

Violation of the Minimum H-H Separation "Rule" for Metal Hydrides

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Using gradient-corrected, full-potential, density-functional calculations, including structural relaxations, it is found that the metal hydrides $RTInH_{1.333}$ ($R = \text{La, Ce, Pr, or Nd}$; $T = \text{Ni, Pd, or Pt}$) possess unusually short H-H separations. The most extreme value (1.454 Å) ever obtained for metal hydrides occurs for $\text{LaPtInH}_{1.333}$. This finding violates the empirical rule for metal hydrides, which states that the minimum H-H separation is 2 Å. The paired, localized, and bosonic nature of the electron distribution at the H site are polarized towards La and In which reduces the repulsive interaction between negatively charged H atoms. Also, R - R interactions contribute to shielding of the repulsive interactions between the H atoms.

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The most attractive aspect of metal hydrides from a technological point of view is their potential use as energy-storing materials. Hydrogen as energy carrier and other visions of the "hydrogen society" are especially attractive from an environmental point of view, but since hydrogen is a low-density gas at STP, the storage of the large quantities required for most applications is a challenge. High-pressure-compressed-gas storage is energy intensive if high volume efficiency is desired, liquid or solid hydrogen storage even more so, and all involve certain hazards. Storage of hydrogen in the form of solid metal hydrides, from which it can readily be recovered by heating, is safe and volume efficient.

The amount of hydrogen per volume unit in metal hydrides is very high; in some cases higher than in liquid or solid hydrogen, e.g., VH_2 stores more than twice the amount of hydrogen than solid H_2 at 4.2 K. It is unfortunate, however, that most metal hydrides are heavy in relation to the amount of hydrogen they contain. FeTiH_2 and LaNi_5H_7 , e.g., contain only 1.9 and 1.6 wt. % hydrogen, respectively. Therefore, efforts in hydride research over the past 25–30 years have been concentrated on designing new, or modifying known, intermetallic hydrides to increase the storing capacity and simultaneously adjusting their properties to make them capable of delivering hydrogen at useful pressures (> 0.1 MPa) and acceptable temperatures (< 425 K) [1]. These aspects are particularly important for most mobile applications where hydrogen would be used directly in combustion engines or indirectly via fuel cells. It has proven difficult to exceed 2 wt. % of stored hydrogen, and it remains a challenge to increase this figure if metal hydrides are to become a viable source for the transportation sector.

The search for efficient hydrogen-storage metal hydrides [2] has to some extent been hampered by the mental barriers which empirical rules have put on the thinking. For example, the interstitial hole size that hydrogen is expected to occupy should be > 0.40 Å. Switendick [3] observed from a compilation of experimental structure data that the

minimum H-H separation in ordered metal hydrides is > 2 Å ("the 2-Å rule"). This empirical pattern is later [4] supported by band-structure calculations which ascribe the effect to repulsive interaction generated by the partially charged hydrogen atoms. A practical consequence of this repulsive H-H interaction in metal hydrides is that it puts a limit to the amount of hydrogen which can be accommodated within a given structural framework. So, if H-H separations less than 2 Å would be possible, this could open for new efforts to identify potential intermetallics for higher hydrogen storing capacity. However, there are indeed metal hydrides which do violate the 2-Å rule, and we have here identified the origin for such behavior.

RNiIn ($R = \text{La, Ce, Pr, and Nd}$) crystallizes in the ZrNiAl -type structure (space group $P\bar{6}2m$) and can formally be considered as a layered arrangement with a repeated stacking of two different planar nets of composition $R_3\text{Ni}_2$ and NiIn_3 along [001] of the hexagonal unit cell. If the hydrides of these materials obey the hole-size demand and the 2-Å rule, one would expect H to occupy the interstitial $2d$ site within $R_3\text{Ni}_2$ trigonal bipyramid. However, proton magnetic resonance (PMR) studies suggest [5,6] that H occupies both the $4h$ and $6i$ sites or either of them with H-H distances in the range 1.5–1.8 Å. Recent powder x-ray and neutron diffraction studies [7] on $\text{RNiInD}_{1.333-x}$ (ideally $R_3\text{Ni}_3\text{In}_3\text{D}_4$) show that deuterium occupies the $4h$ site located on the threefold axis of $R_3\text{Ni}$ tetrahedra that share a common face to form trigonal bipyramid (Fig. 1). This configuration gives rise to extraordinary short H-H separations of around 1.6 Å [7]. As the diffraction techniques generally determine the average structure, neglect of partial H-site occupancies and local lattice distortions may lead one to conclude with shorter H-H separations than actually present in the real structure [8]. Hence, it is of interest to perform structural optimization theoretically.

The present full-potential linear muffin-tin orbital [9] calculations are all electron, and no shape approximation to the charge density or potential has been used. The basis

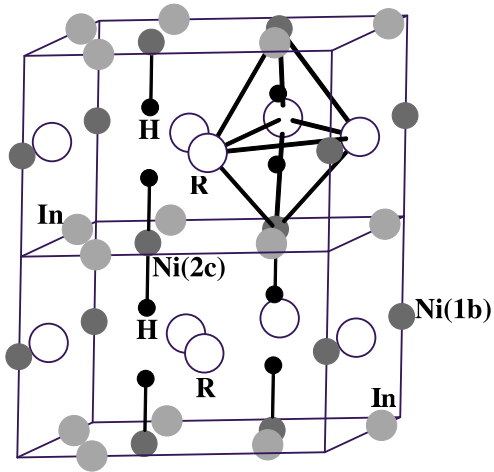


FIG. 1. The $RNiInH_{1.333}$ -type crystal structure. The R_3Ni_2 bipyramid is emphasized with thicker lines.

functions, charge density, and potential were expanded in spherical harmonic series inside the muffin-tin spheres and in Fourier series in the interstitial regions. The ratio of interstitial to unit cell volume is around 0.42. The calculations are based on the generalized-gradient-corrected-density-functional theory as proposed by Perdew *et al.* [10]. Spin-orbit terms are included directly in the Hamiltonian matrix elements for the part inside the muffin-tin spheres. The basis set contained semicore $5p$ and valence $5d$, $6s$, $6p$, and $4f$ states for La (for Ce the $4f$ electrons are treated alternatively as valence and localized core electrons, whereas the Nd- $4f$ and Pr- $4f$ electrons are treated as localized electrons using open core approximation), $3s$, $3p$, $4s$, $4p$, and $3d$ for Ni, $4s$, $4p$, $5s$, $5p$, and $4d$ for Pd, $5s$, $5p$, $6s$, $6p$, and $5d$ for Pt, $5s$, $5p$, and $5d$ for In, and $1s$, $2p$, and $3d$ states for H. All orbitals were contained in the same energy panel. To ensure well-converged wave functions a so-called multibasis was included, implying the use of different Hankel or Neuman functions, each attaching to its own radial functions. The self consistency was obtained with 105 \mathbf{k} points in the irreducible part of the Brillouin zone. To gauge the bond strength and nature of bonding we have used crystal orbital Hamiltonian population and electron localization function (ELF) analyses, as is implemented in TBLMTO-47 [11].

All calculations relate to ideal and fully saturated hydrides with composition $R_3T_3In_3H_4$ ($RTInH_{1.333}$; $R = La, Ce, Pr, \text{ or } Nd$, $T = Ni, Pd, \text{ or } Pt$). For (trivalent) R the $4f$ electrons were treated as core electrons (except for La; $4f$). As Ce- $4f$ electrons are known to take different valence states in intermetallic compounds, different possibilities [12] for the valence states of Ce were considered in both the hydrides and intermetallic phases during the structural optimization. For this optimization all atom positions were relaxed by force minimization and equilibrium c/a , and volumes were obtained by total energy minimization. Optimized structural parameters for the Ce compounds are in good agreement with experimental values (only) when Ce atoms are assumed to be in the trivalent state. The calculated equilibrium lattice parameters and the changes between the intermetallic and corresponding hydride phases are given for selected compounds along with experimental parameters in Table I.

In general, the calculated lattice parameters are in good agreement with the experimental values, and the small differences found may partly be attributed to hydrogen nonstoichiometry (around 10%) in the experimental studies. The hydrogen-induced lattice expansion is strongly anisotropic (Table I): a huge expansion along $[001]$ ($\Delta c/c = 14\% - 20\%$) and a smaller intralayer contraction ($-\Delta a/a = 0\% - 5.8\%$). The calculated cohesive energy and heat of formation for the hydrides are larger than for the corresponding intermetallic phases indicating that it might be possible to synthesize all these hydrides. The electronic structure studies show that all considered phases are in the metallic state consistent with experimental findings. The calculated $R-H$, $T-H$, and $H-H$ distances are given in Table II along with experimentally available values. An interesting observation is that all $RTInH_{1.333}$ materials have unusually short $H-H$ distances. Two explanations have been proposed. Pairing of the hydrogen atoms (either by molecular H_2 -like bonding or by bonding mediated by the intermediate T atom) has been advanced to explain the anomalous PMR spectrum of $CeNiInH_{1.0}$ [13]. The second explanation focuses on the significantly shorter La-La distance in $LaNiInH_{1.333}$ than in closely related phases [7], whereby the La atoms (generally R) may

TABLE I. Calculated lattice parameters (a and c in \AA) and c/a for $LaTiInH_{1.333}$ and relative variation in unit cell dimensions (in %) consequent on hydrogenation from $RTIn$ to $RTInH_{1.333}$.

Compound	a		c		c/a		$\Delta a/a$		$\Delta c/c$		$\Delta V/V$	
	Theor.	Expt.	Theor.	Expt.	Theor.	Expt.	Theor.	Expt.	Theor.	Expt.	Theor.	Expt.
$LaNiInH_{1.333}$	7.2603	7.3810	4.5522	4.6489	0.6270	0.6399	-3.969	-2.76	14.02	14.8	5.14	8.54
$LaPdInH_{1.333}$	7.3501	...	4.8112	...	0.6546	...	-5.42	...	16.64	...	4.33	...
$LaPtInH_{1.333}$	7.7274	...	4.6903	...	0.6070	...	-0.04	...	13.98	...	14.00	...
$CeNiInH_{1.333}$	7.4536	7.2921	4.4871	4.6238	0.6020	0.6341	-1.68	-3.21	12.72	16.3	8.97	8.98
$PrNiInH_{1.333}$	7.3783	7.260	4.4726	4.560	0.6062	0.6281	-2.85	-3.73	13.93	15.4	7.52	7.01
$NdNiInH_{1.333}$	7.2408	7.2255	4.5560	4.5752	0.6292	0.6332	-3.72	-3.92	16.75	16.5	7.60	7.53

TABLE II. Calculated interatomic distances (in Å) for $RTInH_{1.333}$.

Compound	R-H		T-H		H-H	
	Theor.	Expt.	Theor.	Expt.	Theor.	Expt.
LaNiInH _{1.333}	2.379	2.406	1.489	1.506	1.573	1.635
LaPdInH _{1.333}	2.373	...	1.644	...	1.523	...
LaPtInH _{1.333}	2.475	...	1.618	...	1.454	...
CeNiInH _{1.333}	2.427	2.371	1.457	1.508	1.572	1.606
PrNiInH _{1.333}	2.387	...	1.492	...	1.487	...
NdNiInH _{1.333}	2.350	2.350	1.493	1.506	1.492	1.562

act as a shielding that compensates the repulsive H-H interaction.

In order to evaluate these possibilities we have calculated the total energy for (hypothetical) LaPtInH_{1.333} as a function of H-H separation according to three different scenarios: (1) Keeping La, Pt, and In fixed in their equilibrium positions, (2) moving La 0.08 Å out of the equilibrium position toward H, and (3) moving La 0.08 Å out of the equilibrium position away from H. The obtained results are illustrated in Fig. 2. When La, Pt, and In are in their optimized equilibrium positions, the equilibrium H-H separation is 1.454 Å. This scenario corresponds to a lower total energy than the two alternatives. For scenario 3 we obtain a shorter H-H separation (1.438 Å) than for the ground state configuration, and for scenario 2 a correspondingly larger separation (1.462 Å).

As the total energy curves increase steadily on reduction of the H-H separations, the possibility of stabilization of hydrogen in the form of molecular H₂-like units seems completely ruled out. The total energy increases drastically also for increased H-H separation beyond the equilibrium value. This is due to increasing repulsive T-H interaction and decreasing attractive H-H interaction. *The considerable changes in the equilibrium H-H distance on R displacement indicate that R in the R₃T₂ trigonal bipyramidal configuration (Fig. 1) acts as a shielding that to some extent compensates repulsive H-H interactions.*

Owing to charge transfer from metal to hydrogen, the repulsive H-H interaction in metal hydrides are generally larger than that within the H₂ molecule, and this may be the physical basis for the 2-Å rule. Although minimum H-H separation (1.945 Å) in Th₂AlH₄ [14] is less than 2 Å, it is much larger than that found in $RTInH_{1.333}$. In order to quantify the bonding interaction between the constituents in the $RTInH_{1.333}$ series the integrated crystal orbital Hamilton population (ICOHP) were calculated. For example, the ICOHP values up to E_F for LaNiInH_{1.333} are -3.44, -0.14, -0.72, -0.85, -0.86, -1.21, and -0.61 eV for Ni(2c)-H, H-H, La-H, Ni(2c)-In, La-Ni(1b), Ni(1b)-In, and Ni(2c)-La, respectively. This indicates that the strongest bonds are those between Ni(2c) and H. Another important observation is that the bonding interaction between the hydrogens is small, which further confirms that the short H-H separation in these materials

are not rooted in hydrogen pairing or formation of H₂-like molecular units.

In order to substantiate this observation further we have calculated the valence-charge-density distribution in (100) of LaNiInH_{1.333} [Fig. 3(a)]. From this figure, it is apparent that Ni and H form an NiH₂ moleculelike structural subunit. Moreover, Fig. 3(a) demonstrates that there is no substantial charge density distributed between the H atoms. In order to depict the role of charge transfer, we have displayed the charge transfer (the difference in the electron density of the compound and that of constituent atoms superimposed on the lattice grid) for LaNiInH_{1.333} within (100) in Fig. 3(b). From Fig. 3(b) it is clear that electrons are transferred from La, In, and Ni to the H site. So, there is a considerable ionic bonding component between H and the metallic host lattice. The transferred electrons from the metallic host lattice to the H₂-like subunit of the structure enter the antibonding σ^* levels and give rise to repulsive interaction. This repulsive interaction between the negatively charged H atoms could explain why the H-H

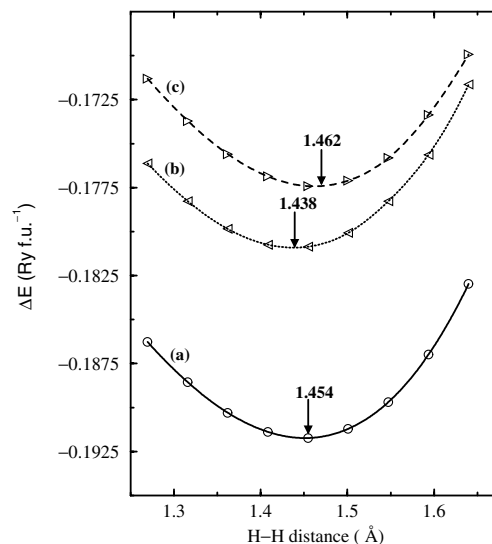


FIG. 2. Total energy versus H-H distance in LaPtInH_{1.333}. (a) All atoms except H are fixed at their equilibrium positions. (b) La atoms are moved 0.08 Å out of their equilibrium position toward H. (c) La atoms are moved 0.08 Å out of their equilibrium position away from H.

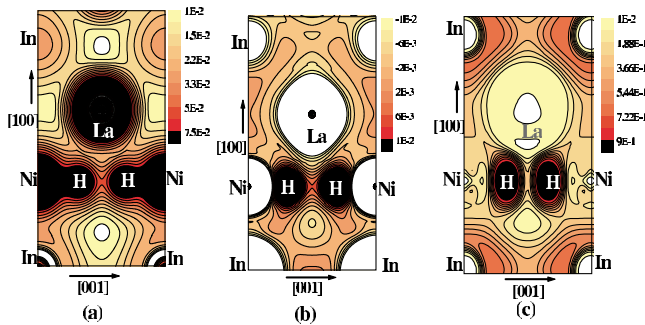


FIG. 3 (color online). (a) Total charge density, (b) charge transfer, and (c) electron localization function plot for $\text{LaNiInH}_{1.333}$ in the (100) plane. The origin is shifted to $(1/3, 0, 0)$, and the charge densities are in $e/a.u.^3$.

separations in these materials are larger than that in the H_2 molecule. If there was strong covalent bonding between Ni and H, one should expect a significant (positive) value of charge transfer distribution between these atoms (contributed by both atoms). The absence of such a feature rules out this possibility. The ELF is an informative tool to distinguish different bonding interactions in solids [15], and ELF for $\text{LaNiInH}_{1.333}$ in (100) is given in Fig. 3(c). The large value of ELF at the H site indicates strongly paired electrons with local bosonic character. Another manifestation of covalent bonding between Ni and H should have been paired electron distribution between these atoms. The negligibly small ELF between Ni and H indicates that the probability of finding parallel spin electrons close together is rather high (correspondingly small for antiparallel spin pairs) in this region confirm metallic bonding consistent with the result obtained from charge transfer analysis and the detailed analysis shows that delocalized metallic Ni(2c)-d electrons are distributed in this region. Even though the charge distribution between Ni and H looks like a typical covalent bonding, the charge transfer and ELF analyses clearly show that the electron distributions between Ni and H are having parallel spin alignment and are purely from the Ni site. Hence, chemical bonding between Ni and H is dominated by metallic components with considerable ionic weight. The partial density of state analysis also shows that the H-s states are well separated from the Ni-d states in the whole valence band and indicates the presence of ionic bonding between Ni and H. Because of the repulsive interaction between the negatively charged H electrons, the ELF contours are not spherically shaped but polarized towards La and In. *The localized nature of the electrons at the H site and their polarization towards La and In reduce significantly the H-H repulsive interaction, and this can explain the unusually short H-H separation in this compound.* The ELF between the H

atoms takes a significant value of 0.35. Considering the small charge density, this indicates a weak metallic type of interaction between the hydrogen atoms.

$\text{RTInH}_{1.333}$ constitutes a series with much shorter H-H separations than other known metal hydrides. We have shown that the short distances between the H atoms in such metal hydrides are governed primarily by the polarization of negative charges on H towards the electropositive La and In. We believe that this conclusion is of more general validity, and may be utilized to search for other metal hydrides of potential interest as hydrogen-storage materials.

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