Hydrogenation-Induced Insulating State in the Intermetallic Compound LaMg$_2$Ni

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(Received 12 August 2004; published 18 February 2005)

Hydrogenation-induced metal-semiconductor transitions usually occur in simple systems based on rare earths and/or magnesium, accompanied by major reconstructions of the metal host (atom shifts > 2 Å). We report on the first such transition in a quaternary system based on a transition element. Metallic LaMg$_2$Ni absorbs hydrogen near ambient conditions, forming the nonmetallic hydride LaMg$_2$NiH$_7$ which has a nearly unchanged metal host structure (atom shifts < 0.7 Å). The transition is induced by a charge transfer of conduction electrons into tetrahedral [NiH$_4$]$^{4-}$ complexes having closed-shell electron configurations.

DOI: 10.1103/PhysRevLett.94.066403 PACS numbers: 71.30.+h, 61.66.Fn, 71.15.Mb, 72.80.Ga

Hydrogenation-induced metal-nonmetal transitions occur in relatively simple systems based on nontransition elements such as yttrium (Y-YH$_{3-}$) and analogues, or main-group elements such as magnesium (Mg-MgH$_2$) [1,2]. For transition (T) elements the only well documented example is the nickel based ternary system Mg$_2$Ni-H. Upon hydrogenation the metallic compound Mg$_2$Ni transforms into a nonmetallic hydride of stoichiometric composition Mg$_2$NiH$_4$ that shows optical mirror properties [3] and provides a safe way of storing hydrogen [4]. The nature of the electron correlations leading to these transitions is of fundamental interest and subject of current research (see, e.g., [5]). One reason why these correlations are still poorly understood is the fact that they are accompanied by major reconstructions of the metal atom arrangements. In the Mg-H system, for example, the Mg atom arrangement changes from hexagonal close packed in metallic Mg to tetragonal in nonmetallic MgH$_2$. In the La-H and Y-H systems the hydrogenation-induced changes in the close-packed metal substructures are somewhat smaller, but on a local level, in particular, around hydrogen defects, they are substantial [6]. Finally, in the Mg$_2$Ni-H system the metal-nonmetal transition leads to atomic shifts of up to 2 Å and a breaking of metal-metal bonds.

Metal-nonmetal transitions in T-metal-hydrogen systems without reconstruction of the metal substructure have not yet been reported. Here we report on the first such transition in the nickel based system LaMg$_2$Ni-H. Intermetallic LaMg$_2$Ni absorbs reversibly hydrogen near ambient conditions hereby forming an ordered stoichiometric hydride of composition LaMg$_2$NiH$_7$ [7]. Hydrogen enters various types of interstices in, but does not lead to a reconstruction of, the metal substructure. In this combined experimental and theoretical work we show that the hydride is nonmetallic and that the electron correlations responsible for the metal-nonmetal transition are presumably identical to those leading to the formation of T-metal-hydrogen “complexes” having closed-shell electron configurations.

Hydrogen-free LaMg$_2$Ni crystallizes with orthorhombic symmetry [8]. Its structure contains a distorted hexagonal honeycomb network of short metal-metal bonds (La-Ni = 2.95 and 3.05 Å, parallel to the $a$-$b$ plane) in which Mg atoms are inserted (Fig. 1). The hydride LaMg$_2$NiH$_7$ forms readily below 200 °C and 8 bar hydrogen pressure and crystallizes with monoclinic symmetry [8]. It is stoichiometric and shows no homogeneity range. Similar to “interstitial” hydrides its metal atom arrangement does not much differ from that of the alloy. It expands in the $a$-$b$ plane, contracts slightly along $c$, and undergoes a small monoclinic lattice distortion (deviation from orthogonality

![FIG. 1 (color online). Structure and resistance of orthorhombic LaMg$_2$Ni (a) and monoclinic LaMg$_2$NiH$_7$ (b) as measured on compacted polycrystalline samples. Tetrahedral [$\text{NiH}_4$]$^{4-}$ complexes and H$^-$ anions are shown; short La-Ni bonds in alloy $\parallel a$-$b$ plane.](image-url)
density functional theory and the projector augmented wave method (PAW) with plane waves [9]. The generalized gradient approximation (GGA) was used. The energy cut-off is 269.6 eV and the k-point set used was $8 \times 4 \times 4$ for LaMg$_2$Ni and $4 \times 8 \times 4$ for LaMg$_2$NiH$_7$, respectively. The outer core shells ($5s$ and $5p$) of La were included as valence states. All calculated lattice constants were within 1–2% of the experimental values.

The projected density of states (PDOS) plot of metallic LaMg$_2$Ni is shown in Fig. 2(a). The peak around 1–2 eV below the Fermi level, $E_F$, is associated with the Ni $d$ band, while the peak around 2 eV above $E_F$ is associated with the (unoccupied) La $f$ bands. The plot shows a normal metal, although the Ni $d$ bands are much narrower than those in the Ni metal. In comparison, the plot for the hydride LaMg$_2$NiH$_7$ is shown in Figs. 2(b) and 2(c) [10]. A gap appears upon hydrogenation. These plots represent averages over the various atoms sites. The peaks in the range from 0 to $-2.0$ eV are associated with Ni $d$ states, while those around $+2.0$ eV are associated with La $f$ states. The
fundamental gap (indirect, $\Gamma \rightarrow A$ or $\Gamma \rightarrow Y$) is about 0.9 eV. This is the GGA value, which is expected to be smaller than the quasiparticle gap. A correction of the order of $+0.5$ to $+1.0$ eV is expected. One can identify three broad peaks for the occupied states. They can be associated with states (in the order of rising energy) from H-$s$ in the complex, H-$s$ interstitial, and Ni-$d$, respectively. Almost all the Ni-$d$ states are below the gap, indicating an approximately closed $d$ shell. An examination of the charge density (not shown) concludes that magnesium behaves like an electron donor with very little valence charge in its vicinity, while both types of hydrogen attracts charge as expected from its relatively large electronegativity.

In order to understand the bonding within the tetrahedral [NiH$_4$]$^{4-}$ complex, in Fig. 3 we plot the difference between the charge density in the crystal and the superposition of the atomic charge density in a plane containing Ni and two H. This contour plot indicates the charge transfer that takes place when the complex is formed from atoms. The contour interval is 0.05 e/$\text{Å}^3$, with solid (dashed) lines representing positive (negative) changes. The contours show a charge redistribution of the Ni $d$ shell compared to the atom, and, most significantly, an increase of charge density near the H sites. It is interesting to note that the maximum of this increase is not exactly located at the H site. Instead, it is shifted along the H-Ni direction, thus confirming the directional character of the Ni-H interactions.

Summarizing, our theoretical calculations and experimental results on the LaMg$_2$Ni-H system confirm the occurrence of a hydrogenation-induced charge transfer and the opening of a band gap. The results suggest a filled $d$ band situation and two sorts of metal-hydrogen interactions, a more covalent one involving $s^p$ bonded [NiH$_4$]$^{4-}$ complexes having closed 18-electron shells (ten Ni $3d$ and four H $s$, plus four valence electrons formally transferred from Mg to the complex) forming four directional 2-center 2-electron (2c-2e) bonds, and a more ionic one involving H$^-$ anions and Mg$^{2+}$ and La$^{3+}$ cations only, as shown by the limiting ionic formula La$^{3+}$:$2$Mg$^{2+}$:$[\text{NiH}_4]^{4-}$:$3$H$^-$. This demonstrates that hydrogen contents and H atom distributions in certain T-metal-hydrogen systems can be rationalized in terms of simple electron counting (18-electron rule) and $s$-$p$-$d$ hybridization schemes ($sp^3$).

Apart from the present LaMg$_2$Ni-H system only two other T-metal-hydrogen systems show a similar behavior, including hydrogenation-induced metal-semiconductor and metal-hydrogen complex formation (see Table I). The historically first one concerns the nickel based system Mg$_2$Ni-H. The hydride Mg$_2$NiH$_4$ is nonmetallic, has a calculated band gap of 1.8 eV [11] and derives from metallic Mg$_2$Ni by a relatively important rearrangement of its hexagonal metal substructure (Ni-Ni bond breaking; atom shift $\sim$2 Å, volume increase $\sim$32%). It displays a disordered hydrogen distribution in its cubic high-temperature phase and has been originally classified as an interstitial hydride. It was only after its monoclinic room-temperature structure had been found to contain an ordered array of tetrahedral 18-electron [NiH$_4$]$^{4-}$ complexes that it was classified as a so-called complex metal hydride (for a recent review on this class of compounds see [12]).

The Ni-H distances in these complexes (1.54–1.57 Å) are closely similar to those in the present LaMg$_2$NiH$_7$ and consistent with covalent interactions, but in contrast to the latter, Mg$_2$NiH$_4$ contains no anionic hydrogen surrounded by magnesium cations only. The second example is the recently reported iridium based system Mg$_2$Ir-H [13]. The stoichiometric hydride Mg$_2$Ir$_2$H$_4$ derives from the intermetallic compound Mg$_2$Ir by a relatively important rearrangement of the metal substructure (atom shifts $\sim$1.9 Å, formation of new metal-metal bonds, volume increase 40%). Hydrogen occupies not less than 26 different interstices, but the structure is better rationalized in terms of four nearly ordered saddelike [IrH$_4$]$^{3-}$ and square-pyramidal [IrH$_4$]$^{4-}$ complexes, all formally 18 electrons and displaying directional 2c-2e iridium-hydrogen bonds, and five hydride anions H$^-$ surrounded by Mg$^{2+}$ cations only, corresponding to the limiting ionic formula $4\text{Mg}_2\text{IrH}_4 = 5\text{MgH}_2 \cdot 19\text{Mg}^{2+} \cdot 2[\text{IrH}_4]^{3-} \cdot 6[\text{IrH}_4]^{4-}$. Although electric properties have not been reported yet the intensely red color of the hydride suggests nonmetallic behavior. As to other nonmetallic metal hydrides showing complex formation such as Mg$_2$CoH$_5$ ([CoH$_5$]$^{3-}$) and Mg$_2$FeH$_6$ ([FeH$_6$]$^{4-}$) they do not fall in this class because stable binary compounds “Mg$_2$Co” and “Mg$_2$Fe” do not exist [12].
Clearly, such simple bonding pictures and electron counting rules cannot be applied to metallic interstitial T-metal hydrides. Given that these usually display wide homogeneity ranges and disordered hydrogen substructures their local hydrogen configurations around the T elements are unknown which precludes their electron requirements from being determined. Nevertheless, for certain systems preferred hydrogen configurations showing directional bonding character do occur, and these can be rationalized in terms of nearly closed-shell electron configurations. Examples are found with MPdH_{2+x} (M = Ca, Sr, Eu, Yb) and MgRhH_{0.94}. Their CsCl-type metal substructures contain formally 14-electron [PD_{2}H_{2}]^{2-} complexes having linear H-Pd-H bonds, and 48-electron [Rh_{8}H_{8}]^{8-} complexes made up by nearly linear Rh-H-Rh bonds in a cyclic squarelike arrangement [12]. The T elements have nearly closed d shells and their H ligands can be rationalized in terms of 2c-2e bonds. Even classical hydrogen storage compounds such as LaNi_{5}H_{7} show a tendency of forming disordered tetrahedral NiH_{4} units whose electron requirements, however, have not yet been estimated. Although none of these systems show hydrogenation-induced metal-nonmetal transitions under the relatively mild pressure-temperature conditions investigated so far, one might speculate that such transitions do occur under more extreme conditions where hydrogenation-induced cell expansion favors electron charge transfer.

In conclusion, our work shows for the first time a hydrogenation-induced metal-nonmetal transition in a quaternary transition-metal-hydrogen system. The transition occurs without major reconstruction of the metal atom network and can be rationalized in terms of a local bonding picture. Insertion of hydrogen leads to a charge transfer of conduction electrons into metal-hydrogen bonds that stabilize T-metal-hydrogen complexes having closed-shell electron configurations. The formation of such complexes, at least on a local level, could be a general phenomenon in metallic interstitial transition-metal hydrides. This could open the door for the discovery of new metal-hydrogen systems showing metal-semiconductor transitions and thus to a better understanding of these transitions.

We thank N. Clayton (Geneva) for help with the resistivity measurements. This work is supported by the Swiss National Science Foundation, the Swiss Federal Office of Energy, the U.S. Department of Energy under Grant No. DE-FG02-97ER45632 (MYC), the U.S. National Science Foundation under Grant Nos. DMR-02-05328 and SBE-01-23532 (MYC), and the National Science Council of Taiwan under Grant No. 92-2112-M001-052 (CMW). The computation used resources of the DOE National Energy Research Scientific Computing Center (NERSC).


\[ \text{TABLE I. Hydrogenation-induced structural and electronic changes in transition-metal compounds} \]

<table>
<thead>
<tr>
<th>Compound (symmetry)</th>
<th>Hydride (symmetry)</th>
<th>$\Delta V/V$</th>
<th>Maximum atomic shift</th>
<th>Complexes and $H^-$ anions</th>
<th>Hydride properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg$_2$Ni (hexagonal)</td>
<td>Mg$_2$NiH$_4$ (monoclinic)</td>
<td>32%</td>
<td>$\sim 2.0$ Å</td>
<td>[NiH$_4$]$^{2-}$</td>
<td>nonmetallic, brownish</td>
</tr>
<tr>
<td>Mg$_3$Ir (hexagonal)</td>
<td>Mg$_3$Ir$_2$H$_1$ (monoclinic)</td>
<td>40%</td>
<td>$\sim 1.9$ Å</td>
<td>3[IrH$_4$]$^{2-}$, 3[IrH$_4$]$^{3-}$, 5H$^-$</td>
<td>nonmetallic, red</td>
</tr>
<tr>
<td>LaMg$_2$Ni (orthorhombic)</td>
<td>LaMg$_2$NiH$_2$ (monoclinic)</td>
<td>19%</td>
<td>$\sim 0.7$ Å</td>
<td>[NiH$_4$]$^{2-}$, 3H$^-$</td>
<td>nonmetallic, dark gray</td>
</tr>
</tbody>
</table>

[8] Crystal data: LaMg$_2$Ni: orthorhombic, space group Cmcm, $a = 4.2266(6)$ Å, $b = 10.303(1)$ Å, $c = 8.360(1)$ Å. $V = 364.0(1)$ Å$^3$, $Z = 4$, one La, one Mg and one Ni site; LaMg$_2$NiH$_2$: monoclinic, space group $P2_1/c$, $a = 13.9789(7)$ Å, $b = 4.7026(2)$ Å, $c = 16.0251(8)$ Å, $Z = 8$, two La, four Mg, two Ni and 14 D sites; cell parameter relationship between the alloy ($a$) and the hydride ($m$) $a_m = b_o - \tilde{c}_o$, $b_m = -\tilde{a}_o$, $c_m = 2\tilde{c}_o$.
[10] The projection radii used were 1.8 Å for La, 1.3 Å for Mg, 1.2 Å for Ni, and 0.7 Å for H. With the small H value, not all the charge was captured, but the energy-distribution trend is visible in these plots.