LaMg$_2$NiH$_7$, a novel quaternary metal hydride containing tetrahedral [NiH$_4$]$^{4-}$ complexes and hydride anions

G. Renaudin, L. Guénéé, K. Yvon

Laboratory of Crystallography, University of Geneva, 24 quai Ernest Ansermet, 1211 Geneva, Switzerland

Received 13 July 2002; accepted 22 July 2002

Abstract

A new ternary compound of composition LaMg$_2$Ni has been found and investigated with respect to structure and hydrogenation properties. It crystallizes with the orthorhombic MgAl$_2$Cu type structure (space group Cmcm, $a=4.2266(6)$, $b=10.303(1)$, $c=8.360(1)$ Å; $V=364.0(1)$ Å$^3$; $Z=4$) and absorbs hydrogen near ambient conditions ($<200^\circ$C, <8 bar) thereby forming the quaternary metal hydride LaMg$_2$NiH$_7$. Neutron powder diffraction on the deuteride revealed a monoclinic distorted metal atom substructure (LaMg$_2$NiD$_7$; space group $P2_1/c$, $a=13.9789(7)$, $b=4.7026(2)$, $c=16.0251(8)$ Å; $\beta=125.240(3)^\circ$, $V=860.39(8)$ Å$^3$; $Z=8$) that contains two symmetry independent tetrahedral [NiD$_4$]$^{4-}$ complexes with Ni–D bond lengths in the range 1.49–1.64 Å, and six D$^-$ anions in tetrahedral metal configuration with bond distances in the ranges 1.82–2.65 Å (Mg) and 2.33–2.59 Å (La). The compound constitutes a link between metallic ‘interstitial’ hydrides and non-metallic ‘complex’ metal hydrides.

Keywords: Rare earth compounds; Hydrogen absorbing materials; Metal hydrides; Crystal structure; Neutron diffraction

1. Introduction

During our search of new hydrogen storage materials we have recently discovered a new ternary compound of composition LaMg$_2$Ni that occurred as a minority phase in LaNi$_5$Mg samples [1]. X-ray powder diffraction indicated an orthorhombic MgAl$_2$Cu type structure [2] that is an ordered derivative of the Re$_2$B type structure [3]. Binary compounds crystallizing with the Re$_2$B type structure are currently investigated with respect to hydrogen storage properties such as Zr$_2$Fe [4,5], Zr$_2$Co [6] and Zr$_2$NiO$_3$ [7]. In this work LaMg$_2$Ni and its hydride (deuteride) are studied by X-ray single crystal diffraction and neutron and synchrotron powder diffraction, respectively. It will be shown that LaMg$_2$Ni reacts with hydrogen to form a quaternary metal hydride of composition LaMg$_2$NiH$_7$. The compound contains [NiH$_4$]$^{4-}$ complexes and H$^-$ anions and thus constitutes a link between typically metallic ‘interstitial’ hydrides such as Zr$_2$FeH$_x$ [4,5], Zr$_2$CoH$_x$ [6] and Zr$_2$NiO$_3$H$_y$ [7] and non-metallic ‘complex’ hydrides such as Mg$_2$NiH$_4$ [8].

2. Experimental

2.1. Synthesis

Samples of nominal composition LaMg$_2$Ni were melted by placing compressed mixtures of La files (Johnson Mathey, 99.99%) and Mg$_2$Ni powder (Hy-Store alloy 301) in an induction furnace. The ingots (~5 g) were crushed into several pieces and powdered under protective argon atmosphere for the purpose of isolating suitable single crystals. X-ray powder diffraction showed that the sample was single-phase and contained the expected ternary compound LaMg$_2$Ni having a C-centred orthorhombic MgAl$_2$Cu-type structure and cell parameters as reported previously ($a=4.21$, $b=10.27$, $c=8.34$ Å [1]). Various hydrogenation experiments were performed. A sample (~0.05 g mass) was placed into a microbalance (Hiden...
Analytical, model IGA001) and hydrogenated at various temperatures (25–400 °C) and pressures (0.01–8 bar). Absorption occurred in one step below 200 °C and led to a hydrogen content of ~7 H atoms per formula unit. This sample was used for subsequent synchrotron diffraction measurements. Another sample was placed on an X-ray powder diffractometer that was equipped with a high-temperature chamber (XRK PAAR) and allowed to work in hydrogen atmosphere. Diffraction patterns were recorded from room temperature up to 673 K under 5 bar H₂ pressure. They showed sharp peaks that could be attributed to the hydrogen free compound below 150 °C and to hydride formation between 150 and 200 °C, and broad peaks suggesting the onset of amorphization. Hydrogenation experiments in an autoclave at temperatures above 300 °C showed that LaMg₂Ni decomposed into the binary hydride LaH₃ and an amorphous phase. However, due to the exothermic nature of the reaction the exact decomposition temperature presumably depends on sample mass. For the neutron diffraction experiment ~4 g of the alloy powder was filled into a steel container and placed into an autoclave that was evacuated. After increasing the temperature to 100 °C for one night deuterium was allowed to enter at a pressure of 5 bar, while the temperature was slowly increased to 200 °C and kept at that level for 24 h. The deuteride obtained had dark grey colour and was stable in air.

2.2. Structure analysis

A single crystal of LaMg₂Ni was measured on a X-ray diffractometer (STOE IPDS) equipped by an image plate (MoKα radiation). The refined cell parameters (a = 4.2266(6), b = 10.303(1), c = 8.360(1) Å, V = 364.0(1) Å³) were consistent with those reported previously [1] and the systematic extinctions indicated space group Cmcm. A structure refinement was performed by placing La, Mg and Ni on the Re1 (4c), Re2 (8f) and B (4c) sites, respectively, of the Re₃B-type structure [3], and by varying the scale factor and 14 atomic parameters (programme Xtal3.7 [9]). Results are summarised in Table 1. A hydride sample was measured by synchrotron powder diffraction because laboratory X-ray data indicated a symmetry lowering during hydrogenation (average space group Pnma, a = 8.0329(6), b = 4.7159(4), c = 11.4553(9) Å; V = 433.95(6) Å³, Z = 4). The experiment was performed on the Swiss–Norwegian beam lines (BM1) at ESRF (Grenoble) in Debye–Scherrer geometry (six Si(111) analysers in the diffracted beam, λ = 0.49949 Å, 2θ range 2.46–27.00°, step size 2θ = 0.01°, glass capillary of 0.3 mm diameter). The data (not shown here) revealed a monoclinic lattice distortion and a doubling of the cell volume (a = 14.0164(6), b = 4.7146(2), c = 16.0572(8) Å, β = 125.222(2)°; V = 866.83(6) Å³, Z = 8). The systematic extinctions indicated space group P2₁/c. The metal atom substructure was solved ab-initio by the program fox [10] and found to consist of two La, two Ni and four Mg sites (all on 4e). The hydrogen positions were determined from neutron data as collected on the deuteride sample by using the high-resolution powder diffractometer D2B at ILL (Grenoble) under the following experimental conditions: wavelength λ = 1.594 Å; 2θ range 6–159°; step size 2θ = 0.05°; temperature 293 K; cylindrical vanadium container (8 mm inner diameter). As expected, the refined cell parameters (a = 13.9789(7), b = 4.7026(2), c = 16.0251(8) Å, β = 125.240(3)°; V = 860.39(8) Å³, Z = 8) were slightly smaller than those obtained for the hydride by the synchrotron data. No impurity phase was detected and vanadium contributed only marginally to the diffraction pattern. Fourteen deuterium sites in general position 4e of space group P2₁/c were located ab-initio by the program fox [10], and a complete structure refinement was performed by Fullprof.2000 [11]. The following 81 parameters were allowed to vary: one scale, 5 profile, 4 cell and 71 atomic (66 positional and five displacements). No indication for a partial occupancy of the deuterium sites was found. The observed and calculated diffraction pattern are presented in Fig. 1 and the refinement results are summarised in Table 2. Attempts to perform joint structure refinements by using the synchrotron data of the hydride and the neutron data of the deuteride did not improve the accuracy of the results.

Table 1
X-ray structure refinement results on a single crystal of LaMg₂Ni

<table>
<thead>
<tr>
<th>Atoms</th>
<th>Site</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>U(eq) (Å²)</th>
<th>Occupancy</th>
</tr>
</thead>
<tbody>
<tr>
<td>La</td>
<td>4c</td>
<td>0</td>
<td>0.44029(2)</td>
<td>1/4</td>
<td>0.0156(2)</td>
<td>1.0</td>
</tr>
<tr>
<td>Ni</td>
<td>4c</td>
<td>0</td>
<td>0.72661(6)</td>
<td>1/4</td>
<td>0.0181(3)</td>
<td>1.0</td>
</tr>
<tr>
<td>Mg</td>
<td>8f</td>
<td>0</td>
<td>0.1543(1)</td>
<td>0.0552(1)</td>
<td>0.0170(5)</td>
<td>1.0</td>
</tr>
</tbody>
</table>

Anisotropic displacement amplitudes (Å²)

<table>
<thead>
<tr>
<th>Atoms</th>
<th>U₁₁</th>
<th>U₂₂</th>
<th>U₃₃</th>
<th>U₁₃</th>
<th>U₁₂</th>
<th>U₂₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>La</td>
<td>0.0153(2)</td>
<td>0.0148(2)</td>
<td>0.0167(2)</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Ni</td>
<td>0.0174(3)</td>
<td>0.0196(3)</td>
<td>0.0175(3)</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Mg</td>
<td>0.0172(5)</td>
<td>0.0176(5)</td>
<td>0.0161(5)</td>
<td>0</td>
<td>0</td>
<td>0.0002(4)</td>
</tr>
</tbody>
</table>

Space group Cmcm, a = 4.2266(6), b = 10.303(1), c = 8.360 (1) Å, V = 364.0(1) Å³; refinement on F², agreement factors Rₑ = 2.0%, wRₑ = 2.3%; GoF=1.49; 1085 measured reflections, 218 unique reflections, R(F) = 10.1%, electron density residuals ±1.1 eÅ⁻³.
3. Results and discussion

LaMg$_2$Ni crystallizes with the orthorhombic MgAl$_2$Cu$_2$ type structure. Similar to the structurally related binary compounds Zr$_2$Fe, Zr$_2$Co and Zr$_2$NiO$_4$, it reacts with hydrogen to yield a quaternary metal hydride of composition LaMg$_2$NiH$_4$ and calculated hydrogen storage efficiencies of 2.8 wt.% and 109.5 g l$^{-1}$. In contrast to the zirconium based hydrides, however, that have partially disordered hydrogen distributions and remain orthorhombic LaMg$_2$NiH$_4$, displays an ordered hydrogen atom distribution and shows a monoclinic lattice distortion. The cell parameter relationships between the alloy (o) and the hydride (m) are $a$ and $c$.

The overall structure of the deuteride is shown in Fig. 2. Clearly, it contains two sorts of deuterium atoms. One appears as a terminal ligand around two symmetry independent nickel sites (see shaded polyhedra around Ni1 and Ni2) while the others are surrounded by lanthanum and magnesium only. The detailed configurations and metal atom environments are shown in Figs. 3 and 4. While the deuterium atoms bonded to nickel (Ni1: D11–D14; Ni2: D21–D24; Fig. 3a1,a2) form tetrahedral complexes reminiscent of those in ‘complex’ transition metal hydrides [12] such as Mg$_2$NiH$_4$ and MMgNiH$_4$ (M=Ca,
Fig. 2. Monoclinic structure of LaMg$_2$NiD$_{3}$. Space group $P2_1/c$, projection along [010], shaded atom polyhedra around Ni1 and Ni2 enlarged in Fig. 3.

Fig. 3. Tetrahedral [NiD$_4$]$^{4-}$ complexes around Ni1 (a1) and Ni2 (a2) and their cation environments in LaMg$_2$NiD$_{3}$, as compared with those in Mg$_2$NiD$_{4}$ (b) and MMgNiD$_{4}$ (M=Ca, Sr, Eu, Yb) (c). Atom labels in a1 and a2 according to list of coordinates. Figures in bold: Ni–D bond lengths (Å); figures in italics: shortest distances between cations and terminal hydrogen ligands; values in c for M=Ca; e.s.d.’s of bond lengths in LaMg$_2$NiD$_{3}$ are ±0.02 Å.
other complex metal hydrides containing symmetry independent complexes such as $K_2ReH_6$ (two $[ReH_6]^{2-}$ [16,17]), $Mg_2CoH_{11}$ (one $[CoH_4]^{2-}$ and three $[CoH_5]^{2-}$ [18]), $Mg_2IrH_{11}$ (one $[IrH_5]^{2-}$ and three $[IrH_6]^{3-}$ [19]) and $Mg_8RhH_{23}$ ($M$ = Ca, Sr) (one $[RhH_6]^{3-}$, one $[RhH_{12}]^{9-}$ and one $[RhH_5]^{4-}$ [20,21]) in which the complexes differ more strongly. As to the deuterium–
˚cation distances in $LaMgNiD$ ($D$–Mg = 1.82–2.65 Å; $D$–La = 2.33–2.59 Å) they are consistent with the sum of ionic radii, except for the anomalous long Mg–D distances ($D$ = 2.65 Å) and Mg–D = 2.63 Å) that suggest a distorted triangular $[LaMg]$ rather than a tetrahedral $[LaMg]$ coordination (Fig. 4). As expected, the D–D contact distances are relatively long ($D$–D = 2.1 Å) and consistent with repulsive D–D interactions.

In conclusion, the $LaMgNi$–$LaMgNiD$ system provides another example for a hydrogenation induced hydrido complex formation in a metallic compound, the other known examples being $MgNi$–$MgNiD$ (rusty coloured hydride) and $MgIr$–$MgIrH$ (red coloured hydride). Whether or not a concomitant transition between metallic (alloy) and non-metallic (hydride) properties occurs also in this system remains to be investigated.

Fig. 4. Tetrahedral environments of deuteride anions (D1–D6) in $LaMgNiD$. Notation as in Fig. 3; e.s.d.’s of distances ~0.02 Å.

Acknowledgements

Help by the staff of the Swiss-Norwegian beamline (BM1) at ESRF (Grenoble) and the D2B powder diffractometer at ILL (Grenoble) is gratefully acknowledged. The authors thank Y. Filinchuk (University of Geneva) and V. Favre-Nicolin (ESRF, Grenoble) for useful discussions and help with the newly developed computer program FOX. This work was supported by the Swiss National Science Foundation and the Swiss Federal Office of Energy.

References