The effect of boron doping on crystal structure, magnetic properties and magnetocaloric effect of DyCo₂

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The magnetic properties and magnetic entropy changes of DyCo₂B_x (x=0, 0.05, 0.1, 0.2) alloys were investigated. The Curie temperature (T_C) increases with increasing B concentration. The frequency dependence of ac magnetic susceptibility of DyCo₂ caused by the narrow domain wall pinning effect is depressed by B doping, but the coercivity and the magnetic viscosity are prominently increased in the B doped alloys. The magnetic transition nature of DyCo₂B_x changes from the first-order to the second-order with increasing x, which leads to the decrease of the maximum magnetic entropy change. However, the relative cooling power (RCP) of DyCo₂ and the B doped alloys remains nearly constant.

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I. INTRODUCTION

The Laves phases RM_2 (R is a rare earth element and M is a transition metal) keep attracting a lot of research attention, because of their rich magnetic properties, such as giant magnetoresistance, magnetostriction, and magnetocaloric effects.¹⁻⁴ A particular property of the $DyCo_2$ compound is the narrow domain wall pinning effect manifested by the irreversibility of ZFC and FCC magnetization, and the ZFC peak just below the transition temperature,⁵ which is also a signature of the spin glass system. The narrow domain wall pinning effect occurs due to the high magnetocrystalline anisotropy of $DyCo_2$,^{6,7} and this effect depends strongly upon the applied magnetic field strength.⁵ For the narrow domain wall systems, there is an energy difference between the center of the wall located at an atomic plane and the one that is located between two planes. Such difference blocks the domain wall motion and leads to the domain wall pinning effect.⁸ Compared to the domain wall pinning caused by the impurities and defects, the narrow domain wall pinning is an intrinsic property in $DyCo_2$.

Magnetic refrigeration is a promising technology, which can replace the traditional vapor-compression refrigeration due to the higher efficiency and eco-friendliness. Since the discovery of the giant magnetocaloric effect (GMCE) in the intermetallic compound $Gd_5Si_2Ge_2$,⁹ increasing attention has been devoted to GMCE near room-temperature resulting in the discovery of other promising GMCE materials such as $La(Fe_{1-x}Si_x)_{13}$ and its hydrides, $MnFeP_{1-x}As_x$, $MnAs_{1-x}Sb_x$, Heusler alloys (e.g. $Ni_{51.5}Mn_{22.7}Ga_{25.8}$), RM_2 Laves phases and others.¹⁰⁻¹⁶

The Laves phase $DyCo_2$ has the highest first-order magnetic transition (FOMT) temperature (140 K) in the RCO_2 family of alloys, but it is still far below the room temperature. To increase the transition temperature of $DyCo_2$, element substitutions have been extensively studied over the past few years. For example, partial replacement of Dy by Gd and Tb,^{17,18} and substitution of Co by Ga, Fe, Al, and

Si^{6,19-21} were investigated. All the results show that the Curie temperature rises with the increase of lattice constant. However, the order of the magnetic transition changes from first to second. The non-monotonic increase of T_C in case of Si substitution was explained by the competition among magnetovolume effect and magnetic dilution effect.⁶ Moreover, the study of the pressure effects on DyCo₂ reveals that the Curie temperature decreases with the application of external pressure due to the contraction of the lattice parameter.²² Doping by interstitial elements (H, C, and B) usually leads to an increase of the lattice constant, and the H absorption has been successfully applied to adjust the Curie temperature of La(Fe_{0.89}Si_{0.11})₁₃ from 190 K to room-temperature, while preserving the first-order of the magnetic transition.¹⁵ However, the hydrogenation treatment for DyCo₂ leads to disproportionation and amorphization of the compound.²³

In this paper, the magnetocaloric effect and magnetic properties (such as ac susceptibilities, magnetic hysteresis, magnetic relaxation and magnetic phase transition at Curie temperature) of DyCo₂B_x (x=0, 0.05, 0.1, 0.2) alloys were studied, due to the influences of interstitial element B on the exchange interaction and the domain wall mobility of DyCo₂.

II. EXPERIMENTAL DETAILS

The DyCo₂B_x (x=0, 0.05, 0.1, 0.2) alloys were prepared by arc-melting of the constituents in an argon atmosphere. The alloys were turned over several times to insure the homogeneity of the sample. The Dy metal was prepared by the Materials Preparation Center²⁴ of the Ames Laboratory and it was 99.8 at.% (99.97 wt.%) pure with the major impurities, given as at. ppm (wt. ppm), as follows: O-802(79), C- 1271(94), N-104(9), Hf-109(120). The Co metal of 99.95 wt.% purity was purchased from Alfa Aesar Inc. The purity of B was 99.5 wt.%. The arc-melted ingots were annealed in evacuated silica tubes at 1173 K for 6 days, and then quenched in ice-water slurry.

Structural and phase analyses were performed by collecting and analyzing the powder x-ray diffraction (XRD) patterns obtained at room temperature on PANalytical X'Pert Pro diffractometer using Cu $K\alpha_1$ radiation. The lattice parameters of the obtained phases and the concentration of the minor phase (when present) were calculated by the Rietveld method using the LHPM Rietica software.²⁵ Magnetic properties of bulk polycrystalline samples were measured by superconducting quantum interference device (SQUID) magnetometer, MPMS-XL7 from Quantum Design Inc. The ZFC, FCC and FCW magnetization measurements were made as follows: the ZFC curve was measured by cooling the sample down to 2 K without magnetic field, then a magnetic field of 100 Oe was applied, and the magnetization of a sample was measured during heating from 2 K to 200 K, with the temperature rate of 2 K/min. The FCC curve was measured by sweeping down the temperature from 200 K to 2 K in applied field of 100 Oe. The field-cooled-warming (FCW) curve was obtained by cooling the sample down in presence of 100 Oe magnetic field, then measuring the magnetization from 2 K to 200 K under magnetic field of 100 Oe.

III. Results and discussion

A. XRD and magnetization measurements

The XRD patterns of DyCo_2B_x ($x=0, 0.05, 0.1, 0.2$) alloys containing the C15 (MgCu_2 -type structure) Laves phase as a main phase are shown in Fig. 1. The impurity phase DyCo_2B_2 (BaAl_4 -type) was found in $\text{DyCo}_2\text{B}_{0.2}$ and its Bragg peaks are marked by black diamonds; the concentration of this phase is about 8 wt.% as determined by Rietveld refinement.

FIG. 1. XRD patterns of DyCo_2B_x ($x=0, 0.05, 0.1, 0.2$), vertical bars indicate the calculated positions of the Bragg peaks of the MgCu_2 -type Laves phase. Diamonds on the $\text{DyCo}_2\text{B}_{0.2}$ alloy signify the impurity phase DyCo_2B_2 (BaAl_4 -type).

The lattice parameters of DyCo_2B_x ($x=0, 0.05, 0.1, 0.2$) calculated by the Rietveld refinement are listed in Table 1. Due to B doping, the lattice parameter expands from $7.191(1) \text{ \AA}$ (DyCo_2) to $7.195(1) \text{ \AA}$ ($\text{DyCo}_2\text{B}_{0.1}$). However, the lattice parameter of $\text{DyCo}_2\text{B}_{0.2}$ and $\text{DyCo}_2\text{B}_{0.1}$ is the same. This indicates that the DyCo_2B_x solid solution terminates near $x = 0.1$. For AB_2 (C15 -type) Laves phase, there are three types of tetrahedral sites available which are presented in the following format, atom type + atom number (Wyckoff sites): $\text{B4}(8b)$, $\text{AB3}(32e)$ and $\text{A2B2}(96g)$, and interstitial atoms prefer AB3 and A2B2 sites.^{26,27} Therefore, those two positions are potential interstitial sites for boron in DyCo_2B_x compounds. Distortions caused by boron atoms may account for the small solid solubility in DyCo_2 .

As shown in Fig. 2, below T_C noticeable thermomagnetic irreversibility between ZFC and FCC magnetizations occurs in 100 Oe magnetic field in DyCo_2 and is attributed to the narrow domain

wall pinning effect.^{8,28} A weak anomaly was found in ZFC curve at 20 K (labeled as T_a , see Fig. 2a). On the further increase of temperature ZFC magnetization forms a broad peak below T_C (136(1) K), and then drops sharply at the Curie temperature showing a magnetic transition from the ferrimagnetic state⁴ to the paramagnetic state. The field cooling process stabilizes the magnetic moments along the magnetic field direction. As a result, both the FCC and FCW curves have a stable magnetization below T_C . An obvious irreversibility of FCC and FCW curves below T_C (Fig. 2a) is often observed in materials that show a significant time dependence of remanent magnetization²⁹ which will be discussed in part B.

The dc magnetization curves of DyCo_2B_x ($x=0.05$ and 0.1) displayed in Fig. 2(b) and (c) are similar. Because of the enhancement of domain pinning effect by interstitial B atoms, the ZFC magnetizations are close to zero below 43 K (T_P , indicated by arrows in Figs. 2b,c). Above T_P the ZFC magnetization increases quickly and reaches maximum just below T_C . The thermomagnetic irreversibility between FCC and FCW curves below T_C exists in both of the doped samples.

The Curie temperatures of DyCo_2B_x ($x=0, 0.05, 0.1, 0.2$) are increased from 136(1) K ($x=0$) to 147(1) K ($x=0.2$) as listed in Table 1. The increase of T_C is a result of the volume expansion which leads to the 3d band narrowing.⁶

FIG. 2. The ZFC-FCC-FCW magnetization of DyCo_2B_x ($x = 0, 0.05, 0.1$) measured in a 100 Oe magnetic field. The insets show a detailed view of dc magnetization curves near the Curie temperature.

The inset of Fig. 3 shows that the paramagnetic susceptibilities of DyCo_2B_x follow the Curie-Weiss law:

$$H/M = Np_{eff}^2 / 3k(T - \theta_p) \quad (1)$$

where H is the applied magnetic field, M is the molar magnetization, N is Avogadro's number, p_{eff} is the effective magnetic moment, k is Boltzmann's constant, T is the absolute temperature, and θ_p is the paramagnetic Weiss temperature. The calculated effective magnetic moment per formula unit p_{eff} and the paramagnetic Weiss temperature θ_p are listed in the Table 1. Similar to T_C , θ_p of DyCo_2B_x increases from 133(1) K ($x=0$) to 142(1) K ($x=0.1$), however, the p_{eff} decreases from 9.56 $\mu_B/\text{f.u.}$ ($x=0$) to 9.23 $\mu_B/\text{f.u.}$ ($x=0.1$). The increase of paramagnetic Weiss temperature with boron concentration also results from the volume expansion which enhances the exchange interaction of Co sublattice. It is important to note that no short range order effects (such as paramagnetic effect³⁰) are observed in the DyCo_2 compound prepared using the high-purity rare earth metal.

FIG. 3. Temperature dependence of dc magnetization of DyCo_2B_x ($x=0, 0.05, 0.1$) measured in 1 kOe field under ZFC condition. The inset shows the inverse susceptibility for the same samples.

The effect of boron on magnetization of DyCo_2 is also examined by saturation magnetization measurement at 5K. By linear fitting the magnetization versus reciprocal magnetic field (not shown here), the saturation magnetizations of DyCo_2B_x ($x=0, 0.05, 0.1$ and 0.2) are estimated as follow:

151, 160, 139 and 132 emu/g. The non-monotonic saturation magnetizations of DyCo₂B_x alloys may result from the competition between lattice expansion and hybridization effect^[31].

The influence of B doping on the ac susceptibility of DyCo₂B_x compounds is studied. The samples were cooled down to 2 K, and then the ac susceptibility was measured from 1 Hz to 1000 Hz during heating in zero dc magnetic field (Fig. 4). At low temperatures the χ' and χ'' of DyCo₂ are both zero due to the domain wall pinning effect, since the 5 Oe ac magnetic field is too small to move the domain walls. With temperature increasing to ~30 K, both real and imaginary parts of ac magnetization begin to increase showing strong frequency dependence. The χ' reaches maximum just below T_C , but the peaks of χ'' are at about half of the T_C .

The imaginary susceptibility of DyCo₂ has two peaks, the broad peak around 50 K that shifts to higher temperature with increasing the frequency, and the sharp peak at T_C , which is frequency independent and small. The nonzero imaginary susceptibility indicates a dissipative process caused by the narrow domain wall pinning. When the temperature is high enough (in this case close to T_C) the domain walls become unrestricted, so the χ'' drops to zero. At these temperatures the frequency dependence of χ' disappears too. Spin glass systems also show frequency dependence of ac susceptibility, but the frequency dependence of freezing temperature (defined as the peak of ac susceptibility³²), which is a typical characteristic of a spin glass system does not occur in DyCo₂.

The frequency dependence of the B doped samples is weaker than that of DyCo₂. This may be due to the fact that the frequency dependence of ac susceptibility mainly results from the narrow domain wall pinning effect, which becomes weaker with the temperature increase, as shown by the χ' of DyCo₂. Because the doping by B increases pinning, the domain walls cannot respond the ac magnetic field until temperature reaches ~80 K, where the thermal energy of the system becomes high enough to suppress the pinning and the frequency effects associated with it. In addition, the

sharp peak of χ'' at T_C disappears, but weak anomaly is still observed.

FIG. 4. The temperature dependence of ac susceptibility of DyCo₂B_x (x=0, 0.05, 0.1) measured in 5 Oe ac field with frequency ranging from 1 Hz to 1000 Hz. χ' is the real part (solid symbols) and χ'' is the imaginary part (open symbols). The inset of DyCo₂ is the amplification of its imaginary susceptibility.

The domain wall pinning effect has an influence on the coercivity determined by measuring the

magnetic hysteresis loop. Hysteresis loops of DyCo_2B_x were performed with magnetic field step of 200 Oe and are shown in Fig. 5. The coercivities of DyCo_2B_x ($x=0, 0.05, 0.1$) samples are 0.28(1), 3.29(1) and 4.41(1) kOe respectively, as listed in Table 1. It is possible that the coercivity is increased due to stronger domain wall pinning effect caused by the introduction of the interstitial B atoms (see above). However, modification of the microstructure, namely the precipitation of the secondary phase at the phase boundaries (even though the phase is not seen in the XRD patterns) may also be responsible for the larger coercivity.

For the B doped samples, one can define a critical field called propagation field (H_p), indicated by arrows in Fig. 5, the initial field at which the magnetization starts rising³³. The propagation fields of DyCo_2B_x ($x = 0, 0.05, 0.1$) increase with x from zero to 1.9 kOe and 2.5 kOe, respectively. This indicates the enhanced stability of the domain walls. Moreover, all of the samples have unusual initial magnetization curves, which go outside of the hysteresis loop at low magnetic field and then cross the loop back inside when the magnetization is nearly saturated. This abnormal region corresponds to the irreversible domain wall motion and rotation, which imply that the domain wall ‘feels’ higher resistance during the first time passing through the irreversible domain wall movement region, than that of the second time.

FIG. 5. Hysteresis loops of DyCo_2B_x ($x = 0, 0.05, 0.1$) measured at 5 K with magnetic field changing from -50 kOe to 50 kOe. The inset to each graph shows the amplification of the first quadrant.

B. Magnetic relaxation

To study the time dependence of remanent magnetization of DyCo_2B_x ($x = 0, 0.05, 0.1$) the isothermal magnetic relaxation measurements were performed and are shown in Fig. 6.

The samples were first cooled down from 300 K to 5 K in magnetic field of 10 kOe, and then kept for 1000 s to stabilize the temperature and magnetization of the sample. After that the magnetic field was turned off and magnetization was measured at 5 K as a function of time. The magnetic relaxation process can be described by the following expression³⁴:

$$M_r = M_0 - S_v \ln(t - t_0) \quad (2)$$

where M_r is the remanent magnetization; M_0 is the initial remanent magnetization; S_v is the magnetic viscosity, and t is time.

The magnetic viscosities S_v of DyCo_2B_x ($x=0, 0.05, 0.1$) calculated using equation 2 are 0.49(1), 1.85(1) and 1.14(1) emu/g, respectively, as listed in Table 1. The increase of magnetic viscosities of the B doped samples may be due to the larger resistance of domain wall movement caused by the B doping.

FIG. 6. The remanent magnetization of DyCo_2B_x ($x = 0, 0.05, 0.1$) magnetized in a field 10 kOe at 5 K.

Table 1. Crystal and magnetic parameters of DyCo₂B_x (x = 0, 0.05, 0.1, 0.2).

Alloy	Lattice parameter	Curie temprature	Paramagnetic Weiss temperature	Effective magnetic moment	Coercivity	Magnetic viscosity	Magnetic entropy change
	a	T_C	θ_P	p_{eff}	H_C	S_v	$ \Delta S $
	(Å)	(K)	(K)	($\mu_B/\text{f.u.}$)	(kOe)	(emu/g)	(J/kgK)
							(50 kOe)
DyCo ₂	7.1910(1)	136(1)	133(1)	9.56	0.28(1)	0.49(1)	13.9
DyCo ₂ B _{0.05}	7.1944(1)	143(1)	141(1)	9.27	3.29(1)	1.85(1)	10.9
DyCo ₂ B _{0.1}	7.1948(1)	145(1)	142(1)	9.23	4.41(1)	1.14(1)	9.0
DyCo ₂ B _{0.2}	7.1950(1)	147(1)	-	-	-	-	7.8

C. Isothermal magnetization and magnetocaloric effect

Isothermal magnetization curves of DyCo₂B_x (x=0, 0.05, 0.1, 0.2) are shown in Fig. 7. Both increasing and decreasing field measurements were carried out in the vicinity of T_C . A weak magnetic hysteresis of DyCo₂ at 137 K, marked by the arrows in Fig. 7, top left plot, supports the weak first-order nature of magnetic transition. No hysteresis is observed in any of the B doped samples confirming a second order nature of these magnetic transitions. The itinerant electron metamagnetism (IEM) of DyCo₂ could be observed just above T_C 136 K, but for the B doped samples the IEM transition is depressed.

FIG. 7. The magnetization isotherms of DyCo_2B_x ($x=0, 0.05, 0.1, 0.2$) measured in magnetic fields up to 50 kOe.

The Arrott plots of DyCo_2B_x ($x=0, 0.05, 0.1, 0.2$) obtained just above their respective Curie temperatures are shown in Fig. 8. According to the Banerjee criterion^[35], positive slopes of the M^2 vs. M/H curves of DyCo_2B_x ($x=0.05, 0.1, 0.2$) at Curie temperature indicate the second-order magnetic transition. The negative slope of DyCo_2 agrees with the first-order nature of magnetic transition. As an alternative to the Banerjee criterion, Bonilla provided a new criterion to distinguish the order of magnetic transitions by rescaling magnetic entropy change in different applied fields^[36]. If the entropy change curves collapse onto a single one, then the magnetic transition is second order, otherwise it is first order. For DyCo_2B_x ($x=0, 0.05, 0.1$) samples, the magnetic entropy change curves are rescaled by two steps: first, normalize each isofield $\Delta S(T)$ to its maximum value ΔS^{peak} , and then rescaling the temperature axis with variable θ ,

$$\theta = \begin{cases} -(T - T_c)/(T_{r1} - T_c), & T \leq T_c \\ (T - T_c)/(T_{r2} - T_c), & T > T_c \end{cases} \quad (3)$$

The reference temperatures T_{r1} and T_{r2} satisfy $T_{r1} < T_c < T_{r2}$, and they are determined by the equation 4, for each curve

$$\frac{\Delta S(T_{r1})}{\Delta S^{peak}} = \frac{\Delta S(T_{r2})}{\Delta S^{peak}} = \frac{1}{2} \quad (4)$$

As shown in Fig. 8, the rescaled magnetic entropy change curves of DyCo_2B_x ($x=0.05, 0.1$) are collapsed onto single one separately, which confirm their second-order magnetic transition; On the contrary, the scattered curves of DyCo_2 demonstrate its first-order magnetic transition.

FIG. 8. The scaled entropy change curves and Arrott plots of DyCo_2B_x ($x=0, 0.05, 0.1, 0.2$).

The plot of magnetic entropy change (ΔS) versus temperature of DyCo_2B_x ($x=0, 0.05, 0.1, 0.2$) in the magnetic field of 50 kOe, calculated from the isothermal $M(H)$ data using the Maxwell relation $\Delta S(T, H) = \int_0^H (\partial M / \partial T)_H dH$ is presented in Fig. 9. With increasing of the B concentration, the temperatures of the $\Delta S(T)$ peaks of DyCo_2B_x alloys shift from 136 K ($x=0$) to 147 K ($x=0.2$)

due to the increase of T_C . But the maximum values decrease from $-13.9 \text{ J/kg}\cdot\text{K}$ to $-7.8 \text{ J/kg}\cdot\text{K}$ because the order of the magnetic transition changes from first to second, as shown in Fig. 8.

FIG. 9. The entropy change of DyCo_2B_x ($x=0, 0.05, 0.1, 0.2$) in the magnetic field of 0-50 kOe.

The relative cooling power (RCP), which is also an important parameter to evaluate the magnetocaloric materials, is given by the following expression:

$$RCP = -\Delta S^{\max} \times \delta T_{FWHM} \quad (5)$$

where δT_{FWHM} is the full width at half maximum of $-\Delta S$ vs. T curve. The RCP values of DyCo_2B_x ($x=0, 0.05, 0.1, 0.2$) in the magnetic field of 50 kOe are 302, 357, 310 and 293 J/kg. Although the doping of B reduces the maximum entropy change, the $\Delta S(T)$ peaks become broader. Therefore, the RCP's of DyCo_2B_x alloys are almost the same with that of their parent compound.

IV. CONCLUSIONS

The discrepancy between the ZFC and FCC curves of DyCo_2B_x is enhanced in the B doped samples.

The Curie temperature of DyCo_2 also increases with the B doping; however, the increase is not linear and when compared with the change in lattice parameters indicates that the DyCo_2B_x solid solution is nearly terminated slightly above $x = 0.05$. It is possible that the precipitation of the secondary phase in the grain boundaries also modifies the magnetic properties, such as coercivity. The dissipation of domain wall movement caused by narrow domain wall pinning effect leads to an obvious frequency dependence of the ac magnetic susceptibility in DyCo_2 . However, this phenomenon is masked in the B doped samples, because the domain walls are further stabilized by B doping at low temperature where narrow domain wall pinning effect is strong, while at higher temperatures the increase in thermal energy overcomes the kinetic effects associated with pinning. The coercivity and viscosity that are related with the mobility of the domain walls are increased by the B doping. The magnetic transition nature is changed from first-order to second-order because of the B doping, which leads to the decrease of the maximum magnetic entropy change values. At the same time the RCP's of DyCo_2B_x for $x=0.1$ and 0.2 are almost the same (within 3%) with that of the parent compound DyCo_2 , while that for $x=0.05$ is about 18% larger.

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