Magnetovolume effect in Ho2Fe17-xMnx compounds

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The structural and magnetic properties of seven compounds in the Ho$_2$Fe$_{17-x}$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 Ho$_2$Fe$_{17-x}$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 Ho$_2$Fe$_{17}$. The maximum magnetic entropy changes for Ho$_2$Fe$_{17-x}$Mn$_x$ with $x = 0$ and 2.0 are 3.2 J kg$^{-1}$ K$^{-1}$ around $T_C \sim 336$ K and 2.7 J kg$^{-1}$ K$^{-1}$ around $T_C \sim 302$ K, respectively, for magnetic field change of B = 0-5 T. © 2012 American Institute of Physics. [doi:10.1063/1.3671422]

INTRODUCTION

Intermetallic compounds R$_2$Fe$_{17}$ (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$_2$Fe$_{17}$ compounds crystallize in two related crystal structures, rhombohedral Th$_2$Zn$_{17}$ type (light R) and hexagonal Th$_2$Ni$_{17}$ type (heavy R), with the two nearest Fe atoms.4–6 Moreover, as the Curie temperatures of a larger magnetovolume effect and the effects of the competition of magnetic transitions to be delineated. The second series ($T = 10$ K, 100 K, 200 K, 300 K, 400 K, and 450 K; counting time $\geq$10 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 Ho$_2$Fe$_{17-x}$Mn$_x$ at 10 K are shown in Fig. 1(a) with the dependence of the spontaneous magnetization $M_s$ on Mn concentration shown in Fig. 1(b) ($M_s$ is derived in the standard way by extrapolation to zero field). $M_s$ for Ho$_2$Fe$_{17-x}$Mn$_x$ decreases with increasing Mn content to $x \approx 3.8$ before increasing with further increase in Mn content. Ho$_2$Fe$_{17}$ is a collinear ferrimagnetic 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 Ho$_2$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

EXPERIMENTAL PROCEDURES

Ho$_2$Fe$_{17-x}$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 $T \sim 5-350$ K using SQUID (MPMS, quantum design) and Physical Property Measurement System (PPMS). Details of the sample preparation methods and experimental procedures are presented elsewhere.9 Neutron powder diffraction experiments (4.2191 Å) have been carried out from 10 to 450 K using the high intensity powder diffractometer Wombat, OPAL.

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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 ($\sim 2.0 \mu_B$/per Mn atom) compared with that expected from the dilution model ($\sim 3.4 \mu_B$/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 Tb$_2$Fe$_{17-x}$Mnx, Er$_2$Fe$_{17-x}$Mnx,11 and Dy$_2$Fe$_{17-x}$Mnx.5

We have investigated the Invar-type anomaly in Ho$_2$Fe$_{17-x}$Mnx by a combination of conventional fixed temperature neutron diffraction patterns and the ramp sequence as described above. As shown for the example of Ho$_2$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 Ho$_2$Fe$_{17-x}$Mnx 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 Ho$_2$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.
The magnetic regions of interest around TC for Ho2Fe17 as a representative example. The corresponding 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 TC 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 (a).

The existence of the Invar effect is related to the strong dependence of TC and the magnetization on the interatomic distances. A pronounced decrease of spontaneous magnetization and Curie temperature of R2Fe17 intermetallic compounds with applied pressure has been reported (dM/dp = −0.1μ0/μ.u. per kbar for Ho2Fe17 (Ref. 13) and dTC/dp = −9.8 K/kbar for Y2Fe17 (Ref. 14)), thus confirming the close link between magnetic and lattice effects in these R2Fe17-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 EF. If EF lies in an energy region with a steep slope of the DOS curve, small changes in the position of EF could induce large changes in the magnetic moment. Theoretical calculations for R2Fe17 (R = Pr and Gd) (Ref. 15) show that the slope of the DOS curve at EF 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 R2Fe17-based compounds7 by measurement of the MCE values for Ho2Fe17-xMnx. Figure 4(a) shows the M versus $\mu_0 H$ curves for the magnetic regions of interest around TC for Ho2Fe17 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 isothermal Arrott plots indicate the second-order nature of the phase transition around TC for Ho2Fe17. The values of the magnetic entropy change $\Delta S$ 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 Ho2Fe17 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 J kg$^{-1}$ K$^{-1}$, 1.8 J kg$^{-1}$ K$^{-1}$, 2.4 J kg$^{-1}$ K$^{-1}$, 2.8 J kg$^{-1}$ K$^{-1}$, and 3.2 J kg$^{-1}$ 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 Ho2Fe15Mn2, with MCE values 0.9 J kg$^{-1}$ K$^{-1}$, 1.5 J kg$^{-1}$ K$^{-1}$, and 2.6 J kg$^{-1}$ K$^{-1}$ in the region of TC ∼ 302 K for ΔB = 0-1 T, 0-2 T, and 0-5 T, respectively.

CONCLUSIONS

Mn substitution for Fe in Ho2Fe17-xMnx 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 T, the magnetic entropy change around $T_C$ has been found to be 3.2 J kg$^{-1}$ K$^{-1}$ and 2.7 J kg$^{-1}$ K$^{-1}$ for Ho2Fe17 ($T_C$ ∼ 336 K) and Ho2Fe15Mn2 ($T_C$ ∼ 302 K), respectively.

12J. L. Wang et al., “Effect of Mn substitution for Fe on the structural and magnetic properties of Ho2Fe17” (unpublished).