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Magnetic properties of $Ho_2Fe_{17-x}Mn_x$ – influence of Mn substitution

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Abstract. The structural and magnetic properties of $Ho_2Fe_{17-x}Mn_x$ (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 $R_2Fe_{17-x}Mn_x$ systems, the unit cell volume generally increases with Mn content other than for low Mn values where a slight maximum is detected around x ~ 0.5. The nature of the magnetic phase transitions around T_C 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 (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_2T_{17} compounds in general exhibit strong magnetism with continuing interest focused on improvement in their magnetic properties [1]. While applications of R_2Fe_{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 $R_2Fe_{17-x}T_x$.

Compared with the substitution of T = Al, Ga and Si where the lattice parameters in $R_2Fe_{17-x}T_x$ exhibit monotonic behaviour with increasing x, it was found that $R_2Fe_{17-x}Mn_x$ (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 $R_2Fe_{17-x}Mn_x$ compounds to the preferential occupation of Mn atoms for the dumbbell pair site 6c (in Th_2Zn_{17}-type structure) or 4*f* (in Th_2Ni_{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 $Dy_2Fe_{17-x}Mn_x$ [6] and $Er_2Fe_{17-x}Mn_x$ [7], here we

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report our experimental investigation on $Ho_2Fe_{17-x}Mn_x$ by x-ray diffraction, magnetic and variable temperature Mössbauer spectroscopy measurements.

2. Experimental process

$Ho_2Fe_{17-x}Mn_x$ 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 Cu$K\alpha$ 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 α-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_2Zn_{17}-type (2:17R) and the hexagonal Th_2Ni_{17}-type (2:17H) structures. For example, in the case of Ho_2Fe_{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 $Ho_2Fe_{17-x}Ga_x$ [2] and $Ho_2Co_{17-x}Mn_x$ [8] with $Ho_2Fe_{14}Ga_3$, Ho_2Co_{17} and $Ho_2Co_{15}Mn_2$ showing coexistence of the Th_2Ni_{17} (H) and Th_2Zn_{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 $Ho_2Fe_{17-x}Mn_x$ at room temperature shown in Figure 1(b). V exhibits a slight maximum around x=0.5 before increasing for Mn content x≥2. This behaviour is similar to those of $R_2Fe_{17-x}Mn_x$ with R=Dy and Er but different from $Ho_2Co_{17-x}Mn_x$ [8] for which the unit-cell volumes increase monotonically with Mn (shown in Figure 1(b) for comparison).

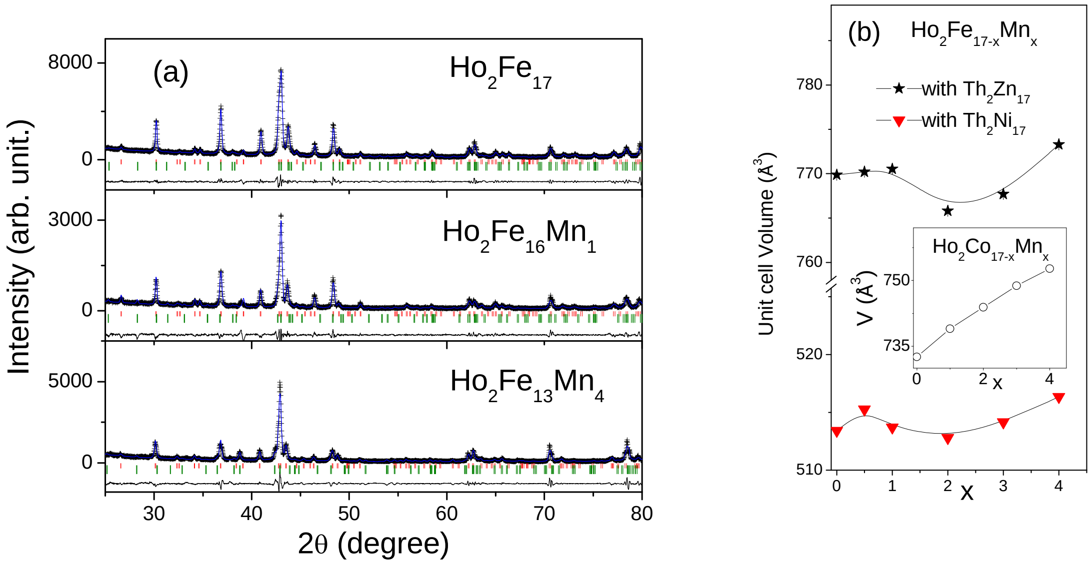

Figure 1 (a) X-ray-diffraction patterns for $Ho_2Fe_{17-x}Mn_x$ compounds (upper markers for Th_2Ni_{17} type (2:17R), lower markers for the Th_2Zn_{17} type (2:17H)). (b) Compositional dependence of the unit-cell volume V of $Ho_2Fe_{17-x}Mn_x$. The behaviour of V for $Ho_2Co_{17-x}Mn_x$ [8] is shown 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_2Zn_{17} and Th_2Ni_{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 $Ho_2Co_{17-x}Mn_x$ for which T_C decrease with increasing Mn content [8], the T_C values for $Ho_2Fe_{17-x}Mn_x$ remains 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 behaviour is similar to the case of $Nd_2Fe_{17-x}Mn_x$ [2] and $Dy_2Fe_{17-x}Mn_x$ [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_2Fe_{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 $R_2Fe_{17-x}Mn_x$, 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 $Ho_2Co_{17-x}Mn_x$, 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.

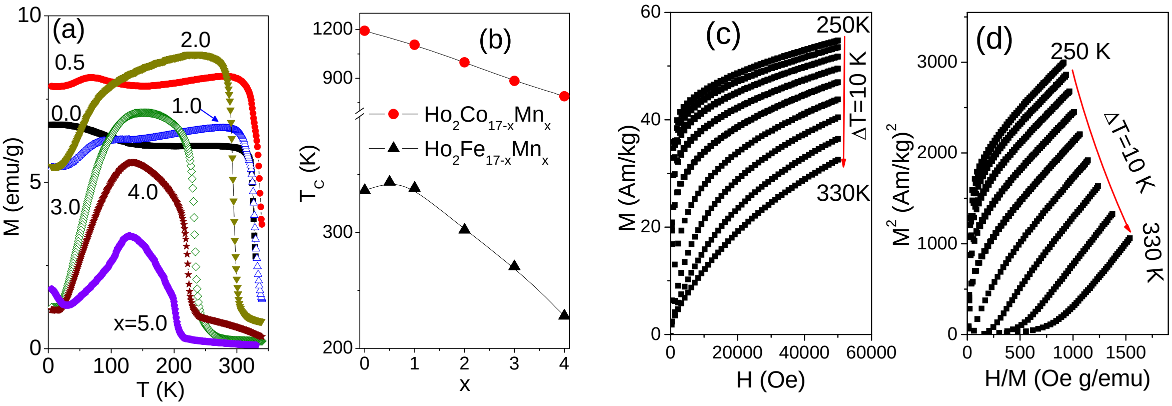

Figure 2. (a) M-T curves (B_{appl}=100 Oe) for $Ho_2Fe_{17-x}Mn_x$ during cooling from higher temperature; (b) Composition dependence of Curie temperature for $Ho_2Fe_{17-x}Mn_x$ (present work) and $Ho_2Co_{17-x}Mn_x$ [8]; (c) M-H curves and (d) the corresponding Arrot-plots at the temperatures indicated for $Ho_2Fe_{15}Mn_2$.

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 $Ho_2Fe_{15}Mn_2$ 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 $Ho_2Fe_{16}Mn_1$ 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_2Fe_{17}-based compounds [6, 11].

Figure 3(b) shows the temperature dependences of the average hyperfine field and isomer shift values for $Ho_2Fe_{16}Mn$. The temperature dependence of the hyperfine field for $Ho_2Fe_{16}Mn_1$ is described well by the equation $B_{hf}(T) = B_{hf}(0)[1 - b(T/T_C)^2]$; similar behavior has been detected in $Dy_2Fe_{17-x}Mn_x$

[6] and ErFe$_{11.4}$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 $\delta_{6c(4f)} > \delta_{18f(12j)} \approx \delta_{18h(12k)} > \delta_{9d(6g)}$.

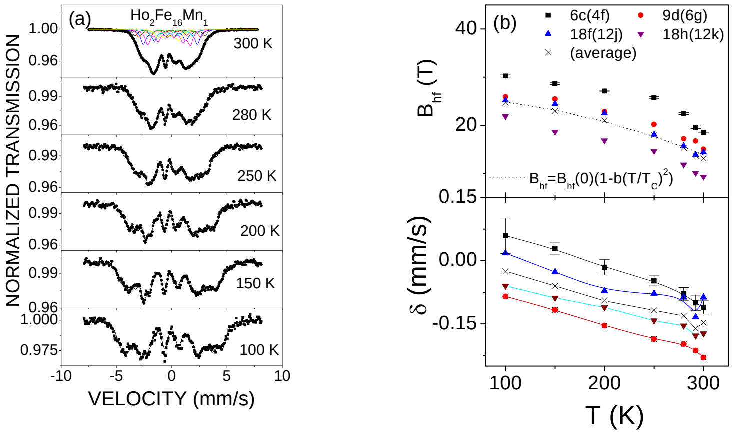

Figure 3 (a) ^{57}Fe Mössbauer spectra of Ho$_2$Fe$_{16}$Mn$_1$ over the temperature range 100 K –300 K. The fits to the spectra (continuous lines) are described in the text. (b) Temperature dependences of the average values of hyperfine field and isomer shift for Ho$_2$Fe$_{16}$Mn$_1$.

4. Conclusions

Ho$_2$Fe$_{17-x}$Mn$_x$ (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

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