to be a reasonable representation of the situation prevailing in these several ternary systems.

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W. E. Wallace
E. B. Boltich

Department of Chemistry
University of Pittsburgh
Pittsburgh, Pennsylvania 15260

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