A study on the effect of hydrogen in the compounds with $ThMn_{12}$-type structure

A study on the effect of hydrogen in the compounds with ThMn$_{12}$-type structure

Weihua Mao†, Jinbo Yang†, Bo Cui†, Benpei Cheng†, Yingchang Yang†, Honglin Du‡, Baisheng Zhang‡, Chuntang Ye‡ and Jilian Yang‡

† Department of Physics, Peking University, Beijing 100871, People's Republic of China
‡ Institute of Atomic Energy, Academica Sinica, Beijing 102413, People's Republic of China

Abstract. The structural and magnetic properties of hydrides with ThMn$_{12}$-type structure have been studied by means of magnetic measurements, the neutron powder diffraction technique and self-consistent spin-polarized band calculations (LMTO-ASA). We found that the hydrides retain the ThMn$_{12}$-type structure, but with an increase of unit-cell volume. The neutron diffraction results indicate that hydrogen atoms occupy the interstitial 2b sites. Magnetic measurements carried out on YFe$_{10}$Mo$_2$, YFe$_{10.5}$V$_x$, YFe$_{11}$Ti and their hydrides show that both the Curie temperature and the saturation magnetization can be enhanced by introducing interstitial hydrogen atoms. Band-structure calculations and spin-fluctuation theory give a fair description of the enhancement of the magnetization and Curie temperature.

1. Introduction

Since the discovery of nitrogenated R$_2$Fe$_{17}$ and R(Fe, M)$_{12}$ [1, 2] (R = rare earth, M = Ti, V, Mo, . . .), the interstitially modified intermetallic materials based on rare-earth and iron compounds have been studied quite intensively. Much attention has focused on nitrides and carbides. In fact, rare-earth intermetallic compounds can also absorb certain quantities of hydrogen, which leads to substantial changes in their structures and magnetic properties [3].

Since 1987, much effort has been devoted to the 1:12-type hydrides [4]. It has been found that the magnetic properties of these compounds can be changed by introducing hydrogen atoms into the crystal lattice. In order to understand the origin of the hydrogen effects, it is necessary to clarify the crystallographic structure of the hydrides. Obbade *et al* [5] have suggested that hydrogen atoms might occupy tetrahedral holes formed by Nd(2a)–V(8i)–Fe(8i)–Fe(8f) in NdFe$_{11}$VH; however, no experimental evidence was provided. And Tomey *et al* [6] have proposed that hydrogen atoms occupy 16l and 32o sites in the 1:12 hydrides. Up to now, explicit experimental results concerning the hydrogen location have been rare in the literature, and the hydrogen location is still controversial in the literature. In practice, deuterides are used instead of hydrides because hydrogen has a higher incoherent scattering cross section for neutrons in the process of neutron diffraction. In 1994, Tomey *et al* reported that deuterium atoms occupy the octahedral 2b site in Er(Fe, M)$_{12}$D$_x$ [7]. But later-reported results of Soubeyroux *et al* [8] indicated that hydrogen could occupy either 16l and 32o or 2b sites. Consequently, more studies of the hydrides with the 1:12-type structure are required.

In this paper, we first investigate detailed aspects of the hydrogen occupation by using the neutron diffraction technique; then, on the basis of the experimental results, the electronic

structures of the parent alloys and hydrides are calculated in order to explain the effects of hydrogen on the site-dependent magnetic moments and Curie temperature.

2. The experiment and the theoretical calculation method

The sample was prepared by arc melting of 99.5% pure materials in a purified argon atmosphere. Hydrides were prepared by passing purified hydrogen gas at atmospheric pressure through finely ground powder samples (about 10–30 μm) at 200–300 °C for 2–6 h, and then rapidly cooling to room temperature. X-ray diffraction was used to determine the crystal structure. Magnetization curves were measured with a field of up to 70 kOe in a temperature range from 1.5 K to 300 K by using an extracting-sample magnetometer. The Curie temperature was determined from the thermomagnetic curve measured by a vibrating-sample magnetometer (VSM) in a temperature range from 300 K to 1000 K. The neutron diffraction measurements were performed on the powder diffractometer at the heavy-water research reactor at the Institute of Atomic Energy in Beijing. The data were collected by scanning the samples from 10° to 80° in steps of 0.2° at room temperature with a neutron wavelength of 1.184 Å. The diffraction patterns were analysed by means of the Rietveld profile technique.

The linear-muffin-tin-orbital (LMTO) method [9] with the atomic sphere approximation (ASA) has been employed to perform a semi-relativistic band calculation in the framework of local spin-density-functional theory [10]. The exchange–correlation term took the von Barth and Hedin form [11, 12]. The core charge density was calculated for a free atom using the Dirac equation, and the result was used as a so-called frozen core. The s, p, d orbits were used for Y, Fe and Mo, and the s orbital was used for H. We calculated the magnetic moments of $YFe_{10}Mo_2$ and $YFe_{10}Mo_2H_x$. The lattice parameters were taken from neutron diffraction results; the ratio of the atomic sphere radii was $R_Y:R_{Fe}:R_{Mo} = 1.35:1:1.12$; the atomic sphere radius for H was set such that $R_H/R_{Fe} = 0.6$.

Table 1. The lattice parameters (a and c) and unit-cell volume (V) of $YFe_{12-x}M_xH_y$ in comparison with $YFe_{12-x}M_x$ and the relative change in the unit-cell volume upon hydrogenation $\Delta V/V$.

	a (Å)	c (Å)	V (Å^3)	$\Delta V/V$ (%)
$YFe_{10}Mo_2$	8.563	4.810	352.7	
$YFe_{10}Mo_2H_x$	8.592	4.817	355.6	0.82
$YFe_{11}Ti$	8.522	4.797	348.4	
$YFe_{11}TiH_x$	8.546	4.800	350.6	0.63
$YFe_{10.5}V_{1.5}$	8.488	4.770	343.7	
$YFe_{10.5}V_{1.5}H_x$	8.503	4.778	345.5	0.52

3. Results and discussion

3.1. Crystal structure

X-ray diffraction patterns and thermomagnetic analysis results proved that $YFe_{12-x}M_x$ (M = Mo, Ti and V) and their hydrides are of single phase. The hydrides are
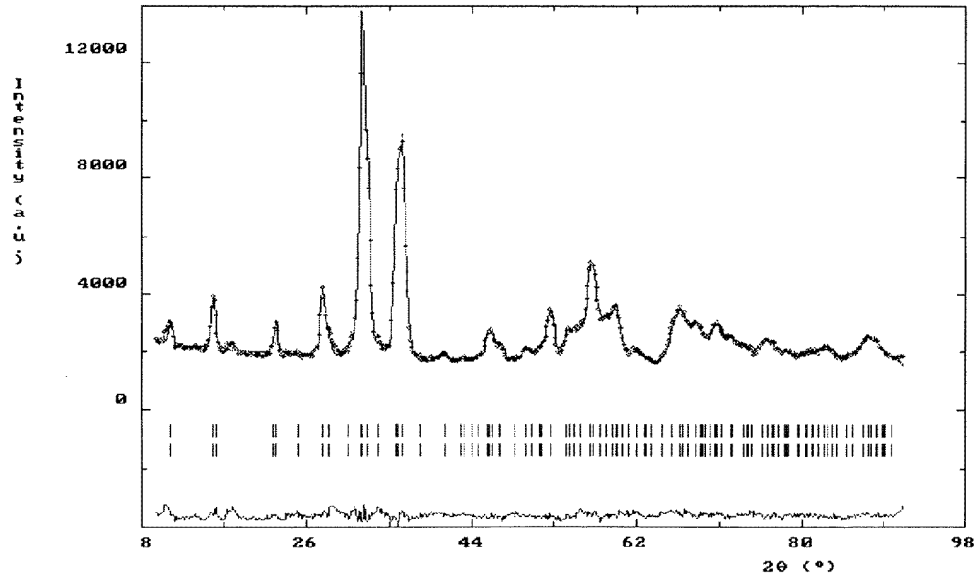
Figure 1. The neutron diffraction pattern of YFe$_{10}$Mo$_2$H$_x$ at room temperature.

Table 2. Neutron diffraction refinement results for YFe$_{10}$Mo$_2$ and YFe$_{10}$Mo$_2$H$_x$.

Atom	Site	x	y	z	n	μ_z (μ_B)
Y	(2a)	0	0	0	2	0
Fe	(8i)	0.3567(49)	0	0	3.745	1.40(6)
Fe	(8j)	0.2808(43)	0.5000	0	8	1.31(7)
Fe	(8f)	0.2500	0.2500	0.2500	8	1.25(9)
Mo	(8i)	0.3567(49)	0	0	4.255	0
		$R_p = 8.03\%$, $R_n = 4.43\%$, $R_m = 5.78\%$				
Y	(2a)	0	0	0	2	0
Fe	(8i)	0.3586(44)	0	0	3.7650	1.57(7)
Fe	(8j)	0.2767(41)	0.5000	0	8	1.37(8)
Fe	(8f)	0.2500	0.2500	0.2500	8	1.51(9)
Mo	(8i)	0.3586(44)	0	0	4.2350	0
H	(2b)	0	0	0.5000	1.6540	0
		$R_p = 7.84\%$, $R_n = 3.91\%$, $R_m = 5.78\%$				

found to retain the same tetragonal ThMn$_{12}$-type structure, but with an increase in lattice parameters, which are listed in table 1. Neutron powder diffraction measurements were performed on YFe$_{10}$Mo$_2$ and YFe$_{10}$Mo$_2$H$_x$ at room temperature. Figure 1 illustrates the neutron diffraction pattern of YFe$_{10}$Mo$_2$H$_x$. The neutron data suggest that hydrogen atoms occupy 2b sites, whereas iron atoms occupy 8j, 8i and 8f sites, and Mo atoms occupy only the 8i sites. The results are listed in table 2. Assuming hydrogen atoms to locate at other sites or irregular sites leads to a larger *R*-factor, and, moreover, the hydrogen atom occupation number would be unreasonable in some cases (see table 3). So we conclude that hydrogen atoms occupy only 2b sites in YFe$_{10}$Mo$_2$H$_x$.

Table 3. Neutron diffraction refinement results for $YFe_{10}Mo_2H_x$ assuming H to occupy different sites.

Site	Refined coordinate	R_t (%)	R_n (%)	R_m (%)	Occupancy of H
2b	$(0, 0, \frac{1}{2})$	7.84	3.91	5.78	1.654
4c	$(0, \frac{1}{2}, 0)$	11.9	5.58	10.5	0.009
4d	$(0, \frac{1}{2}, \frac{1}{4})$	11.5	5.52	7.78	0.112
8g	$(0, \frac{1}{2}, z), z = 0.153$	13.5	7.14	13.7	−0.099
8h	$(x, x, 0), x = 0.129$	13.3	7.10	11.6	0.683
16k	$(x, x + \frac{1}{2}, \frac{1}{4}), x = 0.157$	11.9	5.79	11.3	0.476
16l	$(x, y, 0), x = 0.295, y = 0.134$	12.8	6.81	12.2	−1.551
16m	$(x, x, z), x = 0.079, z = 0.370$	12.7	6.16	11.9	2.465
16n	$(0, y, z), y = 0.187, z = 0.269$	13.6	7.25	13.6	2.542
32o	$(x, y, z), x = 0.556, y = 0.388, z = 0.130$	12.6	6.03	12.5	3.023
No regular site		10.1	5.06	9.58	—

Table 4. The Curie temperature T_C and saturation magnetization σ_s of $YFe_{12-x}M_xH_y$ in comparison with $YFe_{12-x}M_x$ and the relative enhancements of Fe moments upon hydrogenation $\Delta\mu_{Fe}/\mu_{Fe}$.

	σ_s (μ_B/f.u.)		$\Delta\mu_{Fe}/\mu_{Fe}$ (%)			
	1.5 K	300 K	1.5 K	300 K	T_C (K)	$\Delta T_C/T_C$
$YFe_{10}Mo_2$	16.12	9.89			410	
$YFe_{10}Mo_2H_x$	16.70	11.60	3.6%	17.3%	440	7.3%
$YFe_{11}Ti$	20.29	17.81			530	
$YFe_{11}TiH_x$	21.25	19.25	4.7%	8.1%	580	9.4%
$YFe_{10.5}V_{1.5}$	17.30	15.40			580	
$YFe_{10.5}V_{1.5}H_x$	17.69	16.31	2.3%	5.9%	630	8.6%

3.2. The effects of hydrogen on the magnetic properties

Table 4 lists the Curie temperatures (T_C) and saturation magnetizations (σ_s) of $YFe_{10}Mo_2$, $YFe_{10.5}V_x$, $YFe_{11}Ti$ and their hydrides. The interstitial hydrogen atoms have the effect of increasing the Curie temperature T_C and saturation magnetization σ_s. T_C for the hydrides of $YFe_{10}Mo_2$ increases from 410 K to 440 K, and σ_s is increased by 3.6% and 17.3% at 1.5 K and 300 K, respectively. The large increase of σ_s at room temperature is partly due to the increase of the Curie temperature. Since T_C for $YFe_{10}Mo_2$ is just above room temperature, a small increase of T_C results in a large increase in saturation magnetization at room temperature. This result is consistent with that obtained from neutron diffraction data.

The spin-polarized densities of states (DOS) for $YFe_{10}Mo_2$ and $YFe_{10}Mo_2H$ are shown in figure 2. As can be seen from the figure, the DOS are dominated by the Fe d band. The additional structure around −0.6 Ryd in $YFe_{10}Mo_2H$ is due to the H s states. The structure of the Fe d band in the $YFe_{10}Mo_2$ DOS is shifted to higher binding energy due to the reduction in the overlap upon hydrogenation. This leads to a decrease of both the up-
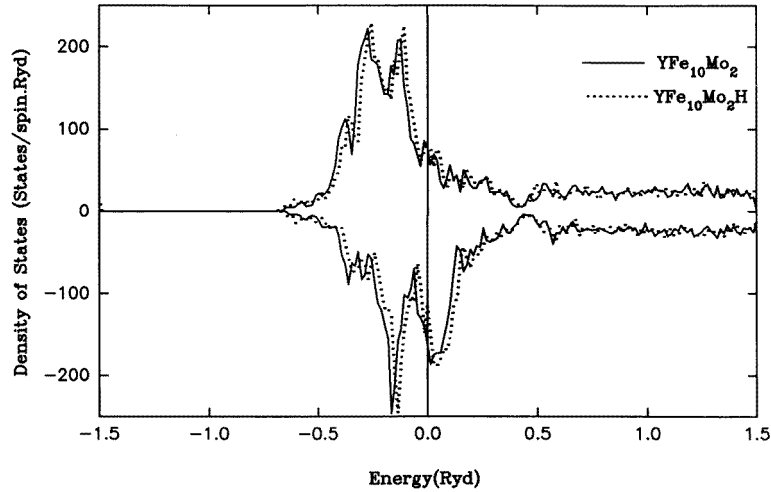
Figure 2. The total densities of states of YFe$_{10}$Mo$_2$ and YFe$_{10}$Mo$_2$H.

Table 5. The results from the theoretical calculation of the site-dependent moments (unit: μ_B).

Atoms	Site	YFe$_{10}$Mo$_2$	YFe$_{10}$Mo$_2$H	
Y	(2a)	−0.44	−0.43	
Fe	(8j)	2.08	2.09	
Fe	(8f)	1.69	1.87	
Fe	(8i)	2.53	2.50	
Mo	(8i)	−0.49	−0.50	
H	(2b)		−0.25	
Total		18.72	19.16	2.4%

Table 6. Band-structure parameters and the spin-fluctuation temperatures T_{SF} of YFe$_{10}$Mo$_2$ and YFe$_{10}$Mo$_2$H.

	DOS (E_F) (eV^{-1}/Fe)		Magnetic moment (μ_B/Fe)	Stoner parameter (eV)	$T_{SF}(H)/T_{SF}$	$T_C(H)/T_C$ (experimental)
	$N_\uparrow$	$N_\downarrow$				
YFe$_{10}$Mo$_2$	0.53	0.47	2.02	0.96	1.10	1.07
YFe$_{10}$Mo$_2$H	0.49	0.42	2.09	0.97		

and down-spin DOS values at Fermi level. The calculated magnetic moments for different atomic sites in these compounds are compared in table 5. The total magnetic moments per formula unit (f.u.) are 18.72 and 19.16 μ_B/f.u. These results are close to the experimental magnetization values of 16.12 and 16.70 μ_B/f.u. As for the total magnetic moment, the value for YFe$_{10}$Mo$_2$H is enhanced by about 2.4%, which is close to the experimental value (3.6%). It can be seen from table 5 that the interstitial effect of hydrogen atoms will increase the magnetic moments at 8f sites, but has little effect on the magnetic moments at Fe(8i) and Fe(8j) sites. As compared to that on the nitrides [13], the effect of interstitial hydrogen

atoms is smaller than that of nitrogen atoms due to the smaller magnetovolume effect and hybridization effect of hydrogen atoms.

Finally, the increase of T_C with the addition of interstitial atoms can be explained with the spin-fluctuation theory of Mohn and Wohlfarth [14–16]. The Curie temperature was defined by $T_C \propto M_0^2 / \chi_0$, where M_0 is the zero-temperature magnetic moment per Fe atom and the susceptibility χ_0 is given by $\chi_0^{-1} \propto [1/2N_\uparrow(E_F) + (1/2N_\downarrow(E_F) - I)]$. Here $N_\uparrow(E_F)$ and $N_\downarrow(E_F)$ are the densities of states (DOS) at the Fermi energy (E_F) for the up- and down-spin states, respectively, and I is the Stoner parameter. Table 6 lists the characteristic parameters obtained from the band-structure calculations. It is found that T_{SF} increases with the absorption of H atoms. Though a quantitative explanation cannot be given, the ratio of T_{SF} before hydrogenation to that after hydrogenation gives a fair estimate of the enhancement of T_C for these systems.

4. Conclusions

In summary, hydrogen atoms occupy 2b sites in $YFe_{10}Mo_2H_x$ and they are found to have the effect of increasing the Curie temperature and saturation magnetization. The LMTO-ASA method and the spin-fluctuation theory give a fair description of the changes of the magnetization and the Curie temperature of the $ThMn_{12}$ compounds.

Acknowledgments

References

[1] Coey J M D and Sun H 1990 *J. Magn. Magn. Mater.* **87** L251
[2] Yang Y C, Zhang X D, Ge S L, Kong L S and Pan Q 1990 *Proc. 6th Int. Symp. on Magnetic Anisotropy and Coercivity in Rare Earth Transition Metal Alloys* ed S G Sankar (Pittsburgh, PA: Carnegie Mellon University Press) p 190
[3] Buschow K H J and Sherwood R C 1978 *J. Appl. Phys.* **49** 1480
[4] Ohashi K, Yokohama T, Osugi R and Tawara Y 1987 *IEEE Trans. Magn.* **5** 23
[5] Obbade S, Miraglia S, Fruchart D, Pre M, L'Heritier P and Barlet H 1988 *C. R. Acad. Sci., Paris* II **307** 889
[6] Tomey E, Isnard O, Fagan A, Desmoulins C, Miraglia S, Soubeyroux J L and Fruchart D 1993 *J. Alloys Compounds* **191** 233
[7] Tomey E, Bacmann M, Fruchart D, Miraglia S, Soubeyroux J L, Gignoux D and Palacios E 1994 *IEEE Trans. Magn.* **30** 687
[8] Soubeyroux J L, Fruchart D, Isnard O, Miraglia S and Tomey E 1995 *J. Alloys Compounds* **219** 16
[9] Anderson O K 1975 *Phys. Rev.* B **12** 3060
[10] Skriver H L 1984 *The LMTO Method* ed M Cardona, P Fulde and H J Queisser (Berlin: Springer)
[11] von Barth U and Hedin L 1972 *J. Phys. C: Solid State Phys.* **5** 1629
[12] Janak J F 1978 *Solid State Commun.* **25** 53
[13] Ishida S, Asano S and Fujii S 1994 *Physica* B **193** 66
[14] Mohn P and Wohlfarth E P 1987 *J. Phys. F: Met. Phys.* **17** 2421
[15] Jaswal S S, Yelon W B, Hajipanayis G C, Wang Y Z and Sellmyer D J 1991 *Phys. Rev. Lett.* **67** 644
[16] Sakuma A 1992 *J. Phys. Soc. Japan* **61** 4119