# Structural and magnetic modifications induced by hydrogen atoms occupying interstitial sites in GdNiInH$_{0.5}$ compound

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## ARTICLE INFO

## ABSTRACT

The structural and magnetic properties of GdNiIn intermetallic compound and its hydride have been studied. The GdNiIn compound crystallizes in the ZrNiAl-type structure. The structural study indicates that after hydrogenation the crystal structure remains the same and suggests that hydrogen atoms likely occupy 4$h$ and 2$d$ interstitial sites; meanwhile the unit cell expands in ~2%. The magnetic characterization shows that the presence of hydrogen modifies the magnetic properties of the host compound. Two main effects have been observed: a decrease of the magnetic moment per formula unit and a reduction of the ferromagnetic Curie temperature ($T_C$). The decrease of the magnetic moment has been speculatively interpreted as follows. The entrance of hydrogen atoms into the intermetallic lattice induces a magnetic moment in Ni atoms. Therefore, the effective magnetic moment determined for GdNiInH$_{0.5}$ comes from Gd and Ni atoms, which magnetic moments are oriented antiparallel to each other. On the other hand, the increase of interatomic distances leads to weakening of the coupling constant of Gd–Gd atoms, resulting in a decrease of $T_C$ after the hydrogen absorption.

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## 1. Introduction

Neither storage of hydrogen as a compressed gas nor as a cryogenic liquid appears suitable and economical for most uses as a fuel for many types of energy converters. However, the hydrogen storage in the form of a metal hydride is a promising alternative with many attractive features [1,2]. Over the past few decades and until now, a major challenge is to identify optimal candidates based on intermetallic compounds for such hydrogen storage. Rare-earth based ternaries are found to be promising alternatives as hydrogen-storage media offering safety advantages over the other types of hydrogen storage. Rare-earth based ternary intermetallic compounds with formulae R–T–X, where R = rare earth, T = transition metal and X = p-electron element, are interesting systems. They are attractive candidates due to their high hydrogen capacity per unit volume and their ability to absorb hydrogen under moderate conditions [1,3].

RNiIn compounds crystallize in the ZrNiAl-type hexagonal crystal structure (space group: $P\bar{6}2m$) and show interesting crystallographic features. R atoms occupy positions that form a triangular structure ($R_3$) in a similar way as a Kagomé lattice does. That triangular coordination symmetry of R atoms can provide the ideal scenario for a geometrical frustration if antiferromagnetic interactions are present. However, the physical properties of those RNiIn compounds have been very little studied so far [4,5]. It is known that GdNiIn, TbNiIn, DyNiIn, HoNiIn and ErNiIn show ferromagnetic order with $T_C$ at 96, 70, 30, 20 and 9 K, respectively [4,6]. When Gd atoms are substituted by Nd atoms in GdNiIn or when Ni atoms are substituted by Pd atoms to form NdNiIn and NdPdIn compounds, the ferromagnetic properties remain [7]. However, antiferromagnetic order has been reported for the GdCuIn compound [8]. Moreover, when Gd atoms are substituted by Ce atoms to form the CeTIn compounds different magnetic properties are observed [7]. It is known that the CeNiIn compound is a valence-fluctuating system having a Kondo temperature of 94 K, but when Ni atoms are replaced by Au or Pd an antiferromagnetic order is observed with Neel temperatures of 5.7 K or 1.8 K, respectively [9].

However, the magnetic properties of those compounds after the hydrogen absorption are scarcely reported. The hydrogen absorption introduces drastic modification in the properties of those compounds. After the hydrogenation to form the CeNiInH$_{1.8}$ hydride, the crystalline structure remains the same, but a pronounced anisotropic expansion of the unit cell is observed. The insertion of hydrogen favors the transition from a Kondo behavior in the CeNiIn compound to a ferromagnetic behavior in the hydride with a $T_C \sim 7$ K [10,11]. To the best of our knowledge, there are no reports about the structural and/or magnetic properties of GdNiInH$_x$ hydride.

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In this work, the study of the structural and magnetic properties of polycrystalline GdNiIn is presented. Besides that, the effects on those properties due to the absorption of hydrogen to form the $GdNiInH_{0.5}$ hydride are reported for the first time.

## 2. Experimental

The polycrystalline GdNiIn samples were prepared by arc melting high-purity elements (99.9% Gd, 99.99% Ni, and 99.99% In) under argon atmosphere. The samples were re-melted several times to ensure homogeneity. After arc-melting, the samples were annealed in vacuum at 800 °C for 48 h. The hydrogenation was carried out using a process based on the Sievert's method with a high purity (99.9999%) hydrogen gas. Prior to hydrogenation, the sample was activated under a hydrogen atmosphere for 30 min at 800 °C. Subsequently, the sample was cooled to room temperature while keeping the hydrogen pressure constant (1.2 bar). The hydrogen absorption results in the formation of $GdNiInH_{0.5}$ compound. Powder X-ray diffractograms were obtained by using Cu Kα radiation, with 0.05° steps in the $20° < 2\theta < 90°$ range. Magnetization measurements were carried out using a commercial Physical Properties Measurements System (PPMS) from Quantum Design and conventional Foner-type vibrating sample magnetometer. The measurements were obtained by applying magnetic fields up to ±9 T and at temperatures between 4.2 and 300 K.

## 3. Results and discussion

### 3.1. Structural properties

The X-ray powder diffraction (XRD) pattern of GdNiIn is shown in Fig. 1a. The observed reflections correspond to the hexagonal structure with a space group: $P\bar{6}2m$. The XRD data were additionally analyzed by the Rietveld refinement method. This analysis confirms
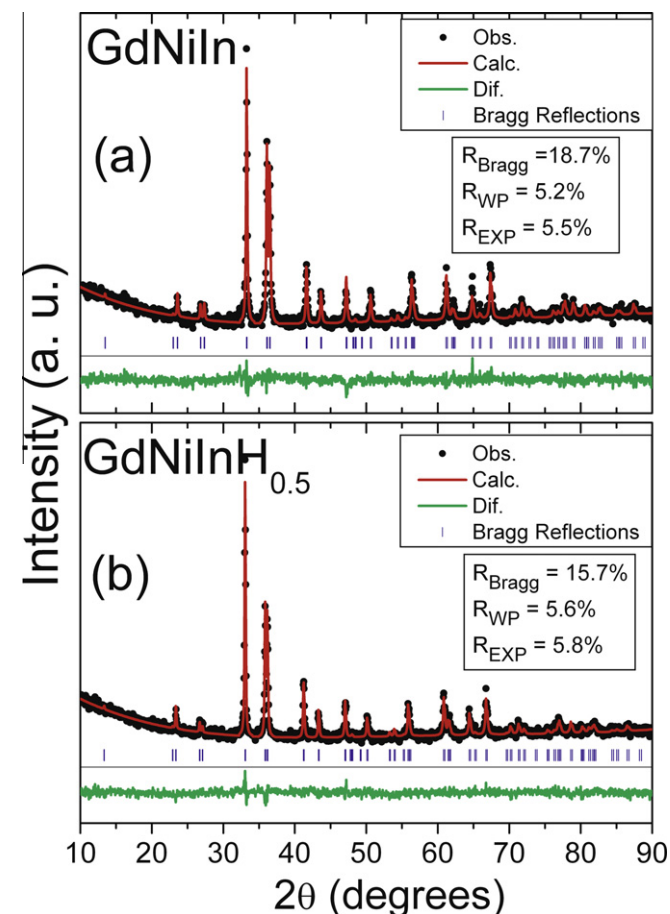


**Fig. 1.** X-ray diffraction patterns of (a) the GdNiIn intermetallic compound and (b) its hydride. The calculated curves are obtained from the Rietveld refinement. The reliability factors are also included.

the formation of a single phase (no additional Bragg reflections were determined within the resolution limits). Structural parameters obtained from the refinement are presented in Table 1. Values of the isotropic thermal parameters ($B = 8\pi^2 U_{eq}$) were obtained from Ref. [4] and they are kept fixed during the refinement. The lattice constants obtained from the fit ($a = b = 7.4771(1)$ Å and $c = 3.8341(1)$ Å) are in good agreement with values reported in the literature [4]. Although the hexagonal crystal structure remains the same after the hydrogen absorption, as observed in Fig. 1, some structural modifications were determined as shown in Table 1. Larger lattice constants are obtained for the hydride ($a = b = 7.5422(4)$ Å and $c = 3.8443(2)$ Å), which provide a larger volume of the unit cell. The unit cell expansion after the hydrogen absorption is estimated to be $\Delta V/V = 2.02\%$ with anisotropic expansions along the $a$ and $b$ axes ($\Delta a/a \sim 0.9\%$, $\Delta c/c \sim 0.3\%$). This anisotropic expansion has also been observed in $LaNiInD_{0.48}$ [12]. Due to the low level of hydrogen absorption, the compound studied in this work is considered as a "lower" hydride [12], where hydrogen atoms are randomly located in the crystal lattice as in a "solid solution".

When hydrogen atoms enter the lattice structure they are expected to occupy interstitial sites. Size calculations based on interatomic distances (see Table 2) suggest that the hydrogen atoms likely occupy the trygonal bipyramidal (2d) interstices and the tetrahedral (4h) interstices depicted in Fig. 2. Although for lower deuterium or hydrogen contents an isotropic expansion of the unit cell is expected in $RENiInDH_x$ with $x < 0.8$ [12–14], the anisotropic expansion determined in $GdNiInH_{0.5}$ could be an evidence for the preferential occupation of interstitial sites such as 2d sites, which can favor the significant enlargement along the $a$ (and $b$) axis. This finding requires more detailed studies to confirm that preferential occupation.

### 3.2. Magnetic properties

Fig. 3 shows the magnetization as a function of the magnetic field for GdNiIn and $GdNiInH_{0.5}$ compounds obtained at $T = 5$ K. As observed in the figure both compounds show ferromagnetic features, although the saturation magnetization of the system becomes smaller when hydrogen absorption happens. Using the law of approach to saturation: $M = M_s(1 - a/H + \ldots) + \chi H$, where $a$ is a constant related to non-magnetic inclusions and $\chi$ is the high field susceptibility, a saturation magnetization value of $M_s = 130.9(1)$ and $88.5(1)$ emu/g have been determined for the intermetallic and hydride compounds, respectively. The saturation magnetization value of the intermetallic compound provides an atomic magnetic moment of $\mu_{at.} = 7.70 \mu_B$ and a $5.25 \mu_B$ for the hydride. On the other hand, no hysteretic behavior is shown by the intermetallic even at the lowest temperature ($T = 5$ K), i.e. magnetization and demagnetization curves coincide. The presence of hydrogen atoms does not modify this anhisteretic behavior. This finding suggests the presence of a strong magnetic anisotropy or a high magnetic texture [15,16] which could favor alignment of the magnetic moments perpendicular to the applied field.

In order to estimate the ferromagnetic Curie temperature ($T_C$), several $M$ vs. $H$ curves were obtained at different temperatures and the Arrot's plots [17] were mounted. Fig. 4 shows the Arrot's plot for the GdNiIn. At each temperature, the linear region of the $M^2$ vs. $H/M$ curves (not steep tangent) was extrapolated towards the $M^2$ axis to provide the intercept. The plot of the intercept as a function of the temperature is shown in the inset of Fig. 4. As the value of $M^2 = 0$ provides the temperature at which the inverse of the susceptibility ($1/\chi = H/M$) goes to zero (i.e. the ferromagnetic Curie temperature), the linear fit of the intercept values provide a $T_C = 85.4(1)$ K for the GdNiIn compound. Similar analysis were carried out for $GdNiInH_{0.5}$ and this provides a $T_C = 53.3(8)$ K.

**Table 1**
Compilation of the structural parameters determined from the Rietveld refinement analysis for both GdNiIn and GdNiInH$_{0.5}$ compounds.

| | GdNiIn | | | | GdNiInH$_{0.5}$ | | | |
|---|---|---|---|---|---|---|---|---|
| Atom | Gd | Ni(1) | Ni(2) | In | Gd | Ni(1) | Ni(2) | In |
| Site | 3g | 1b | 2c | 3f | 3g | 1b | 2c | 3f |
| x/a | 0.5898(8) | 0 | 1/3 | 0.2548(10) | 0.6010(8) | 0 | 1/3 | 0.2560(9) |
| y/a | 0 | 0 | 2/3 | 0 | 0 | 0 | 2/3 | 0 |
| z/c | 1/2 | 1/2 | 0 | 0 | 1/2 | 1/2 | 0 | 0 |
| B (Å$^2$) | 0.83 | 0.80 | 0.87 | 0.81 | 0.83 | 0.80 | 0.87 | 0.81 |
| a = b (Å) | 7.4771(1) | | | | 7.5422(4) | | | |
| c (Å) | 3.8341(1) | | | | 3.8443(2) | | | |
| V (Å$^3$) | 185.636(7) | | | | 189.385(17) | | | |

**Table 2**
Selected interatomic distances in the hexagonal structure of GdNiIn and GdNiInH$_{0.5}$. Gd atoms occupy the 3g site and Ni(2) atoms occupy the 2c site (see Fig. 2).
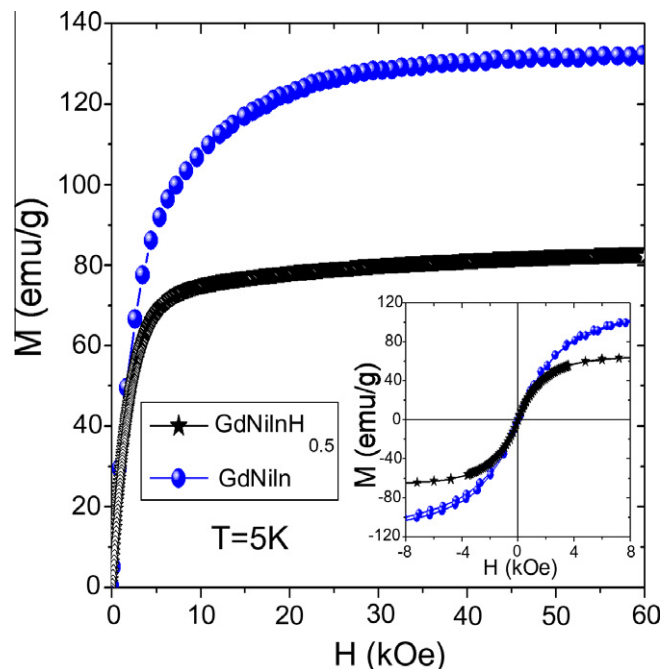
| | $d_{Gd-Gd}$ (Å) | $d_{Gd-Ni(2)}$ (Å) | $d_{Ni(2)-Ni(2)}$ (Å) |
|---|---|---|---|
| GdNiIn | 3.9153 | 2.9639 | 3.8341 |
| GdNiInH$_{0.5}$ | 3.9953 | 3.0026 | 3.8443 |
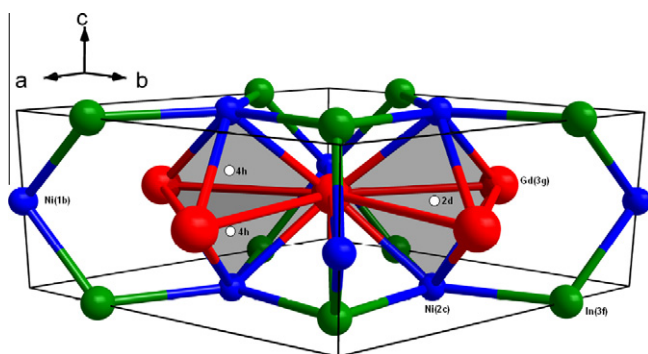


**Fig. 2.** Schematic representation of the crystal structure of GdNiIn compound. The interstitial sites likely occupied by H atoms are indicated in the illustration.



**Fig. 3.** Plot of the magnetization (*M*) as a function of the magnetic field (H) obtained at 5 K for the GdNiIn and its hydride. The inset shows the absence of hysteresis in both compounds.

Magnetization measurements as a function of the temperature were carried out in a magnetic field of *H* = 1000 Oe and the curves are shown in Fig. 5. Both compounds show features of a ferromagnetic behavior, but the ferro-paramagnetic transition happens at lower temperature for the GdNiInH$_{0.5}$ compound in agreement with the previous results. The magnetic susceptibility of both compounds follows the Curie Weiss law $\chi = \chi_0 + C/(T - \theta)$ in the high-temperature region, where $\chi_0$ is the temperature-independent susceptibility, C is the Curie constant and $\theta$ is the paramagnetic Curie temperature. The $\chi^{-1}$ vs. *T* plot is shown in the inset of Fig. 5 and the linear fit provides a $\theta$ = 79.6(3) K and an effective magnetic moment of $\mu_{eff}$ = 8.05(5) $\mu_B$ for GdNiIn. However, lower values of $\theta$ = 62.3(5) K and $\mu_{eff}$ = 6.93(5) $\mu_B$ has been determined for GdNiInH$_{0.5}$.

The effective magnetic moment determined for GdNiIn is consistent with the calculated magnetic moment of Gd$^{3+}$ free ion ($\mu_{cal.}$ = 7.94 $\mu_B$) and this result is in agreement with those obtained from saturation magnetization experiments. This finding suggests that the magnetic contribution to the effective magnetic moment of the intermetallic comes only from Gd atoms and implies that the magnetic contribution of Ni atoms to the effective moment is very small or negligible.

Two main effects are determined after the entrance of hydrogen atoms into the lattice structure: both the magnetic moment per Gd atom and the ferromagnetic Curie temperature notoriously decrease. The reduction in the magnetic moment must be related to the electron transfer from the host lattice to H placed in interstitial sites to establish a H$^-$ with a paired $s^2$ state [18,19]. It is

reported that the electronic states of R atoms forming the triangular R$_3$ structural units hybridize with the electronic states of H atoms. This hybridization seems to be stronger when the full occupation of 4h sites occurs, since the repulsive interaction between neighboring H–H atoms located in neighboring 4h interstitial sites is compensated by the shield carried out by R atoms forming the R$_3$ units [20–23]. This R–H hybridization must modify the background electronic state of R atoms in the hydride with respect to that one in the intermetallic compound. Other effect produced by the entrance of H atoms is the conformation of H-Ni-H linear chains which provides Ni–H bonds, strongly covalent-like in nature [18,19]. Those H-induced modifications must provide the adequate scenario for an effective reduction of the magnetic moment per formula unit.

Speculatively, one might consider a change in the electronic configuration of Ni atoms in order to explain the magnetic moment reduction. In this scenario, Ni atoms with negligible magnetic moment in the intermetallic become Ni atoms or Ni–H units with finite magnetic moment in the GdNiInH$_{0.5}$ compound. These H-induced magnetic moments should have an antiparallel orientation with respect to the Gd magnetic moments, in which case a reduced magnetic moment per formula unit is expected.

On the other hand, the entrance of hydrogen expands the unit cell and increases the interatomic distances of Gd atoms. Since the $T_C$ depends on the exchange coupling constant (J) and this
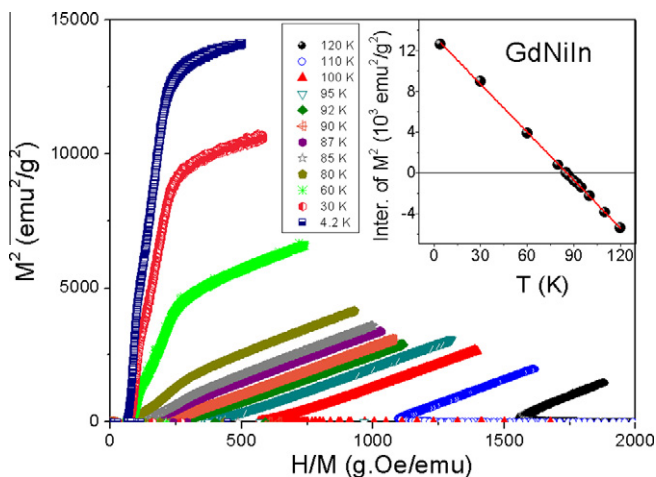
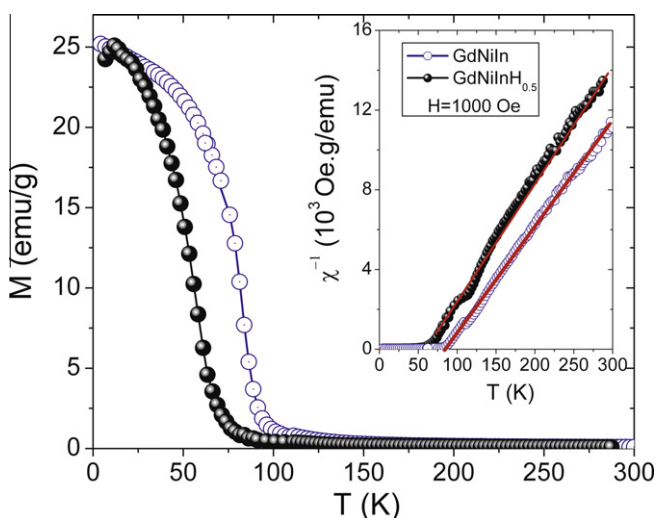**Fig. 4.** Arrot's plot obtained at the indicated temperatures for the GdNiIn compound.



**Fig. 5.** Magnetization as a function of the temperature curves for the intermetallic and the hydride compound obtained by applying a magnetic field of 1000 Oe. The inset shows the $\chi^{-1}$ vs. $T$ curves and their linear fits.

constant varies inversely with the interatomic distance, it is expect that the entrance of hydrogen leads to the decrease of the ferromagnetic Curie temperature in agreement with what is experimentally observed for the GdNiInH$_{0.5}$ compound studied in this work.

## 4. Conclusions

A single-phased GdNiIn intermetallic compound has been synthetized. The entrance of hydrogen to occupy $4h$ and $2d$ interstitial sites does not modify this crystalline structure, but it expands the unit cell in ~2% instead. The magnetic measurements reveal that the hydrogen presence modifies the magnetic properties of the GdNiIn compound. It has been determined that the effective magnetic moment of the intermetallic compound comes uniquely from the Gd atoms. However, the magnetic moment per formula unit decreases after the hydrogenation. This decrease has been speculatively interpreted as the result of the rising of a magnetic moment in Ni atoms induced by the presence of hydrogen. These H-induced magnetic moments must have an antiparallel orientation with respect to the magnetic moments of Gd atoms in GdNiInH$_{0.5}$. The increase in the interatomic distances must weaken the coupling constant of Gd–Gd atoms and that weakening results in a decrease of the ferromagnetic Curie temperature after the hydrogen absorption.

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