Magnetic properties of Ho2Fe17-xMnx - Influence of Mn substitution

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Abstract
The structural and magnetic properties of Ho2Fe17-xMnx (x=0-5) have been investigated by x-ray diffraction, Mössbauer spectroscopy and DC magnetization measurements (0-5 T) over the temperature range 4.5-350 K. Similar to other ferrimagnetic R2Fe17-xMnx systems, the unit cell volume generally increases with Mn content other than for low Mn values where a slight maximum is detected around x ~ 0.5. The nature of the magnetic phase transitions around TC is shown by Arrot plot analysis to be second order for all samples. The Curie temperature remains essentially unchanged for Mn contents up to x=1.0 (TC =336 K for x=0.0, TC =338 K for x=1.0) before decreasing steadily with further increase in Mn content (TC =209 K for x=5). The 57Fe hyperfine interaction parameters have been determined from variable temperature Mössbauer spectra.

Keywords
Magnetic, properties, Ho2Fe17, xMnx, Influence, substitution

Disciplines
Engineering | Physical Sciences and Mathematics

Publication Details

This journal article is available at Research Online: https://ro.uow.edu.au/aiimpapers/28
Magnetic properties of Ho$_2$Fe$_{17-x}$Mn$_x$ – influence of Mn substitution

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Abstract. The structural and magnetic properties of Ho$_2$Fe$_{17-x}$Mn$_x$ ($x=0-5$) have been investigated by x-ray diffraction, Mössbauer spectroscopy and DC magnetization measurements (0-5 T) over the temperature range 4.5-350 K. Similar to other ferrimagnetic R$_2$Fe$_{17-x}$Mn$_x$ systems, the unit cell volume generally increases with Mn content other than for low Mn values where a slight maximum is detected around $x \sim 0.5$. The nature of the magnetic phase transitions around $T_C$ is shown by Arrott plot analysis to be second order for all samples. The Curie temperature remains essentially unchanged for Mn contents up to $x=1.0$ ($T_C =336$ K for $x=0.0$, $T_C =338$ K for $x=1.0$) before decreasing steadily with further increase in Mn content ($T_C =209$ K for $x=5$). The $^{57}$Fe hyperfine interaction parameters have been determined from variable temperature Mössbauer spectra.

1. Introduction
R$_2$T$_{17}$ compounds in general exhibit strong magnetism with continuing interest focused on improvement in their magnetic properties [1]. While applications of R$_2$Fe$_{17}$ compounds are restricted by their low Curie temperatures and poor magnetocrystalline anisotropy at room temperature, significantly improvements to magnetic properties (such as increase in $T_C$; change of magnetocrystalline anisotropy at room temperature from easy-plane to easy axis) can be obtained on introduction of the interstitial atoms C or N [1], and substitution of T = Al, Ga, Si and Mn [2] for Fe in R$_2$Fe$_{17-x}$T$_x$.

Compared with the substitution of T = Al, Ga and Si where the lattice parameters in R$_2$Fe$_{17-x}$T$_x$ exhibit monotonic behaviour with increasing x, it was found that R$_2$Fe$_{17-x}$Mn$_x$ ($R=$Nd [3], Pr [4], Tb [5], Dy [6], Er [7]) shows unexpected behaviour in that the unit-cell volume first exhibits a slight maximum around $x=0.5-2$ before increasing monotonically with further increase in x. Some authors ascribed this unexpected composition dependence of lattice volume with Mn content in R$_2$Fe$_{17-x}$Mn$_x$ compounds to the preferential occupation of Mn atoms for the dumbbell pair site 6c (in Th$_2$Zn$_{17}$-type structure) or 4f (in Th$_2$Ni$_{17}$-type structure) which has the largest Wigner–Seitz cell (WSC) volumes [3], while others suggested that the magnetovolume effect in these compounds - for which the Curie temperature $T_C$ is close to or above room temperature - should be responsible for this unexpected anomaly [5-7]. Following our previous studies of Dy$_2$Fe$_{17-x}$Mn$_x$ [6] and Er$_2$Fe$_{17-x}$Mn$_x$ [7], here we...
report our experimental investigation on Ho$_{2}$Fe$_{17-x}$Mn$_x$ by x-ray diffraction, magnetic and variable temperature Mössbauer spectroscopy measurements.

2. Experimental process

Ho$_{2}$Fe$_{17-x}$Mn$_x$ alloys (x=0, 0.5, 1.0, 2.0, 3.0, 4.0, 5.0) were prepared by arc melting Ho, Fe and Mn (> 99.95% purity) in an argon atmosphere. Ingots were melted at least five times to ensure their homogeneity. Each arc-melted ingot was sealed in a silica vacuum tube, annealed at 1000°C for one week, and then quenched in water. The ingot was then ground into powder and the structure examined by x-ray diffraction using CuK$_\alpha$ radiation. The temperature dependence of the magnetization, $M(T)$, was measured in a magnetic field of $B_{appl}=100$ Oe in a SQUID from 5 K to 350 K. The Curie temperatures $T_C$ were derived from $M^2$ versus $T$ plots and by extrapolating $M^2$ to zero. $^{57}$Fe Mössbauer spectra were obtained between 4.5 K and 298 K using a standard constant-acceleration spectrometer and a $^{57}$CoRh source. The spectrometer was calibrated at room temperature with an $\alpha$-iron foil.

3. Results and discussion

As shown by the X-ray diffraction patterns of Figure 1(a), all samples display both the rhombohedral Th$_2$Zn$_{17}$-type (2:17R) and the hexagonal Th$_2$Ni$_{17}$-type (2:17H) structures. For example, in the case of Ho$_2$Fe$_{17}$; (Figure 1(a)), refinement of the XRD pattern shows a ratio of ~ 80:20 for H:R. Our results are consistent with related studies which show that $R_2T_{17}$ ($T$=Fe or Co) can be formed in the 2:17H or 2:17R structures and that both structures can co-exist depending on the preparation conditions [2, 8]. Similar affects have been found in Ho$_2$Fe$_{17-x}$Ga$_x$ [2] and Ho$_2$Co$_{17-x}$Mn$_x$ [8] with Ho$_2$Fe$_{14}$Ga$_3$, Ho$_2$Co$_{17}$ and Ho$_2$Co$_{15}$Mn$_2$ showing coexistence of the Th$_2$Ni$_{17}$ (H) and Th$_2$Zn$_{17}$ (R) structures.

The lattice parameters $a$ and $c$ have been determined using the La Bail method [9] of FULLPROF with values of the unit-cell volume $V$ for Ho$_2$Fe$_{17-x}$Mn$_x$ at room temperature shown in Figure 1(b). $V$ exhibits a slight maximum around $x=0.5$ before increasing for Mn content $x\geq2$. This behaviour is similar to those of $R_2Fe_{17-x}Mn_x$ with $R$=Dy and Er but different from Ho$_2$Co$_{17-x}$Mn$_x$ [8] for which the unit-cell volumes increase monotonically with Mn (shown in Figure 1(b) for comparison).

![Figure 1](image-url)  

Figure 1 (a) X-ray-diffraction patterns for Ho$_2$Fe$_{17-x}$Mn$_x$ compounds (upper markers for Th$_2$Ni$_{17}$ type (2:17R), lower markers for the Th$_2$Zn$_{17}$ type (2:17H)). (b) Compositional dependence of the unit-cell volume $V$ of Ho$_2$Fe$_{17-x}$Mn$_x$. The behaviour of $V$ for Ho$_2$Co$_{17-x}$Mn$_x$ [8] is shown for comparison as an insert.

The temperature dependent magnetization curves of Figure 2(a) ($B_{appl}=100$ Oe) indicate that all compounds exhibit a single magnetic transition from the ferrimagnetic to the paramagnetic states...
confirming that both the Th$_2$Zn$_{17}$ and Th$_2$Ni$_{17}$ structures have the same Curie temperature in agreement with earlier studies [e.g. 2, 8].

The variation of the Curie temperature $T_C$ with composition is shown in Figure 2(b). Compared with Ho$_2$Co$_{17-x}$Mn$_x$ for which $T_C$ decreases with increasing Mn content [8], the $T_C$ values for Ho$_2$Fe$_{17-x}$Mn$_x$ remain essentially unchanged up to $x=1.0$ ($T_C=336$ K for $x=0.0$, $T_C=338$ K for $x=1.0$) before decreasing steadily with further increase in Mn content ($T_C=209$ K for $x=5$). This behavior is similar to the case of Nd$_2$Fe$_{17-x}$Mn$_x$ [2] and Dy$_2$Fe$_{17-x}$Mn$_x$ [6] where competition between the variation of the T-T interaction strengths and the variation of M$_T$ with the Mn content play a role. It is accepted that in Ho$_2$Fe$_{17}$ compounds there exist both positive and negative exchange interactions that are very sensitive to the spacing between Fe atoms [e.g. 1]. Due to the preferential occupation of the 6$c$/4$f$ Fe sites by the Mn atoms [2], for low levels of Mn doping ($x<2$) the negative T-T interaction will be reduced due to the increase in Fe-Fe bond distances (Mn atomic radius 1.35 Å; Fe atomic radius 1.26 Å) while the positive interaction also decreases due to the decrease in 3d sublattice magnetic moments (the magnetic moments of the 3d sublattice in R$_2$Fe$_{17-x}$Mn$_x$, as determined by neutron diffraction, decrease as the Mn content increases [2]). These two competing effects lead to the total T-T interaction remaining almost unchanged within the composition range $x=0-1$. For Ho$_2$Co$_{17-x}$Mn$_x$, with the strongest T-T exchange interaction and absence of negative exchange interactions, Mn substitution for Co will decrease the total T-T interaction throughout the entire Mn doping range.

The order of the phase transitions at $T_C$ was determined for all samples from M-H curves at various temperatures around the transition temperatures and the corresponding Arrot plots ($M^2$ versus $H/M$). Figure 2(c) show a typical example for Ho$_2$Fe$_{15}$Mn$_2$ with the corresponding Arrot plot presented in Figure 2(d). The positive slope derived from the Arrot plots demonstrates clearly that all phase transitions in the present set of samples are second order [10].

Figure 3(a) shows $^{57}$Fe Mössbauer spectra of Ho$_2$Fe$_{15}$Mn$_1$ at selected temperatures. The spectra have been fitted with a self-consistent model [6, 11] taking into account the orientation of the iron magnetic moments, the correlation between the iron isomer shifts and the Wigner-Seitz cell (WSC) volumes [6, 11] and the correlation between the hyperfine fields and the number of iron near neighbors. The subspectra were assigned by taking the nearest-neighbor environment of each respective site and the Fe-Fe distances into account. The sequences of hyperfine fields assigned to the different sites - 4f(6c)>6g(9d)>12j(18f)>12k(18h) - have also been observed in other R$_2$Fe$_{17}$-based compounds [6, 11].

Figure 3(b) shows the temperature dependences of the average hyperfine field and isomer shift values for Ho$_2$Fe$_{15}$Mn. The temperature dependence of the hyperfine field for Ho$_2$Fe$_{15}$Mn$_1$ is described well by the equation $B_{hf}(T) = B_{hf}(0)[1 - b(T/T_C)^2]$; similar behavior has been detected in Dy$_2$Fe$_{17-x}$Mn$_x$.  

![Figure 2](image-url)  

**Figure 2.** (a) M-T curves ($B_{appl}=100$ Oe) for Ho$_2$Fe$_{17-x}$Mn$_x$ during cooling from higher temperature; (b) Composition dependence of Curie temperature for Ho$_2$Fe$_{17-x}$Mn$_x$ (present work) and Ho$_2$Co$_{17-x}$Mn$_x$ [8]; (c) M-H curves and (d) the corresponding Arrot-plots at the temperatures indicated for Ho$_2$Fe$_{15}$Mn$_2$. 

![Figure 3](image-url)  

**Figure 3.** (a) $^{57}$Fe Mössbauer spectra of Ho$_2$Fe$_{15}$Mn$_1$ at selected temperatures; (b) Temperature dependences of the average hyperfine field and isomer shift values for Ho$_2$Fe$_{15}$Mn; (c) Arrot plots for Ho$_2$Fe$_{15}$Mn$_1$; (d) Arrot plots for Ho$_2$Fe$_{15}$Mn$_2$. 

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and ErFe$_{1.4}$Nb$_{0.6}$ [12]. The $T^2$ dependence of the hyperfine fields in the present series of compounds suggests that single-particle excitations may be responsible for suppressing the 3$d$-sublattice magnetization with increasing temperature [13]. Similar to other R$_2$Fe$_{17}$-based systems, Figure 3(b) also shows the correlation [6, 11] between isomer shift and the WSC with $\delta_{6c(4f)}$ $\approx$ $\delta_{18h(12k)}$ $\approx$ $\delta_{9d(6g)}$. 

![Figure 3](image)

**Figure 3** (a) $^{57}$Fe Mössbauer spectra of Ho$_2$Fe$_{16}$Mn$_1$ over the temperature range 100 K –300 K. The fits to the spectra (continuous lines) are described in the text. (b) Temperature dependences of the average values of hyperfine field and isomer shift for Ho$_2$Fe$_{16}$Mn$_1$.

### 4. Conclusions

Ho$_2$Fe$_{17-x}$Mnx (x=0-5) exhibits an unusual dependence of unit cell volume at room temperature with increase in Mn content (Figure 1(b)). The Curie temperature remains essentially unchanged for Mn content up to x=1.0 before decreasing steadily with further increase in Mn. The magnetic phase transitions around $T_C$ are determined to be second order. The $T^2$ dependence of the magnetic hyperfine field (Figure 3(b)) suggests that single-particle excitations may be responsible for suppressing the 3$d$-sublattice magnetization with increasing temperature.

### Acknowledgements

This work is supported by grants from ANSTO and UNSW (Joint Agreement; Silverstar).

### References

[9] We thank J M Cadogan for introducing us to the La Bail feature of the FULLPROF program.