Violation of the Minimum H-H Separation “Rule” for Metal Hydrides

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Using gradient-corrected, all-electron, full-potential, density-functional calculations, including structural relaxations, it is found that the metal hydrides \( RTnH_{1.33} \) (\( R = \text{La, Ce, Pr, or Nd} \); \( T = \text{Ni, Pd, or Pt} \)) 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. Electronic structure, charge density, charge transfer, and electron localization function analyses on \( RTnH_{1.333} \) show dominant metallic bonding with a non-negligible ionic component between \( T \) and \( H \), the H–H interaction being weakly metallic. 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. This could explain the unusually short H–H separation in these materials. Also, \( R–R \) interactions contribute to shielding of the repulsive interactions between the H atoms.

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., \( \text{VH}_3 \) stores more than twice the amount of hydrogen than solid \( \text{H}_2 \) at 4.2 K. It is unfortunate, however, that most metal hydrides are heavy in relation to the amount of hydrogen they contain. \( \text{FeTiH}_2 \) and \( \text{LaNi}_{5} \text{H}_2 \), e.g., only contain 1.9 and 1.6 wt.% hydrogen, respectively. Therefore, efforts in hydride research have over the past 25–30 years 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). 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 has to some extent been hampered by the mental barriers which empirical rules have put on the thinking. For example, the interstitial hole size where hydrogen is expected to occupy should be >0.40 Å. Switendick 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 supported by band-structure calculations which ascribe the effect to repulsive interactions 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.

\( \text{RNiIn} (R = \text{La, Ce, Pr, and Nd}) \) crystallizes in the \( \text{ZrNiAl-type structure (space group } \overline{F}2m \) and can formally be considered as a layered arrangement with a repeated stacking of two different planar nets of composition \( \text{R}_3\text{Ni}_2 \) and \( \text{NiIn}_3 \) 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 \( \text{H} \) to occupy the interstitial \( 2d \) site within \( \text{R}_3\text{Ni}_2 \) trigonal bipyramid. However, proton magnetic resonance (PMR) studies suggest that \( \text{H} \) occupies both the \( 4h \) and \( 6i \) sites or either of them with \( \text{H}–\text{H} \) distances in the range 1.5–1.8 Å. Recent powder X-ray and neutron diffraction studies on \( \text{RNiD}_{1.333–x} \) (ideally \( \text{R}_3\text{Ni}_3\text{In}_3\text{D}_4 \)) show that deuterium occupies the \( 4h \) site located on three-fold axis of \( \text{R}_3\text{Ni} \) 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. As the diffraction techniques generally determine the average structure, neglect of partial H-site occupancies and local lattice distortions may lead one to conclude...
FIG. 1: The \( R \text{NiInH}_{1.333} \)-type crystal structure. The \( R_3 \text{Ni}_2 \) bipyramid is emphasized with thicker lines.

with shorter H–H separations than actually present in the real structure. Hence, it is of interest to perform structural optimization theoretically.

The present full-potential LMTO calculations are all electron, and no shape approximation to the charge density or potential has been used. The basis 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. 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 \( 1s, 2p, 3d \) states for H. All orbitals were contained in the same energy panel. To ensure well-converged wave functions a so-called multi basis was included, implying the use of different Hankel or Neuman functions each attaching to its own radial functions. This allows reliable description of the higher-lying unoccupied states and low-lying semicore states. The self consistency was obtained with 105 \( \mathbf{k} \) points in the irreducible part of the Brillouin zone. Test calculations were made for 210 \( \mathbf{k} \) points to check for convergence, but the optimized \( c/a \) ratio for 105 and 210 \( \mathbf{k} \) points for \( \text{LaNiInH}_{1.333} \) is essentially the same. To gauge the bond strength and nature of bonding we have used crystal orbital Hamiltonian population (COHP) and electron localization function (ELF) analyzes, as is implemented in TBLMTO-47.

All calculations relate to ideal and fully saturated hydrides with composition \( \text{R}_3\text{T}_3\text{In}_3\text{H}_4 \) (\( \text{RTInH}_{1.333} \); \( \text{R} = \text{La, Ce, Pr, or Nd}, \text{T} = \text{Ni, Pd, or Pt} \)). For (trivalent) \( \text{R} \) 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 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 volume 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.

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 non-stoichiometry (around 10%) in the experimental studies. The hydrogen-induced lattice expansion is strongly anisotropic (Table). 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 \( \text{R}–\text{H}, \text{T}–\text{H}, \) and \( \text{H}–\text{H} \) distances are given in Table along with experimentally available values. An interesting observation is that all \( \text{RTInH}_{1.333} \) materials have unusually short \( \text{H}–\text{H} \) distances. Two explanations have been proposed. Pairing of the hydrogen atoms (either by molecular \( \text{H}_2 \)-like bonding or by bonding mediated by the intermediate \( \text{T} \) atom) has been advanced to explain the anomalous PMR spectrum of \( \text{CeNiInH}_{1.0} \). The second explanation focuses on the significantly shorter \( \text{La}–\text{La} \) distance in \( \text{LaNiInH}_{1.333} \) than in closely related phases, whereby the La atoms (generally \( \text{R} \)) may act as a shielding that compensates the repulsive \( \text{H}–\text{H} \) interaction.

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

As the total energy curves increase steadily on reduction of the \( \text{H}–\text{H} \) separations, the possibility of stabilization of hydrogen in the form of molecular \( \text{H}_2 \)-like units...
TABLE I: Calculated lattice parameters (a and c in Å) and c/a for LaTInH$_{1.333}$ and relative variation in unit cell dimensions (in %) consequent on hydrogenation from RTIn to RTInH$_{1.333}$.

| Compound   | a (Å) | c (Å) | c/a | $\Delta a/a$ | $\Delta c/c$ | $\Delta V/V$ |
|------------|-------|-------|-----|--------------|--------------|--------------|
| LaNiInH$_{1.333}$ | 7.293 | 7.3810 | 0.6270 | 0.6399 | -3.969 | -2.76 | 14.02 | 14.8 | 5.14 | 8.54 |
| LaPdInH$_{1.333}$ | 7.3501 | 4.8122 | 0.6546 | -5.42 | -5.42 | 16.64 | 4.33 | - |
| LaPtInH$_{1.333}$ | 7.7274 | 4.6903 | 0.6070 | -0.04 | -0.04 | 13.98 | 14.00 | - |
| CeNiInH$_{1.333}$ | 7.4536 | 4.8712 | 0.6341 | -1.68 | -3.21 | 12.72 | 16.3 | 8.97 | 9.98 |
| PrNiInH$_{1.333}$ | 7.3783 | 4.7562 | 0.6062 | -2.85 | -3.73 | 13.93 | 15.4 | 7.52 | 7.01 |
| NdNiIn$_{1.333}$ | 7.2408 | 4.5560 | 0.6292 | -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 |
|------------|-----|-----|-----|
| The. | Exp. | The. | Exp. | The. | Exp. | The. | Exp. | The. | Exp. |
| 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 | — | 1.545 | — |
| 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 |

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.

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 R$_3$T$_2$ trigonal bipyramidal configuration (Fig. 3) acts as a shielding that to some extent compensates repulsive H–H interactions. When the R–H separation is reduced the H atoms are allowed to approach each other more closely.

Owing to charge transfer from metal to hydrogen the repulsive H–H interaction in metal hydrides are generally larger than that with the H$_2$ molecule and this may be the physical basis for “the 2-Å rule”. Another example of violation of “the 2-Å rule” is found for Th$_2$AlH$_4$ [3], but here the minimum H–H separation (1.945 Å) within the Th$_5$ trigonal bipyramids is much larger than the bond distance in the H$_2$ molecule and the H–H separations 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 Er 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 H$_2$-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). From this figure, it is apparent that Ni and H form an NiH$_2$ molecule-like structural subunit. Moreover, Fig. 3a demonstrates that there is considerable ionic bonding component between H and the metallic host lattice. The transferred electrons from the metallic host lattice to the H$_2$-like subunit of the structure enter the antibonding $\sigma^*$ levels and gives rise to repulsive interaction. This repulsive interaction between the negatively charged H atoms could explain why the H–H separation 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...
FIG. 3: (a) Total charge density, (b) Charge transfer and (c) Electron localization function plot for 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.$^3$.

of such a feature rules out this possibility. The ELF is an informative tool to distinguish different bonding interactions in solids and ELF for LaNiInH$_{1.333}$ in (100) is given in Fig. 3c. 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 show 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 analyzes clearly show that the electron distribution between Ni and H are having parallel spin alignment and purely from Ni site. Hence, chemical bonding between Ni and H is dominated by metallic components with considerable ionic weft. The partial density of state analysis also show that the H-s states are well separated from the Ni-d states in the whole valence band indicates the presence of ionic bonding between Ni and H. Due to 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 atom takes a significant value of 0.35. Considering the small charge density, this indicates a weak metallic type of interaction between the hydrogen atoms.

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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