Hydrogenation Induced Structure and Property Changes in GdGa

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Abstract

Hydrides GdGaH_x were obtained by exposing the Zintl phase GdGa with the CrB structure to a hydrogen atmosphere at pressures from 1.5 to 50 bar and temperatures from 50 to 500 °C. Structural analysis by powder X-ray diffraction suggests that conditions with hydrogen pressures in a range between 15 and 50 bar and temperatures below 500 °C afford a uniform hydride phase with the NdGaH_{1.66} structure (*Cmcm*, $a = 3.9867(7)$ Å, $b = 12.024(2)$ Å, $c = 4.1009(6)$ Å) which hosts H in two distinct positions, H1 and H2. H1 is coordinated in a tetrahedral fashion by Gd atoms, whereas H2 atoms are inserted between Ga atoms. The assignment of the NdGaH_{1.66} structure is corroborated by first principles DFT calculations. Modeling of phase and structure stability as a function of composition resulted in excellent agreement with experimental lattice parameters when $x = 1.66$ and revealed the presence of five-atom moieties Ga-H2-Ga-H2-Ga in GdGaH_{1.66}. From in situ powder X-ray diffraction using synchrotron radiation it was established that hydrogenation at temperatures above 200 °C affords a hydride with $x \approx 1.3$, which is stable up to 500 °C, and that additional H absorption, yielding GdGaH_{1.66}, takes place at lower temperatures. Consequently, GdGaH_{1.66} desorbs H above $T = 200$ °C. Without the presence of hydrogen, hydrides GdGaH_x decompose at temperatures above 300 °C into GdH₂ and an unidentified Gd-Ga intermetallics. Thus the hydrogenation of GdGa is not reversible. From magnetic measurements the Curie-Weiss constant and effective magnetic moment of GdGaH_{1.66} were obtained. The former indicates antiferromagnetic interactions, the latter attains a value of $\sim 8 \mu_B$ which is typical for compounds containing Gd³⁺ ions.

I. Introduction

The great majority of rare earth (RE) metals form monogallides REGa which all crystallize with the orthorhombic CrB structure featuring linear zigzag chains of Ga atoms (Figure 1a) [1-3]. The REGa compounds display interesting magnetic properties and have recently attracted attention due to their potential as magnetocaloric materials [4-10]. In general they are ferromagnets and across the lanthanide series the Curie temperature T_C increases from 32 K for PrGa to a maximum of ~190 K for GdGa and then decreases to 15 K for TmGa [11-13]. On cooling, ferromagnetically ordered REGa compounds undergo spin reorientation transitions [4,7,8,14].

The ferromagnetic properties of REGa are a consequence of the coupling of magnetic moments arising from localized 4f electrons, which is mediated via conduction electrons according to the Ruderman-Kittel-Kasuya-Yosida (RKKY) coupling mechanism [15]. First principles calculations based on the RKKY interaction reproduce well observed ferromagnetic transition temperatures [16]. The validity of the RKKY coupling mechanism, however, contradicts the simple description of REGa compounds as Zintl phases [17]. Following the Zintl concept and assuming trivalent RE, Ga will correspond to six-electron species Ga^{3-} , which are connected to polyanionic zigzag chains via single bonds. Within this simple picture all valence electrons are then localized as bonds and lone pairs, i.e. a charge balanced Zintl phase $\text{RE}^{3+}\text{Ga}^{3-}$ with singly bonded chains would not leave any excess electrons for mediating ferromagnetic coupling.

To reconcile RKKY coupling within the Zintl concept one may assume that Ga is just reduced to Ga^{2-} species, now forming π -bonded zigzag chains in a charge imbalanced (electron excess) Zintl phase $\text{RE}^{3+}\text{Ga}^{2-}\text{e}^-$. Hydrogen incorporation in REGa represents a possibility to probe the electronic structure of REGa systems and, thus, to provide insight into the interplay between chemical bonding in the polyanion and magnetic properties. In particular, itinerant electrons may be localized as H^- through the formation of interstitial hydrides [18,19]. This should express in a change of the strength and possibly also the sign of the magnetic interaction. Provided that hydrogen uptake and desorption are easily reversible, one could even envision switchable magnetic properties with systems REGa/REGaH_x.

Previously we explored the structure and magnetic property changes of NdGa upon hydrogenation [20]. We found that NdGa transforms into a hydride NdGa_{1.66} by incorporating H into two distinct positions, H1 and H2. Interstitial H1 atoms are exclusively coordinated by RE atoms, whereas H2 atoms are inserted between Ga atoms and part of a two-dimensional Ga-H polyanion (Figure 1b). At the same time the magnetic interaction changed from ferromagnetic to antiferromagnetic nature. In this paper we report on the hydrogenation behavior of GdGa which possesses the highest T_C among REGa compounds.

II. Methods

1. *Synthesis.* GdGa was synthesized by arc-melting mixtures of pieces of Gd (99.99%, Sigma-Aldrich) and Ga (99.999%, Sigma-Aldrich) metal in a glove box. A slight excess of Gd (2 %) was applied. Sample batches corresponded to 0.5 – 1.0 g in total mass. To ensure homogeneity, samples were re-melted five times and flipped between each melting. The total mass loss was less than 1 %. Arc-melted GdGa samples were then heat-treated at 900 °C in an evacuated fused silica ampoule for 10 – 20 days and subsequently ground for hydrogenation experiments. Hydrogenous GdGa was produced by exposing GdGa in an autoclave to a H₂ atmosphere using temperatures from 50 to 600 °C, pressures from 1.5 to 80 bar, and dwelling times from 15 min to 20 h. GdGa and its hydrides appear stable in air.

2. *Structural Characterization of GdGa and hydrogenous GdGa.* Powder X-ray diffraction (PXRD) patterns of GdGa and hydrogenated GdGa samples were recorded on a Panalytical X'Pert Pro diffractometer in θ -2 θ diffraction geometry employing CuK α radiation ($\lambda = 1.5418$ Å). For room temperature measurements powder samples were mounted on a Si wafer zero-background holder and diffraction patterns were measured in a 2 θ range 5 - 90°. For high temperature PXRD studies powder samples were heated in dynamic vacuum ($\sim 10^{-5}$ bar) to 450 °C using an Anton Paar XRK 900 chamber equipped with Be windows and connected to a temperature controller. Data in a 2 θ range 20 – 50° were collected from 100 °C in steps of 50 °C, 20 min acquisition time and 3 °C/min heating rate between the steps. The Rietveld method [21] as implemented in the FullProf program [22] was used for structure and phase analysis. Structure refinements were based on the established structure models for GdGa [2] and NdGaH_{1.66} [20].

3. *In-situ diffraction.* The hydrogen uptake of GdGa was studied in situ by PXRD using synchrotron radiation at the I711 beam line ($\lambda = 0.991$ Å) at the MAX-IV laboratory [23]. A small amount of powder sample was placed in a fused silica capillary which was in turn placed in a single crystal sapphire tube mounted in a sample cell. This cell is dedicated for in situ studies using high gas pressures, high temperatures as well as magnetic fields [24, 25]. The sample was subjected to 20 bar H₂ after being flushed three times with high purity Ar. Subsequently the sample was heated with a constant rate from room temperature to 500 °C using a Kanthal resistive wire coiled around the sapphire tube and then cooled to room temperature. During the experiment a series of diffractograms were recorded using a Titan area CCD detector. The resulting data was reduced from 2D images to 1D diffractograms using the FIT2D software [26]. Sequential Rietveld refinement with the FullProf program [22] was performed to obtain the lattice parameters as a function of time (and temperature). The background was refined as a six-coefficient polynomial and the peaks were described by a Lorentzian function. After fitting the background, peak function, lattice parameters and scale factor to the first pattern the sequential refinement was performed. During the sequential refinement nine parameters were refined: five background parameters; the a , b and c lattice parameters and the scale factor.

4. *Computations.* The theoretical calculations of the electronic structure and total energies of GdGa and structure models for GdGaH _{x} ($1 \leq x \leq 2$) were performed using the first-principles

all-electron projector augmented waves (PAW) method [27,28] within the Vienna *ab initio* Simulation Package (VASP) [29,30]. Exchange-correlation effects were treated within the generalized gradient approximation (GGA) via the Perdew–Burke–Ernzerhof parametrization PBE [31]. A conjugate gradient algorithm was used to relax the atomic nuclei positions to a local minimum in the total energy landscape. Structure relaxations for GdGaH_x did not employ any symmetry restrictions. The findsym program [32] was used to check for symmetry of atom arrangements after relaxations. Forces were converged to better than 10⁻³ eV/Å. The plane wave basis set was terminated at a kinetic energy cutoff of 600 eV. Partial occupancy of hydrogen was accounted for in a 3 × 1 × 1 supercell based on the orthorhombic CrB type structure with Z = 12 and considering the compositions GdGaH_{1.33}, GdGaH_{1.50}, GdGaH_{1.66}. The number of calculations of random H distributions was large enough so that convergence was reached in the total energy, i.e. adding more calculations of random distributions made insignificant difference to the mean total energy. Stoichiometric GdGa, GdGaH and GdGaH₂ were calculated both within a 3 × 1 × 1 supercell and a single unit cell (Z = 4). The heat of formation, referring to zero Kelvin, is given by:

$$\Delta H = 1/x [(E(\text{GdGaH}_x) - E(\text{GdGa}) - x/2 E(\text{H}_2))] \quad (1 \leq x \leq 2)$$

where E denotes the total energy of the in brackets enclosed system. The number of H atoms in the calculation is denoted by x. For the H₂ molecule, a box of 8 × 8 × 8 Å³ dimensions was used with Γ -point sampling of the Brillouin zone. Electronic structure calculations for single unit cells used a grid of 21 × 7 × 21 k-points to sample the Brillouin zone [33]. For this work theoretical calculations were used for assessing structural variations and enthalpy changes upon H incorporation. As both GdGa and its hydrides do not show magnetic correlations at temperatures above 200 K the contribution of magnetic coupling to total energies was assumed negligible. Hence, for simplicity, all systems were treated as non-magnetic and calculations were thus non spin-polarized.

5. Magnetic Measurements. Magnetization measurements were performed as a function of temperature using a Quantum Design MPMS SQUID magnetometer. M vs. T measurements were done both at low field (H = 4 kA/m) in order to determine the transition temperature of the samples, as well as in high field (H = 80 kA/m) in order to do a Curie-Weiss fit and estimate the effective number of bohr magnetons (μ_{eff}) and Curie-Weiss temperature (Θ_{CW}) of the samples. M vs. H measurements were performed using a Quantum Design PPMS VSM magnetometer at 6K in the field range of ±7200 kA/m to determine the saturation magnetization as well as study the field dependence of the samples.

III. Results and Discussion

A. Hydrogenation behavior of GdGa.

GdGa was exposed to a hydrogen atmosphere at various conditions in order to explore temperature, pressure and time aspects of the hydrogenation reaction. Figure 2 shows selected PXRD patterns of reaction products when varying temperature and pressure, respectively, and

keeping dwelling time constant (2 h). GdGa is remarkably susceptible to H uptake. As a matter of fact, kinetic barriers appear to be small. Quantitative hydride formation is observed at lowest T in the temperature series (~50 °C, 20 bar) and lowest p in the pressure series (~1.5 bar, 100 °C). The great similarity of the PXRD patterns of obtained products from reactions performed between 50 and 400 °C and at a pressure of 20 bar suggests that a uniform hydride was obtained. At higher temperatures (above 500 °C) GdH₂ can be identified in the PXRD, which indicates H-induced oxidative decomposition of GdGa [18]. When varying pressure (and keeping annealing temperature constant at 100 °C) the hydride seen in the temperature series is produced between 15 and 50 bar. At lower pressures differences in the PXRD patterns indicate the formation of different (“intermediate”) hydrides. Similar to high temperatures, high hydrogen pressures (80 bar) result in a decomposition of GdGa (formation of GdH₂).

The diffraction patterns of the temperature series can be indexed in a *C*-centered orthorhombic cell with lattice parameters $a \approx 3.99$ Å, $b \approx 12.02$ Å, $c \approx 4.10$ Å resembling the ones of the starting material GdGa ($a = 4.340(3)$ Å, $b = 11.012(2)$ Å, $c = 4.105(3)$ Å (cf. Figure S1 in the supporting information)). This is similar to NdGa for which hydrogenation leads to a phase NdGaH_{1.66} with lattice parameters closely related to the starting material. As a matter of fact, the PXRD patterns of the uniform hydride product can be satisfactorily fit to the NdGaH_{1.66} structure model (Figure 3a). When applying it to the data of “intermediate” hydrides obtained at H₂ pressures below 15 bar unindexed peaks remain (Figure 3b), which may be accounted for by doubling the *a* or *c* axis (or both) with respect to the original *C*-centered orthorhombic cell. Results of the *Cmcm* structure refinements are compiled in Table 1.

In conclusion, the T and p dependent hydrogenation reactions with GdGa suggest great similarities to earlier investigated NdGa [20]. We assign the hydride phase yielding a *C*-centered orthorhombic PXRD pattern to GdGaH_{1.66} – in analogy with NdGa. This assignment is strongly supported by DFT simulations of GdGaH_x structures with $x > 1$ (see below). We note that the exceptionally high neutron capture cross section of Gd prohibits the application of neutron diffraction for structural analysis of hydrogenous GdGa.

To investigate the time aspect of GdGa hydrogenations we performed an in situ PXRD experiment where GdGa was heated to 500 °C in a hydrogen atmosphere of 20 bar at a rate of 10 °C/min and subsequently cooled. The results are compiled in Figure 4. Upon heating PXRD patterns changed abruptly after 35 min (~370 °C), and more subtly and gradually upon cooling at temperatures below 200 °C (Figure 4a). The diffraction patterns were indexed in a *C*-centered orthorhombic cell and Figure 4b shows the relative change of the cell parameters with respect to the starting material GdGa. The structure change upon heating corresponds to an expansion of the *b* axis and a contraction of the *a* axis by 7.5 and 6.5%, respectively. (At 500 °C diffraction peaks from GdH₂ appear, which is consistent with the observation from ex-situ investigations, see above). The structure change upon cooling corresponds to a further increase of *b*/decrease of *a*. During heating and cooling the *c* parameter varies only very slightly. In Figure 4b are inserted the values from DFT simulations for phases GdGaH_{1.0}, GdGaH_{1.33} and GdGaH_{1.66}. It can be recognized that there is a close correspondence of the

parameters of the product after cooling (which is identical to that obtained from ex-situ experiments at 20 bar H_2) with the ones of the simulated $GdGaH_{1.66}$ structure.

There are two important observations with the in situ experiment: (i) Hydrogenation proceeds already at low temperatures (as seen in the gradual change of lattice parameters) and above ~ 350 °C kinetic barriers are absent (abrupt change of lattice parameters). Hydrogen absorption at these (high) temperatures leads to the formation of a hydride phase $GdGaH_{\sim 1.3}$ which is stable to up to 500 °C (onset of decomposition). (ii) At lower temperatures (below 200 °C) additional H is absorbed leading to a hydride $GdGaH_{1.66}$, which is also the final product in synthesis experiments using H_2 pressures above 15 bar. Consequently, $GdGaH_{1.66}$ is thermally labile. When heating $GdGaH_{1.66}$ in dynamic vacuum ($\sim 10^{-5}$ bar) and recording simultaneously PXRD patterns, changes are apparent already at 100 °C (see supporting information, Figure S2). At temperatures above 300 °C hydrogenous GdGa decomposes into GdH_2 and a poorly crystalline Gd-Ga intermetallics which could not be identified. Thus, in contrast with NdGa the hydrogenation of GdGa is not reversible. It is clear that the hydride phase $GdGaH_x$ ($x = 1 - 1.33$) seen in the in situ experiment between 200 and 500 °C (in the presence of H_2) cannot be obtained from desorption experiments. We also observed that $GdGaH_{1.66}$ samples lose H over time when storing at room temperature (see supporting information, Figure S3).

B. Structural variations and energetics of H incorporation

In the orthorhombic CrB type structure of GdGa (space group *Cmcm*, $Z = 4$) both Gd and Ga atoms are situated on sites 4c (0,y,1/4). Ga atoms center Gd_6 trigonal prisms and form polyanionic zigzag chains running along [001]. The arrangement of Gd atoms in “Ga-free” layers corresponds to an array of edge sharing tetrahedra (cf. Figure 1). The center of these tetrahedra, which also corresponds to a 4c site, is occupied by H in the $NdGaH_{1.66}$ structure. Its structure was unambiguously characterized from powder neutron diffraction data (Figure 1b). The tetrahedral, interstitial, H position was termed H1. Additional H (H2) is incorporated between Ga atoms of neighboring chains. The H2 position is partially occupied ($\sim 2/3$). The implications of two chemically different H for $NdGaH_{1.66}$, interstitial H1 primarily leading to an oxidation of the Ga polyanion and H2 being part of a novel two-dimensional polyanion $[GaH]^{2-}$, have been described in detail [20].

For structure analysis of hydrogenous GdGa neutron diffraction cannot be applied. However, the structural consequences of H incorporation in GdGa can be assumed to be very similar to NdGa. In order to corroborate this (and also to obtain insight into the distribution of H in hydrogenous GdGa) structure and phase stability of various compositions $GdGaH_x$ ($x \geq 1$) were investigated by DFT calculations. The salient results are presented in Table 2 and as supporting information, Table S1. First we note that the *Cmcm* structure of GdGa is excellently reproduced by DFT structure optimization (cf. Tables 1, 2, S1), which validates the use of non spin-polarized calculations for this purpose. The occupation of the H1 position is energetically preferred over H2 (by 0.43 eV per formula unit $GdGaH$) and, thus, is assumed to represent the first step in the hydrogenation of GdGa. The transition from GdGa to $GdGaH$ with the H1 position filled is accompanied with a shortening of the *a* and an elongation of the *b* axis by 7.2 and 6.0%, respectively. This trend proceeds gradually when filling the H2

position up to $x = 0.66$. At the same time the c parameter (which coincides with the direction of the Ga zigzag chains in the $Cmcm$ structure) changes very little. As already mentioned, the calculated changes of the lattice parameters compare well with the observation of the in situ PXRD experiment. It is interesting to note that the associated changes of the unit cell volume are minute. As a matter of fact, $GdGaH_{1.66}$ attains virtually the same unit cell volume as the starting material $GdGa$. Upon completely filling of the H2 position (and thus arriving at a hydride composition $GdGaH_2$) the trend in the cell parameter changes is reversed, i.e. when going from $x = 1.66$ to 2 the a parameter increases and the b parameter decreases.

Figure 6 shows the evolution of structures when going from $x = 1$ to 1.66 according to DFT modeling. $GdGaH$ with a fully occupied H1 position ($x = 1$) was described with a single unit cell ($Z = 4$). Partial occupancy of the H2 position ($x > 1$) was simulated by model structures using a $3 \times a$ supercell containing 12 formula units. For $x = 1.33$ the most stable arrangement corresponds to H2 atoms connecting two neighboring Ga zigzag chains into three-atom Ga-H-Ga strands. H2 atoms are symmetrically located between two Ga atoms at a distance 2.11 Å. In addition, this structure model contains original Ga-Ga zigzag chains. The ratio between zigzag chains and three-atom strands is 1:1. In the most stable arrangement for $x = 1.66$ H2 atoms bridge all Ga zigzag chains into five-atom strands Ga-H-Ga-H-Ga. Here H2 atoms are asymmetrically located between two Ga atoms at distances 1.92 and 2.33 Å. (For more details see supporting information, Table S1). The calculated powder pattern for this $GdGaH_{1.66}$ model (Figure 6b) matches very well the experimental pattern of the uniform hydride product obtained from hydrogenations using pressures above 15 bar (Figure 2, 3a).

The electronic density of states (DOS) of stoichiometric $GdGa$, $GdGaH$ and $GdGaH_2$ is shown as supporting information, Figure S3. The energy of formation of $GdGaH_x$ according to $GdGa + x/2 H_2$ is shown in Figure 7 and compared with $NdGa + x/2 H_2$. Upon filling the H2 position (i.e. for $1 < x \leq 2$) its magnitude decreases in a linear fashion with increasing x . This is similar to $NdGaH_x$ but values for $GdGaH_x$ are lower. This may relate to its different desorption behavior. $NdGaH_{1.66}$ desorbs H in two distinct steps, at around 250 and 450 °C, after which CrB-type $NdGa$ is quantitatively reformed [20]. In contrast, although $GdGaH_{1.66}$ starts desorbing H below 200 °C $GdGa$ is not obtained by thermal decomposition. It appears likely that in the early desorption products both H1 and H2 positions are partially occupied. The same may be the case for products from hydrogenations at low p (below 15 bar, i.e. the intermediate hydrides). The diffraction patterns of hydrogenous $GdGa$ from both processes are similar (cf. Figure 2b, Figures S2 and S3).

C. H-induced magnetic property changes

$GdGa$ is known to be ferromagnetic with a reported T_C of ~190 K and a spin reorientation at 85 K [4,14,16,33,34]. A similar behavior is confirmed in our sample; Figure 7a shows zero field cooled (ZFC) and field cooled (FC) magnetization vs. temperature curves of $GdGa$ measured in an applied field of 4 kA/m. The sharp rise of the magnetization at about 180 K indicates the ferromagnetic transition and the peak close to 70 K reflects the spin reorientation. There is a substantial change in the behavior of the magnetization after hydrogenation, as seen in Figure 7b (which shows ZFC and FC magnetization vs. temperature

curves for GdGaH_{1.66} in an applied field of 4 kA/m) indicating an antiferromagnetic transition by the sharp maxima at about 45 K. The separation between the ZFC and FC curves at temperatures below the transition temperature reveals a weak excess moment due to formation of spin domains with residual ferromagnetic components. In order to fit the behavior at higher temperatures to the Curie-Weiss law ($C/(T-\theta_{CW})$), data for both samples were also recorded at a higher field, 80 kA/m. The derived Curie-Weiss constant θ_{CW} and the effective number of bohr magnetons (μ_{eff}) are tabulated in Table 3. Both GdGa and GdGaH_{1.66} have an effective magneton number close to 8, which is the expected number for Gd³⁺. As in the case of NdGa [20] there is a change of sign of θ_{CW} after hydrogenation, again indicating that GdGa transforms from a ferromagnet to an antiferromagnet upon hydrogenation. The full hysteresis curve of GdGa plotted in Figure 7c shows typical ferromagnetic behavior with a low coercive field of ~5 kA/m and an expected saturation magnetization amounting to about 6.9 μ_B /Gd. On the other hand, the antiferromagnetic low temperature state of GdGaH_{1.66} is certified by Figure 7d which shows a linear increase of the magnetization as a function of magnetic field at 6 K. Because GdGaH_{1.66} easily desorbs H, we checked and confirmed the integrity of the sample after the magnetization measurement by PXRD.

IV. Conclusions

GdGa absorbs hydrogen at slightly elevated temperatures. Structural analysis by a combination of X-Ray powder diffraction and DFT modeling suggests that conditions with hydrogen pressures above 15 bar yield GdGaH_{1.66} with the NdGaH_{1.66} structure. GdGaH_{1.66} desorbs H above $T = 200$ °C. Without the presence of hydrogen, hydrides GdGaH_x decompose at temperatures above 300 °C into GdH₂ and an unidentified Gd-Ga intermetallics. Thus the hydrogenation of GdGa is not reversible. This is in contrast with the system NdGa/NdGaH_{1.66} which exhibits reversible H storage capability [20]. Hydrogenation induces a change in the magnetic properties: coupling changes from being ferromagnetic in GdGa to antiferromagnetic in GdGaH_{1.66}. The effective number of bohr magnetons is close to that of GdGa above T_c , indicating that Gd possesses the same oxidation state (+3) in both systems.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at XXXXX

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Figures

Figure 1

a) *Cmcm* CrB-type structure of rare earth (RE) monogallides. RE and Ga atoms are depicted as grey and red circles, respectively. RE atoms are arranged as slabs of trigonal prisms hosting linear zigzag chains of Ga atoms. b) The crystal structure of $\text{NdGaD}_{1.66}$. H atoms are depicted as green circles. Stacking of slabs of RE_6 trigonal prisms in the CrB structure produces layers of edge sharing tetrahedra which are centered by H (H1) atoms. Additional H atoms (H2, not fully occupied) are inserted between Ga atoms which results in quasi linear fragmented chains -Ga-H2-.

Figure 2

PXRD patterns ($\lambda = 1.5418 \text{ \AA}$) of products from the hydrogenation of GdGa at (a) $p = 20 \text{ bar}$ and over a T range of $50 - 600 \text{ }^\circ\text{C}$, (b) at $T = 100 \text{ }^\circ\text{C}$ and over a p range of $1.5 - 80 \text{ bar}$. Dwelling time was 2 h for all experiments. The pattern of the GdGa starting material is shown as black line. Red patterns: hydride phase $\text{GdGaH}_{1.66}$; green patterns: intermediate hydride phase; blue patterns: decomposed products (reflections from GdH_2 are marked with asterisks).

Figure 3

Rietveld fits to the PXRD data of hydrogenous GdGa samples obtained from annealing GdGa for two hours at 100 °C and (a) 20 bar H₂ pressure and (b) 10 bar H₂ pressure. The structure model of NdGaH_{1.66} can be fit satisfactorily to the data of the sample obtained at 20 bar. When applying it to the data of the sample obtained at 10 bar (“intermediate hydride phase”, cf. Figure 2b) unindexed peaks remain (the most prominent ones are marked by arrows), which may be accounted for by a 2×a or 2×c supercell of the NdGaH_{1.66} (*Cmcm*) structure.

Figure 4

a) Densitometric view of the in-situ PXRD patterns ($\lambda = 0.991 \text{ \AA}$) recorded during heating and cooling of GdGa using 20 bar H_2 pressure. b) Relative change of lattice parameters as a function of time (red). DFT-calculated changes for GdGaH, GdGaH_{1.33} and GdGaH_{1.66} are inset as green, blue, and orange symbols, respectively.

Figure 5

Compilation of DFT relaxed structures for GdGaH_x (a) and corresponding powder patterns (b). The calculated patterns for GdGaH_{1.66} and GdGaH_{1.33} relate to the experimental PXRD patterns shown in Figure 3a and 3b, respectively.

Figure 6

Heat of formations $\text{REGa} + x/2 \text{H}_2 = \text{REGaH}_x$ as a function of x . (RE = Gd (upper line) and Nd (lower line)). $x = 1.0$ corresponds to REGaH ($Z = 4$ cell). $x = 1.33, 1.5, 1.66, 2.0$ represent results from $3 \times a$ supercell ($Z = 12$) calculations. The line connects average values from 50 random starting configurations, and the red bars indicate the standard deviation. Blue symbols represent the obtained lowest energy values.

Figure 7

Top: Zero field cooled M vs T curves of (a) GdGa and (b) $\text{GdGa(H)}_{1.66}$ at $H = 4$ kA/m. Bottom: M vs H curves at $T = 6$ K for (c) GdGa and (d) $\text{GdGa(H)}_{1.66}$

Tables:

Table 1. Crystallographic data and structure refinement for GdGa and GdGaH_{1.66} from PXRD data (T = 295 K)

empirical formula	GdGa	GdGaH _{1.66} 20 bar/100 °C	GdGaH _x 10 bar/100 °C
space group	<i>Cmcm</i>	<i>Cmcm</i>	<i>Cmcm</i>
unit cell (Å)	<i>a</i> = 4.340(3) <i>b</i> = 11.012(2) <i>c</i> = 4.105(3)	<i>a</i> = 3.9867(7) <i>b</i> = 12.024(2) <i>c</i> = 4.1009(6)	<i>a</i> = 4.038(7) <i>b</i> = 11.77(2) <i>c</i> = 4.109(6)
Gd 4c (0,y,1/4)	0.1414(3)	0.151(2)	0.1509(3)
Ga 4c (0,y,1/4)	0.4245(5)	0.445(5)	0.4457(7)
<i>V</i> (Å ³)	196.2(4)	196.6(5)	195.4(5)
<i>R</i> _f	2.05	2.40	2.47
<i>R</i> _{wp}	2.65	3.06	3.39

Table 2. Lattice parameters and unit cell volumes of DFT optimized structures GdGaH_x. Relative changes (in %) with respect to GdGa (x = 0) are given in parentheses. (See also Table S1, supporting information)

composition	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	<i>V</i> (Å ³)
0	4.3891	11.0250	4.0970	198.3
1	4.0728 (-7.2)	11.6885 (+6.0)	4.1199 (+0.5)	196.1 (-1.1)
1.33	4.0346 (-8.1)	11.8071 (+7.1)	4.1105 (+0.3)	195.8 (-1.2)
1.50	4.0298 (-8.2)	11.9021 (+8.0)	4.1022 (+0.1)	196.8 (-0.8)
1.66	4.027 (-8.3)	12.0092 (+8.9)	4.0906 (-0.2)	197.8 (-0.2)
2	4.1023 (-6.5)	11.8529 (+7.5)	4.0834 (-0.3)	198.5 (+0.1)

Table 3. Effective number of bohr magnetons (μ_{eff}) and Curie-Weiss constants (θ_{CW}) obtained from Curie-Weiss fits to the high temperature susceptibility data.

Sample	μ_{eff}	θ_{CW} (K)
GdGa	8.4	190
GdGaH _{1.66}	7.9	-13

TOC

Ferromagnetic GdGa absorbs hydrogen in two steps to yield antiferromagnetic GdGaH_{1.66}.

GdGa

GdGaH_{1.66}