Structural, electronic and magnetic properties of YFeMnH₅

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ABSTRACT

YFeMn alloy exposed to high hydrogen pressure transforms into hydrides with hydrogen concentration higher than 5 H p.f.u. Rietveld's refinement of XRD data indicates the presence of two hydrides corresponding to YFeMnH₅.₄₆ and YFeMnH₅.₀₂ with the cubic structure of a parent intermetallics. YFeMnH₅.₄₆ was found to be unstable. It desorbs hydrogen yielding YFeMnH₅.₀₂ (referred as YFeMnH₅) which was used for further X-ray absorption near edge structure (XANES) and magnetic measurements. Based on XANES studies at the Mn and Fe K-edges, Mn and Fe atoms in YFeMn alloy are in the metallic state, whereas they exhibit partially anionic character in the hydride. Hydrogenation influences the valence state of Mn and Fe in YFeMn, modifies the density of states (DOS) near the Fermi level and induces an increase of the Curie temperature and a decrease of magnetization at 5 K.

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1. Introduction

Intermetallic Laves phases with ideal AB₂ composition counting more than 1400 representatives have been extensively studied because of their structural, magnetic and hydrogen storage properties [1]. Hydrogen absorption in the interstices of RM₂ (R = rare earth, and M = transition metals) intermetallic compounds substantially modifies their structural, electronic and magnetic properties. These changes in properties due to hydrogenation are of fundamental interest and have been examined in details [2–4]. Generally, hydrogen absorption affects magnetic order in various ways such as by expanding the crystal lattice, exerting negative pressure and stabilizing the localized magnetic moments [5,6]. Magnetic properties are also affected by the formation of superstructures due to hydrogen ordering, which induces symmetry breaking of the surroundings of magnetic atoms. The formation of M–H bonds also alters the electronic structure and shifts the Fermi level [7].

Laves phase intermetallics based on YMn₂ and their hydrides have been investigated because of their fascinating magnetic and electronic properties which depend on Mn–Mn interatomic distances [8,9]. Modification of the Mn–Mn interaction by hydrogen absorption leads to the interesting magnetic properties, which are governed by the number of hydrogen atoms per formula unit. The interplay between the atomic order in the hydrogen sublattice and the magnetic structure of rhombohedral YMn₂D₄.₃ studied by neutron diffraction suggests that structural order in the H sublattice and antiferromagnetic order in the Mn sublattice are strongly correlated [10]. At ambient pressure, a first-order magnetostructural transition involving the magnetic sublattice transformation from the paramagnetic state to an...
2. Materials and methods

2.1. Synthesis of alloy

YFeMn alloy was synthesized by arc-casting a melt of 99.9% pure metals in a vacuum chamber. To prevent the precipitation of YFe3Mn23, 3–5% excess yttrium was added during melting process. The synthesized alloy was annealed in an evacuated quartz tube at 800 °C for five days to improve homogeneity.

2.2. Synthesis of hydride

YFeMn alloy was hydrogenated under 7 kbar hydrogen pressure at 120 °C. The pressure of the hydrogen was increased very slowly from very low value to 7 kbar over a period of 5 h. The temperature was then increased to 120 °C and both the temperature and pressure conditions were maintained for three days. Then, the vessel was cooled down to −5 °C, the sample was removed and stored in liquid nitrogen in order to prevent hydrogen desorption.

Synchrotron XRD experiments were performed at the BL01C1 beam line (National Synchrotron Radiation Research Center (NSRRC), Taiwan) using an ACCM Si(111) monochromator with a wavelength of synchrotron radiation 1.3332 Å. The 2D XRD patterns were recorded using a curved Fuji imaging plate (20 cm × 20 cm) and read by Fuji BAS2500 scanner. 2D diffraction patterns were integrated using FIT2D software. Diffraction angles were calibrated according to the NBS 640b Si powder standard. Structural refinements were made using Rietveld’s method and GSAS software [18]. Magnetic susceptibility measurements were made between 5 and 380 K in an external field of 1000 Oe by a superconducting quantum interference device (SQUID) magnetometer (Quantum Design; MPMS-XL7). Complementary magnetic measurements were made using a system to measure physical properties (PPMS-9, Quantum Design). Mn and Fe K-edge XANES spectra were obtained at the BL17C Wiggler beam line (National Synchrotron Radiation Research Center, Taiwan) using a double-crystal Si(111) monochromator in transmission mode. The ion chambers utilized to measure the incident (I0) and transmitted (I) beam intensities were filled with a mixture of N2 and H2 gases and a mixture of N2 and Ar gases, respectively. Energy calibration was performed with reference to the first inflection point in the spectra of Mn and Fe metal foils (Mn K-edge: 6539 eV and Fe K-edge: 7112 eV). Each in situ reference spectrum was obtained using Mn and Fe metal foils.

3. Results and discussion

Fig. 1 displays the calculated and experimental powder synchrotron XRD patterns of YFeMn alloy and YFeMnHx hydride. XRD pattern of YFeMn was refined in C15 type cubic Laves phase structure (a = 7.4646(1) Å). The unit cell volume of YFeMn (415.92(1) Å3) alloy is close to the mean of the unit cell volumes of YMn2 (454.22 Å3) [21] and YFe2 (396.66 Å3) [22]. Small amount of YMn2YFe11.5Mn11.5 phase was found to be present in the sample in spite of the precautions taken to avoid this phase formation.

antiferromagnetic state was observed. However, increase in the pressure decouples both hydrogen and magnetic orders, which does not occur at the same temperature. Relatable, we have already reported [11,12] YMn2H6 hydride with the highest number of hydrogen atoms per formula unit (p.f.u.) obtained by now. A complete reorganization of the structure was observed leading to a cubic structure containing MnH6 complexes instead of interstitial H atoms. Moreover, half Mn and all Y atoms are statistically located on the same crystallographic site. Magnetic curves of YMn2H6 were refined as a superposition of Pauli and Curie–Weiss paramagnetic components that results from two different types of Mn atoms (with 6 H and without H neighbors) [11,12]. Thermal properties of YMn2H6 and YMn2H4.5 hydrides were studied by differential scanning calorimetry (DSC) and X-ray diffraction (XRD), showing that YMn2H6 is thermally more stable.

YFe2 alloy has a cubic structure with Y atoms forming a diamond-type lattice and Fe atoms building up a corner linked tetrahedral array. The absorption of hydrogen by YFe2 leads to the hydrides with several crystal structures which can be derived from the C15 structure of a parent material [13]. Up to 4.2 H p.f.u., the hydrides are ferromagnetic at low temperature. However, the hydride YFe2Hx with the highest obtained to date hydrogen concentration is paramagnetic [14].

Hilscher et al. [15] studied magnetic properties of the pseudobinary system Y(Fe1−xMnx)2 and reported ferromagnetic–paramagnetic transition at x = 0.7, accompanied by a decrease of the Curie temperature. The magnetic properties were found to be strongly influenced by annealing suggesting that the magnetism in Y(Fe1−xMnx)2 arises heterogeneously. The loss of antiferromagnetism in Fe-substituted YMn2 [16] and the effect of hydrogenation on the magnetic properties of Y(Fe1−xMnx)2 for various x values have been described by Oesterreicher et al. [17]. They observed a larger Curie temperature for the hydride compared to the intermetallics for low Fe content and then a lower Curie temperature in the hydrides compared to the

structural, electronic and magnetic properties of the parent alloy and corresponding hydride were examined by XRD (X-ray diffraction), XANES (X-ray absorption near edge structure) and SQUID (Superconducting quantum interference device) measurements.

The reference measurement to avoid this phase formation.
The XRD pattern of YFeMnH$_x$ was indexed with two cubic phases (phase I and phase II) and their structures were refined in Fd-3m space group. Table 1 summarizes the results of Rietveld's refinement. Since the expansion of molecular volume per one H atom is 2.95 Å$^3$ for YFe$_2$H$_4$ [4] and 3.05 Å$^3$ for YMn$_2$H$_4$ [9], we assumed 3.00 Å$^3$ value for YFeMnH$_x$. In such a case phases I and II have compositions YFeMnH$_{5.46}$ and YFeMnH$_{5.02}$, respectively. The phase I soon desorbed hydrogen to form single phase YFeMnH$_{5.02}$ (labeled as YFeMnH$_5$) which was used for further XANES and SQUID measurements. The YFeMnH$_5$ sample was stable for more than one month but after one year of storage at ambient conditions it lost part of hydrogen yielding the final hydride YFeMnH$_{4.7}$ with the same cubic Fd-3m crystal lattice symmetry. It is notable that previously only hydrides YFeMnH$_4$ [8] or at least YFeMnH$_{4.3}$ [19] have been reported.

Fig. 2 (a) presents the Mn K-edge spectra of YFeMn, its hydride, and a reference Mn foil. Having reference spectrum as a fingerprint at the absorption edge, it is possible to use it as a standard for oxidation state and site symmetry. Additionally the difference between energy values corresponding to normalized absorption $\mu_x$ near half-height can usually indicates the change in oxidation state, but it should be considered that the comparison is applicable only when the atoms are present in the same or similar coordination environment [11]. The valence state can also be determined from the inflection point of the XANES spectra. Fig. 2(b) presents the second derivative of Mn K-edge for YFeMn alloy and YFeMnH$_5$. The inflection point energies of the alloy and hydride were found to be 6538.6 and 6536.4 eV, respectively, as indicated by the arrows in Fig. 2(b). As it is clearly seen in Fig. 2(a), the Mn K-edge XANES spectrum of YFeMn has almost the same inflection point as that of Mn foil, indicating that the Mn is in the same valence state in the alloy. In contrast, the inflection point of the Mn K-edge XANES spectrum of YFeMnH$_5$ is below that of Mn foil, suggesting the partially anionic character of Mn in the hydride. As it is also seen in Fig. 2 (a), the intensity of the pre-edge peak of the Mn K-edge XANES spectra of YFeMnH$_5$ is reduced compared to the parent compound. According to dipolar selection rules, K-edge corresponds to an electronic transition from 1s core state to empty p state thus the XANES spectrum probes the empty projected local electronic density of p state [25]. The Mn 4p states are hybridized with partially filled Mn 3d states near Fermi level which results appearance of prominent peak at pre-edge region. Therefore due to hydrogenation, hydrogen acts as an electron donor and filled up these empty 3d states and reduced the peak intensity as the number of hydrogen increases per formula unit. This decreases the number of 3d holes and pushes the 3d band below Fermi level results in drastic reduction of the pre-edge feature [24]. Additionally, the large cell volume increase of the hydride compared to the inter-metallics, can also reduce the 4p–3d hybridization and therefore the pre-peak intensity [7,23,24].

### Table 1 – Crystal structure parameters of cubic (s.g. Fd-3m) YMnFe and YFeMnH$_x$.

<table>
<thead>
<tr>
<th></th>
<th>YMnFe</th>
<th>YFeMnH$_{5.02}$</th>
<th>YFeMnH$_{4.6}$</th>
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<tr>
<td>$a$, Å</td>
<td>7.4646(1)</td>
<td>8.1350(1)</td>
<td>8.1893(1)</td>
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<tr>
<td>$V$, Å$^3$</td>
<td>415.93(1)</td>
<td>538.36(1)</td>
<td>549.22(1)</td>
</tr>
<tr>
<td>$Y$ (5/8, 5/8, 5/8), $B_{iso}$, Å$^2$</td>
<td>0.023(2)</td>
<td>0.0533(7)</td>
<td>0.0514(7)</td>
</tr>
<tr>
<td>(Fe, Mn) (0,0,0), $B_{iso}$, Å$^2$</td>
<td>0.0192(2)</td>
<td>0.0375(7)</td>
<td>0.0386(7)</td>
</tr>
<tr>
<td>$R_{wp}$, %</td>
<td>2.73</td>
<td>2.20</td>
<td></td>
</tr>
<tr>
<td>$R_p$, %</td>
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<td>1.47</td>
<td></td>
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<tr>
<td>$\chi^2$</td>
<td>0.42</td>
<td>0.61</td>
<td></td>
</tr>
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</table>

Fig. 1 – Calculated (+) and experimental (−) XRD patterns of YFeMn and YFeMnH$_x$. 

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normalized absorption $\mu_x$ near half-height can usually indicates the change in oxidation state, but it should be considered that the comparison is applicable only when the atoms are present in the same or similar coordination environment [11]. The valence state can also be determined from the inflection point of the XANES spectra. Fig. 2(b) presents the second derivative of Mn K-edge for YFeMn alloy and YFeMnH$_5$. The inflection point energies of the alloy and hydride were found to be 6538.6 and 6536.4 eV, respectively, as indicated by the arrows in Fig. 2(b). As it is clearly seen in Fig. 2(a), the Mn K-edge XANES spectrum of YFeMn has almost the same inflection point as that of Mn foil, indicating that the Mn is in the same valence state in the alloy. In contrast, the inflection point of the Mn K-edge XANES spectrum of YFeMnH$_5$ is below that of Mn foil, suggesting the partially anionic character of Mn in the hydride. As it is also seen in Fig. 2(a), the intensity of the pre-edge peak of the Mn K-edge XANES spectra of YFeMnH$_5$ is reduced compared to the parent compound. According to dipolar selection rules, K-edge corresponds to an electronic transition from 1s core state to empty p state thus the XANES spectrum probes the empty projected local electronic density of p state [25]. The Mn 4p states are hybridized with partially filled Mn 3d states near Fermi level which results appearance of prominent peak at pre-edge region. Therefore due to hydrogenation, hydrogen acts as an electron donor and filled up these empty 3d states and reduced the peak intensity as the number of hydrogen increases per formula unit. This decreases the number of 3d holes and pushes the 3d band below Fermi level results in drastic reduction of the pre-edge feature [24]. Additionally, the large cell volume increase of the hydride compared to the inter-metallics, can also reduce the 4p–3d hybridization and therefore the pre-peak intensity [7,23,24].
Fig. 3(a) presents the Fe K-edge XANES spectra of YFeMn, its hydride, and the metal Fe foil as a standard. These spectra are similar to the Mn K-edge spectra. Fig. 3(b) plots the second derivative of the Fe K-edges of YFeMn and YFeMnH$_5$ and the respective inflection point energies are 7112.0 and 7109.6 eV. As noted, the inflection point of the Fe K-edge XANES spectrum of YFeMnH$_5$ is below that of the Fe foil, suggesting that Fe is partially anionic in the hydride. The decrease in the intensity and change in the shape of Fe K-edge spectra was observed for YFeMnH$_5$. Hydrogenation causes the filling up of d-orbitals and reduces the number of d-orbital holes that results in the disappearance of the peak.

Hydrogenation alters not only the electronic structure of YMnFe but its magnetic properties as well. Fig. 4 plots magnetic susceptibility of YFeMn as a function of temperature. In the YFeMn alloy, the magnetization rapidly increases from 150 to
90 K in an external magnetic field (1 kOe) and a Curie temperature $T_C = 125$ K can be extrapolated from the curve. A positive Curie–Weiss temperature ($\Theta_{CW}$) around 262.2 K of YFeMn is derived from data on the field-cooled magnetization (FC). The magnetization curves at 5 K saturate above 25 kOe and the saturation magnetization extrapolated at zero field is 30 emu/g or 1.1 $\mu_B$/mol. For YFeMnH$_5$, a Curie temperature at 293 K can be extrapolated whereas an irreversibility is observed below 50 K as seen in Fig. 5(a). The hydride had a larger value of $\Theta_{CW}$ than that of the parent compound at approximately 293.9 K. Hydrogenation probably increased the ferromagnetic interaction, as suggested by the higher Curie temperature and $\Theta_{CW}$ of YFeMnH$_5$. This result is very different from that observed in Ref. [18], were ferromagnetism was found to be unstable for Y(Fe$_{1-x}$Mn$_x$)$_2$H$_y$ with $x$ = 0.4 and 3.7 $\leq$ $y$ $\leq$ 4. However, Cadaves-Peres et al. [19], found an ordering temperature near 225 K for YFeMnH$_{6.3}$. Below this temperature a short-range magnetic order corresponding to an incommensurate antiferromagnetic order was observed by NPD. The decrease in the lower magnetic moment of the hydride phase, YFeMnH$_5$ was also consistent with previous results. Figs. 6 and 7 plot the hysteresis loops of YFeMn alloy and YFeMnH$_5$ at three different temperatures. At 280 K, YFeMn alloy is paramagnetic, as indicated by the linear response of the magnetization to the external field. However, at 280 K the hydride exhibits hysteresis with a very small coercivity, suggesting soft-ferromagnetic behavior. As the temperature decreases, the hysteresis loops of both alloys exhibit soft-ferromagnetic character, even down to 5 K. The magnetization curve of YFeMnH$_5$ at 5 K does not reach saturation even at 9 T (measurement with PPMS) and the extrapolation to zero field of the magnetization curve leads to $M_s = 16$ emu/g or 0.57 $\mu_B$/mol. This saturation moment of the hydride at 5 K, is weaker than that of YFeMn (30 emu/g or 1.1 $\mu_B$/mol). The magnetic moment of the (YFe$_{1-x}$Mn$_x$) series is caused mainly by Fe–Fe (ferromagnetic), Mn–Mn (antiferromagnetic) and Fe–Mn (antiferromagnetic) interactions [25–27]. Therefore, the presence of an irreversibility below 50 K and the absence of saturation in the M(H) curve at 5 K should result from the coexistence of antiferromagnetic and ferromagnetic short-range order at low temperature. This can also be a canting of the Fe moment, induced by the hydrogen distribution as Ferro and Antiferromagnetic behaviour exist in the intermetallic YFeMn. Another possible cause is the hydrogen disorder in the interstitial sites,
since interstitial sites are not all occupied, which strongly increases the width of the distribution of magnetic moment orientation above that of the intermetallic. This effect of H disorder on magnetic order was also observed in Y(Mn,Al)D4 [28], Tb(Mn,Al)Dx [29] and YMn2Dx [12] alloys in the paramagnetic region.

4. Conclusions

YFeMn alloy and its hydride were synthesized by arc-melting and using the high-pressure method, respectively. At high hydrogen pressure — high temperature conditions YFeMn absorbs hydrogen, showing expansion of crystal lattice without change the symmetry yielding mixture of two cubic phases: YFeMnH5.46 and YFeMnH5.02. Within few days YFeMnH5.46 lost part of hydrogen forming more stable YFeMnH5.02. The parent YFeMn alloy and YFeMnHx were further examined using XANES and SQUID to study their electronic and magnetic properties. A XANES study at the K-edges of Mn and Fe indicated that Mn and Fe atoms in YFeMn alloy were in metallic state, while Mn and Fe were anionic in the hydride. Hydrogenation influenced the valence state of Mn and Fe in YFeMnHx, reducing the density of states (DOS) near the Fermi level. The magnetization measurements demonstrated that the magnetic moment decreased greatly by hydrogenation.

The magnetization measurements show an increase of the Curie temperature from 125 to 293 K and a decrease of the extrapolated saturation magnetization from 1.1 to 0.57 \( \mu_B \). These results indicate an increase of the Fe–Fe interaction but at the same time a strong canting of the Fe moments due to the hydrogen distribution inside the lattice. These results, compared to that of previous work in the literature indicate an increase of the magnetic ordering temperature with H content. This magnetic behavior is opposite to that observed for YFeHx hydrides as a ferromagnetic behavior was observed up to YFeH4.2, whereas YFe2H5 becomes paramagnetic.

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REFERENCES


