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Magnetovolume effect in $\text{Ho}_2\text{Fe}_{17-x}\text{Mn}_x$ compounds

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The structural and magnetic properties of seven compounds in the $\text{Ho}_2\text{Fe}_{17-x}\text{Mn}_x$ series ($x = 0-5$) have been investigated. The spontaneous magnetization M_s at 10 K exhibits a minimum at $x \approx 3.8$ while the $3d$ -sublattice magnetization M_T is found to decrease at $\sim -3.4 \mu_B$ /per Mn atom compared with the rate of $\sim -2.0 \mu_B$ /per Mn atom expected from a simple dilution model. All of the $\text{Ho}_2\text{Fe}_{17-x}\text{Mn}_x$ compounds exhibit anisotropic thermal expansion below their Curie temperatures leading to the presence of strong magnetovolume effects and Invar-type behavior below T_C . An approximately zero volume thermal expansion has been detected between 10 K and 270 K for $\text{Ho}_2\text{Fe}_{17}$. The maximum magnetic entropy changes for $\text{Ho}_2\text{Fe}_{17-x}\text{Mn}_x$ with $x = 0$ and 2.0 are $3.2 \text{ J kg}^{-1} \text{ K}^{-1}$ around $T_C \sim 336 \text{ K}$ and $2.7 \text{ J kg}^{-1} \text{ K}^{-1}$ around $T_C \sim 302 \text{ K}$, respectively, for magnetic field change of $B = 0-5 \text{ T}$. © 2012 American Institute of Physics. [doi:10.1063/1.3671422]

INTRODUCTION

Intermetallic compounds R_2Fe_{17} (R = rare-earth) with a high concentration of iron continue to attract significant experimental and theoretical interest due to their anomalous magnetic properties.¹⁻³ R_2Fe_{17} compounds crystallize in two related crystal structures, rhombohedral $\text{Th}_2\text{Zn}_{17}$ type (light R) and hexagonal $\text{Th}_2\text{Ni}_{17}$ type (heavy R), with the two structures coexisting for some elements in the middle of the lanthanide series.²

The $\text{R}_2\text{Fe}_{17-x}\text{Mn}_x$ compounds also continue to attract attention due to their interesting magnetic behavior including a larger magnetovolume effect and the effects of the competition of positive and negative exchange interactions between nearest Fe atoms.⁴⁻⁶ Moreover, as the Curie temperatures of R_2Fe_{17} are close to room temperature, the magnetocaloric behavior of several R_2Fe_{17} compounds has been investigated⁷ (e.g., the magnetocaloric effect (MCE) of $\text{Er}_2\text{Fe}_{17}$ is $\sim 3.68 \text{ J/kg K}$ around $T_C = 294 \text{ K}$ for magnetic field change $B = 0-5 \text{ T}$). Here, we investigate the magnetic properties and magnetovolume effect of $\text{Ho}_2\text{Fe}_{17-x}\text{Mn}_x$ compounds with $x = 0.0-5.0$ together with their magnetocaloric behavior.

EXPERIMENTAL PROCEDURES

$\text{Ho}_2\text{Fe}_{17-x}\text{Mn}_x$ ingots were prepared by arc-melting and annealed at 1000°C for a week. Magnetic measurements were carried out over the temperature range $T \sim 5-350 \text{ K}$ using SQUID (MPMS, quantum design) and Physical Property Measurement System (PPMS). Details of the sample preparation methods and experimental procedures are presented elsewhere.⁸ Neutron powder diffraction experiments ($\lambda = 2.4191 \text{ \AA}$) have been carried out from 10 to 450 K using the high intensity powder diffractometer Wombat, OPAL,

Australia.⁹ Two series of variable temperature neutron diffraction measurements were undertaken on each sample after first cooling to base temperature $T = 10 \text{ K}$. The samples were initially investigated using a ramp sequence with a step of 1 K and counting time of 1 min at each temperature; this enabled the overall trends of the peak intensities and magnetic transitions to be delineated. The second series ($T = 10 \text{ K}, 100 \text{ K}, 200 \text{ K}, 300 \text{ K}, 400 \text{ K},$ and 450 K ; counting time $\geq 10 \text{ min}$) provided statistically high quality data for Rietveld refinements. The diffraction patterns were analyzed with the Fullprof package.

RESULTS AND DISCUSSION

The magnetization curves of free powder samples of $\text{Ho}_2\text{Fe}_{17-x}\text{Mn}_x$ at 10 K are shown in Fig. 1(a) with the dependence of the spontaneous magnetization $M_s(10 \text{ K})$ on Mn concentration shown in Fig. 1(b) (M_s is derived in the standard way by extrapolation to zero field). M_s for $\text{Ho}_2\text{Fe}_{17-x}\text{Mn}_x$ decreases with increasing Mn content to $x \approx 3.8$ before increasing with further increase in Mn content. $\text{Ho}_2\text{Fe}_{17}$ is a collinear ferrimagnetic² and the appearance of this minimum in the M_s versus x curve can be understood in terms of a compensation concentration originating from the ferrimagnetic coupling between the Ho-sublattice magnetization and the $3d$ -sublattice magnetization. In $\text{Ho}_2\text{Fe}_{17}$, the magnetic moments of the Fe ions in all crystallographic positions are collinear to each other but antiparallel to the magnetic moments of the Ho-sublattice.² We have calculated the transition-metal sublattice magnetization M_T from the measured M_s by subtracting the Ho-sublattice magnetization (we assume that the Ho sublattice magnetization is the same for all compounds and has the same value, $10 \mu_B$, as the free ion magnetic moment). As shown in Fig. 1(b), the calculated M_T values decrease with Mn content x with the full line representing a linear fit of M_T . A second calculation of the compositional dependence of M_T based on a

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FIG. 1. (Color online) (a) Magnetization curves at 10 K for $\text{Ho}_2\text{Fe}_{17-x}\text{Mn}_x$ ($T = 5$ K for $\text{Ho}_2\text{Fe}_{15}\text{Mn}_2$); (b) Composition dependence of the spontaneous magnetization M_s and the transition-metal sublattice moment M_T at 10 K for $\text{Ho}_2\text{Fe}_{17-x}\text{Mn}_x$ ($T = 5$ K for $\text{Ho}_2\text{Fe}_{15}\text{Mn}_2$). As discussed in the text, the full line represents a linear fit to the M_T values with the dashed line corresponding to M_T values calculated from a dilution model. The dashed-dotted line through the M_s values is a guide to the eye.

simple dilution model, in which the Mn atoms do not have a magnetic moment, is also shown for comparison (dashed line, Fig. 1(b)). The decrease of M_T with increasing Mn content ($\sim -3.4 \mu_B/\text{per Mn atom}$) compared with that expected from the dilution model ($\sim -2.0 \mu_B/\text{per Mn atom}$) indicates that Mn atoms have a magnetic moment which is aligned antiparallel to the Fe moments. Similar behaviors have been found for $\text{Tb}_2\text{Fe}_{17-x}\text{Mn}_x$,¹⁰ $\text{Er}_2\text{Fe}_{17-x}\text{Mn}_x$,¹¹ and $\text{Dy}_2\text{Fe}_{17-x}\text{Mn}_x$.⁵

We have investigated the Invar-type anomaly in $\text{Ho}_2\text{Fe}_{17-x}\text{Mn}_x$ by a combination of conventional fixed temperature neutron diffraction patterns and the ramp sequence as described above. As shown for the example of $\text{Ho}_2\text{Fe}_{17}$ (Fig. 2; for clarity only the patterns taken at 10 K steps are shown), the changes in magnetic peak intensities with temperature (inset of Fig. 2) lead to a magnetic transition temperature that agrees well with our magnetic data.⁸ Figure 3 shows the temperature dependence of the volume expansion $\Delta V/V$ for the $\text{Ho}_2\text{Fe}_{17-x}\text{Mn}_x$ compounds of T_C values close to room temperature (the lattice parameters were derived from the ramp data using the Le Bail approach; detailed refinements will be presented elsewhere¹²). Figure 3 reveals that the $\Delta V/V$ values for all samples tend toward linear behavior at high temperatures above T_C , whereas pronounced Invar-type behavior is observed below T_C .

The magnetic contribution to the thermal expansion which gives rise to Invar behavior can be obtained by comparing the experimental results with, $(\Delta V/V)_{\text{latt}}$, the lattice contribution to the volume. We have calculated $(\Delta V/V)_{\text{latt}}$

from the Grüneisen relation using a Debye temperature of $\theta_D = 450$ K.^{5,11} The thermal dependence of $(\Delta V/V)_{\text{latt}}$ was fitted to the experimental results in the paramagnetic regime leading to the extrapolations shown by the dashed lines in Fig. 3. The deviations from the calculated nonmagnetic anharmonic phonon contributions above T_C reveal contributions to the spontaneous magnetostriction even in the paramagnetic phase, indicating the existence of strong short range magnetic correlations above T_C .¹² In the case of $\text{Ho}_2\text{Fe}_{17}$, this anisotropic thermal expansion (inset to Fig. 3) leads to approximately zero volume thermal expansion with negligible volume change between 10 K and 270 K as shown in Fig. 3.

FIG. 2. (Color online) Representative neutron diffraction patterns for $\text{Ho}_2\text{Fe}_{17}$ at 10 K intervals ($\lambda = 2.4191$ Å). The inset shows a graph of the peak height vs temperature for the (101) and (112) peaks.

FIG. 3. (Color online) Volume expansion, $\Delta V/V$, for $\text{Ho}_2\text{Fe}_{17-x}\text{Mn}_x$ ($x = 0.0$ – 3.0) as a function of temperature. The dashed line represents the calculated nonmagnetic anharmonic phonon contribution. The inset shows the a (closed symbols) and c (open symbols) lattice parameters vs temperature for $\text{Ho}_2\text{Fe}_{17}$.

FIG. 4. (Color online) (a) Magnetization as a function of applied DC field ($\mu_0 H = 0-5$ T) for $\text{Ho}_2\text{Fe}_{17}$ around $T_C \sim 336$ K. (b) Arrott-plots of M^2 as a function of $\mu_0 H/M$ for the magnetization data of (a). The positive slopes indicate that the transition at T_C is second-order. (c) Temperature dependence of the isothermal magnetic entropy change $-\Delta S_M(T, H)$ as measured in magnetic fields up to 5 T and derived from the magnetic data of 4(a).

The existence of the Invar effect is related to the strong dependence of T_C and the magnetization on the interatomic distances. A pronounced decrease of spontaneous magnetization and Curie temperature of R_2Fe_{17} intermetallic compounds with applied pressure has been reported ($dM/dp = -0.1 \mu_B/\text{f.u.}$ per kbar for $\text{Ho}_2\text{Fe}_{17}$ (Ref. 13) and $dT_C/dp = -9.8 \text{ K/kbar}$ for Y_2Fe_{17} (Ref. 14)), thus confirming the close link between magnetic and lattice effects in these R_2Fe_{17} -based compounds. This behavior can be understood within the classical model of itinerant ferromagnetism in which the magnetovolume effect is related to the gradient of the density of states (DOS) at the Fermi level E_F . If E_F lies in an energy region with a steep slope of the DOS curve, small changes in the position of E_F could induce large changes in the magnetic moment. Theoretical calculations for R_2Fe_{17} ($\text{R} = \text{Pr}$ and Gd) (Ref. 15) show that the slope of the DOS curve at E_F for $3d$ and $4p$ densities of states of Fe is indeed very steep, consistent with the above discussion.

We have extended the MCE investigations of R_2Fe_{17} -based compounds⁷ by measurement of the MCE values for $\text{Ho}_2\text{Fe}_{17-x}\text{Mn}_x$. Figure 4(a) shows the M versus $\mu_0 H$ curves for the magnetic regions of interest around T_C for $\text{Ho}_2\text{Fe}_{17}$ as a representative example. The corresponding Arrott plots of M^2 versus $\mu_0 H/M$ are shown in Fig. 4(b). The positive slopes in the isotherm Arrott plots indicate the second-order nature of the phase transition around T_C for $\text{Ho}_2\text{Fe}_{17}$. The values of the magnetic entropy change ΔS have been obtained from the Maxwell relation,⁷

$$-\Delta S_M(T, H) = \mu_0 \int_0^H \left(\frac{\partial M}{\partial T} \right)_H dH. \quad (1)$$

The magnetic entropy changes of $\text{Ho}_2\text{Fe}_{17}$ as a function of temperature and change in external field are shown in Fig. 4(c) with the maximum of $-\Delta S$ derived to be $1.1 \text{ J kg}^{-1} \text{ K}^{-1}$, $1.8 \text{ J kg}^{-1} \text{ K}^{-1}$, $2.4 \text{ J kg}^{-1} \text{ K}^{-1}$, $2.8 \text{ J kg}^{-1} \text{ K}^{-1}$, and $3.2 \text{ J kg}^{-1} \text{ K}^{-1}$, for external field changes from 0 to 1 T, 0 to 2 T, 0 to 3 T, 0 to 4 T, and 0 to 5 T, respectively. Similar results have been obtained for $\text{Ho}_2\text{Fe}_{15}\text{Mn}_2$, with MCE values $0.9 \text{ J kg}^{-1} \text{ K}^{-1}$, $1.5 \text{ J kg}^{-1} \text{ K}^{-1}$, and $2.6 \text{ J kg}^{-1} \text{ K}^{-1}$ in the region of $T_C \sim 302 \text{ K}$ for $\Delta B = 0-1 \text{ T}$, $0-2 \text{ T}$, and $0-5 \text{ T}$, respectively.

CONCLUSIONS

Mn substitution for Fe in $\text{Ho}_2\text{Fe}_{17-x}\text{Mn}_x$ leads to a minimum in the composition dependence of the spontaneous magnetization M_s at 10 K around Mn content $x = 3.8$. Pronounced magnetovolume effects have been observed below the magnetic ordering temperatures; this leads to Invar-type behavior which can be linked to the character of the density of states of Fe atoms. With a magnetic field change of $0-5 \text{ T}$, the magnetic entropy change around T_C has been found to be $3.2 \text{ J kg}^{-1} \text{ K}^{-1}$ and $2.7 \text{ J kg}^{-1} \text{ K}^{-1}$ for $\text{Ho}_2\text{Fe}_{17}$ ($T_C \sim 336 \text{ K}$) and $\text{Ho}_2\text{Fe}_{15}\text{Mn}_2$ ($T_C \sim 302 \text{ K}$), respectively.

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