Structural and magnetic properties of $DyCo_{4-x}Fe_xGa$ compounds

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The structural and magnetic properties of the $DyCo_{4-x}Fe_xGa$ compounds with $x=0$, 0.5, 1, and 1.5 have been investigated by X-ray diffraction and magnetic measurements. Powder X-ray diffraction analysis reveals that each of the $DyCo_{4-x}Fe_xGa$ compounds has a hexagonal $CaCu_5$-type structure (space group $P6/mmm$). The Fe solubility limit in $DyCo_{4-x}Fe_xGa$ is $x<1.5$. The higher the value of x, the larger the unit-cell parameters a, c, V, and the $3d$-sublattice moment but the smaller the $3d$ uniaxial anisotropy. Magnetic measurements show that the Curie temperature of $DyCo_{4-x}Fe_xGa$ increases from 498 K for $x=0$ to 530 K for $x=1.5$, the compensation temperature T_{comp} decreases from 286 K for $x=0$ to 238 K for $x=1.5$, and the spin-reorientation transition temperature increases from 403 K for $x=0$ to 530 K for $x=0.5$. No spin-reorientation transition was found in the samples with $x=1.0$ and 1.5. The saturation magnetization of $DyCo_{4-x}Fe_xGa$ measured at 173 K increases but the magnetization measured at 300 K decreases with increasing Fe content x. © *2010 International Centre for Diffraction Data.* [DOI: 10.1154/1.3478562]

Key words: transition metal compounds, crystal structure, magnetic properties

I. INTRODUCTION

Rare earth–transition metal (R-T) intermetallics are an important group of compounds with interesting magnetic and hydrogen absorption properties (Buschow, 1977). The magnetic performances of the intermetallics are caused by a combination of the complementary characteristics of $3d$-itinerant and $4f$-localized magnetisms. Their technological importance and interesting properties have resulted in a continuous experimental and theoretical research (Buschow, 1977; Richter, 1998) over the past several decades. Among the R-T intermetallics, the hexagonal Haucke compounds RCo_5 ($CaCu_5$-structure type, space group $P6/mmm$) are one of the most interesting subclasses, which have been widely studied for a fundamental research as well as their possible applications as permanent magnets (Strnat, 1988). Studies of the structural and magnetic properties for $DyCo_4M$ (M = Al, Ga) (Klosek *et al.*, 2003, 2004), $DyCo_{5-x}Cu_x$ (Banerjee *et al.*, 2006), and $Dy_{1-x}Y_xCo_5$ (Banerjee *et al.*, 2008) have also been reported. The results show that the substitutions of nonmagnetic atoms, Al, Ga, and Cu for Co or Y for Dy, have remarkable influences on both crystal structure and magnetic properties, such as the Curie temperatures (T_C), compensation temperatures T_{comp}, spin-reorientation transitions, and magnetization of the compounds. To further study the magnetic properties of the $3d$ sublattice of RCo_4Ga compounds, we reported in this paper the effects of the substitution of Fe for Co on both crystal and magnetic properties in $DyCo_4Ga$.

II. EXPERIMENTAL

Polycrystalline samples $DyCo_{4-x}Fe_xGa$ with $x=0$, 0.5, 1, and 1.5 were prepared by arc melting using a nonconsumable

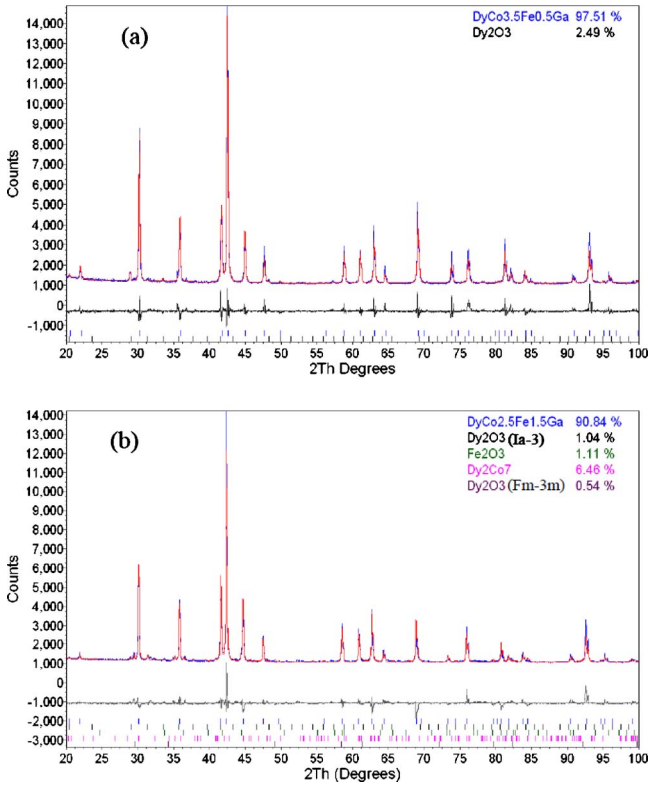

Figure 1. (Color online) Rietveld refinement results for the $DyCo_{3.5}Fe_{0.5}Ga$ sample (a) and the $DyCo_{2.5}Fe_{1.5}Ga$ sample (b).

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TABLE I. Structure and refined parameters for hexagonal $DyCo_{4-x}Fe_xGa$.

Compound	$DyCo_4Ga$	$DyCo_{3.5}Fe_{0.5}Ga$	$DyCo_3FeGa$	$DyCo_{2.5}Fe_{1.5}Ga$
a (nm)	0.497 80 (2)	0.499 33 (3)	0.501 02 (1)	5.0087 (2)
c (nm)	0.402 04 (1)	0.402 52 (2)	0.403 58 (1)	4.0517 (2)
V (nm^3)	0.086 348 (6)	0.0869 20 (1)	0.087 733 (6)	0.088 030 (8)
ρ ($g\ cm^{-3}$)	8.999 (6)	8.898 (1)	8.7955 (6)	8.7387 (8)
R_p (%)	2.77	3.15	2.70	3.15
R_{wp} (%)	5.10	5.21	4.23	5.24
R_{exp} (%)	2.82	2.72	2.77	2.77
GOF	1.81	1.92	1.52	1.89

tungsten electrode and a water-cooled copper tray in argon. The alloy samples, each with 2 g in total weight, were prepared from Dy (99.99 wt %), Co (99.9 wt %), Fe (99.99 wt %), and Ga (99.999 wt %). The alloy samples were remelted at least three times to ensure homogeneity. No composition analysis was carried out since the weight lost of each sample was less than 1% during the preparation. Each sample was further sealed in an evacuated quartz tube, annealed at 950 °C for 1 week, and then cooled to room temperature. X-ray powder diffraction (XRD) data were collected using a Bruker D8 Advance SS/18 kW diffractometer with Cu $K\alpha$ radiation (40 kV and 250 mA) and a diffracted-beam graphite monochromator. A step-scan mode was employed with a step width of $\Delta 2\theta\_ = 0.02°$ and a sampling time of 5 s. The scan range for all samples is from 20° to 100° 2θ. JADE 5.0 and TOPAS 3.0 software programs were used for phase identification and structure determination. The temperature dependence and field dependence of the magnetization of the samples were measured using a vibrating sample magnetometer (VSM) (VSM-HH20, Nanjing University). The Curie temperature of each sample was determined from the minimum of the first derivatives of its magnetization curve.

III. RESULTS AND DISCUSSION

A. Crystal structure

Using the TOPAS 3.0 program, Rietveld refinements of the XRD data of the $DyCo_{4-x}Fe_xGa$ samples were performed with the assumption that each $DyCo_{4-x}Fe_xGa$ compound has a hexagonal $CaCu_5$-type structure with space group $P6/mmm$, and the Dy atom occupies the 1a (0, 0, 0) site, two Co atoms occupy the 2c (1/3, 2/3, 0) and the 3g (1/2, 0, 1/2) sites, and the Ga and Fe atoms prefer to occupy the 3g sites, as those of $DyCo_4M$ and $PrCo_{4-x}Fe_xM$ (M=Al and Ga) as reported by Klosek *et al.* (2003) and Zlotea and Isnard (2003). Representative results obtained by the Rietveld refinements are depicted in Figure 1(a) for the $DyCo_{3.5}Fe_{0.5}Ga$ sample and Figure 1(b) for $DyCo_{2.5}Fe_{1.5}Ga$. The refinement results for all four samples are listed in Tables I and II. As shown in Table I, the values of R factors are reasonably small from 2.72% to 5.24% and the values of goodness of fit (GOF) (or χ^2) are between 1.52 and 1.92. The refinement analysis reveals the presences of small amounts of dysprosium and/or iron oxides [for examples, see Figures 1(a) and 1(b)]. It should be noted that two forms of structures with different space groups of $Ia\bar{3}$ and $Fm\bar{3}m$ were found to present the compound $DyCo_{2.5}Fe_{1.5}Ga$ [see Figure 1(b)]. The larger the Fe content x, the larger the total amount of impurity oxides. The total amount of oxides presented in $DyCo_{2.5}Fe_{1.5}Ga$ is almost 1.0% [Figure 1(b)]. Figures 1(a) and 1(b) reveal that Dy_2Co_7 only appears in the x=1.5 compound, not the x=0.5 compound. This suggests that the iron solubility limit in $DyCo_4Ga$ should be $x<1.5$, which is comparable to that of other $CaCu_5$-type structure compounds. The iron solubility limits were previously reported to be $x<2.0$ in $PrCo_{4-x}Fe_xAl$ by Zlotea and Isnard (2003), $x<1.5$ in $NdCo_{4-x}Fe_xAl$ by Konno *et al.* (1992), and $x<1.8$ in $YCo_{4-x}Fe_xAl$ and $x<1.5$ in $HoCo_{4-x}Fe_xAl$ phases by Thang *et al.* (1995). The compositional dependences of lattice parameters a, c, c/a, and unit-cell volume V for $DyCo_{4-x}Fe_xGa$ as a function of the Fe content x are depicted in Figures 2(a)–2(c). As shown in Figures 2(a) and 2(b), both the values of the unit-cell parameters a and c increase with the content of Fe between x=0 and 1.0. However, a relatively smaller value of the unit-cell parameter a and a significantly larger value of c were obtained for the x=1.5 compound. As a result, the unit-cell volume V increases linearly with x in the

TABLE II. Atomic parameters for hexagonal $DyCo_{4-x}Fe_xGa$ ($P5/mmm$).

					Occupations			
Atom	Site	x	y	z	$DyCo_4Ga$	$DyCo_{3.5}Fe_{0.5}Ga$	$DyCo_3FeGa$	$DyCo_{2.5}Fe_{1.5}Ga$
Dy	1a	0	0	0	1	1	1	1
Co1	2c	1/3	2/3	0	1	1	1	1
Co2	3g	1/2	0	1/2	0.667	0.5	0.333	0.167
Fe	3g	1/2	0	1/2	0	0.167	0.333	0.5
Ga	3g	1/2	0	1/2	0.333	0.333	0.333	0.333

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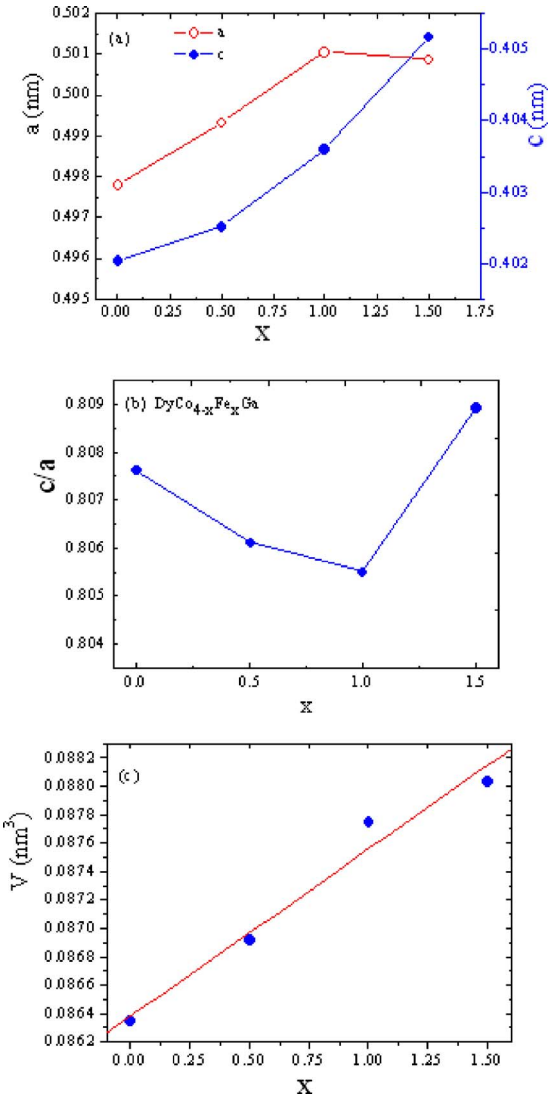

Figure 2. (Color online) Compositional dependence of unit-cell parameters a and c (a), c/a (b), and unit-volume V (c) for $DyCo_{4-x}Fe_xGa$ compounds with $x=0$, 0.5, 1.0, and 1.5.

range of $0 \leq x \leq 1.5$ [see Figure 2(c)]. The expansion of the unit-cell parameters is more pronounced along the a axis at lower Fe substitutions with $0 \leq x \leq 1.0$ but along the c axis at higher Fe substitutions with $1.0 \leq x \leq 1.5$. This anisotropic expansion and contraction may be the cause for the nonstability of crystal structures reported by Taylor and Poldy (1975).

B. Magnetic properties

The temperature dependence and field dependence of the magnetization of the samples were measured using a VSM. Figure 3 shows the temperature dependence of the magnetization (M-T curves) for $DyCo_{4-x}Fe_xGa$ with $x=0$, 0.5, 1.0, and 1.5 measured in the applied field of 0.1 T and the temperature range from 80 to 850 K. All $DyCo_{4-x}Fe_xGa$ samples have magnetic ordering. The M-T curve of $DyCo_4Ga$ has the same magnetic behavior with that reported by Klosek *et al.* (2003). Compensation transition and a spin-reorientation transition were found in $DyCo_4Ga$ at $T_{comp}=286$ K and $T_{SRT}=403$ K, respectively. According to the results of a

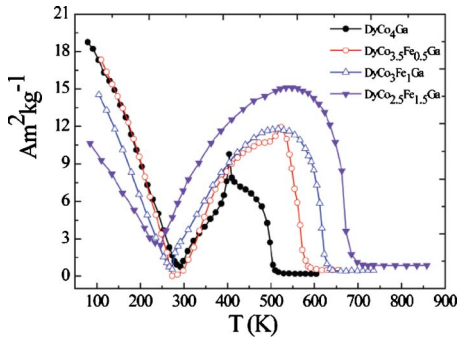

Figure 3. (Color online) Temperature dependence of the magnetization (M-T curves) for $DyCo_{4-x}Fe_xGa$ with $x=0$, 0.5, 1.0, and 1.5 measured in the applied field of 0.1 T and the temperature range from 80 to 850 K.

powder neutron diffraction analysis reported by Klosek *et al.* (2003), the Dy-sublattice magnetization is antiparallel to the Co-sublattice magnetization in $DyCo_4Ga$. The composition dependences of the compensation temperature T_{comp}, the spin-reorientation temperature T_{SRT}, and the Curie temperature T_C for the $DyCo_{4-x}Fe_xGa$ with $x=0$, 0.5, 1.0, and 1.5 are shown in Figure 4. The magnetic parameters are summarized in Table III. The compensation temperatures T_{comp} decrease with increasing Fe concentration from 286 K for $x=0$ to 238 K for $x=1.5$, which may due to the increase of the 3d-sublattice moment by substitution of Fe for Co in this compound. The Dy-sublattice magnetic moment was found to be much more temperature dependence than that of the Co sublattice. Almost cancellation of Dy- and Co-sublattice magnetizations was found to occur at its compensation temperature T_{comp}. The spin-reorientation transitions appear in the $DyCo_{4-x}Fe_xGa$ at $T_{SRT}=403$ K for $x=0$ and at $T_{SRT}=530$ K for $x=0.5$ but disappear for $x=1.0$ and 1.5, suggesting that a weakening of the 3d uniaxial anisotropy upon Fe substitution. Klosek *et al.* (2003) reported that the spin-reorientation transition occurs when the magnetic moments rotate continuously with temperatures near temperature T_{SRT}, which is originated from the competition between axial Co (3d) and planar Dy (4f) magnetocrystalline anisotropic in $DyCo_4Ga$. As shown in Figure 4, the Curie temperature (T_C) of $DyCo_{4-x}Fe_xGa$ increases from 498 K for $x=0$ to 673 K for $x=1.5$. The Curie temperature is mainly determined by the 3d-3d exchange interaction. The observed increase in T_C is due to the magnitudes of both the Fe magnetic moment to be

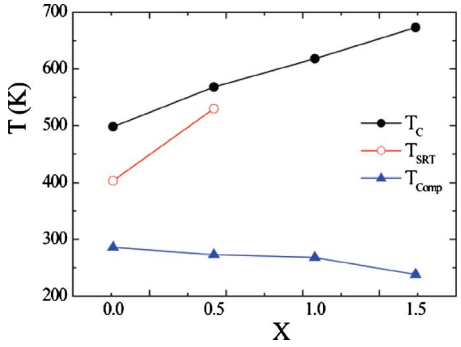

Figure 4. (Color online) Composition dependences of the compensation temperature T_{comp}, the spin-reorientation temperature T_{SRT}, and the Curie temperature T_C for $DyCo_{4-x}Fe_xGa$ with $x=0$, 0.5, 1.0, and 1.5.

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TABLE III. Magnetic properties for $DyCo_{4-x}Fe_xGa$ with $x=0$, 0.5, 1.0, and 1.5.

Compound	T_C (K)	T_{sr} (K)	T_{comp} (K)	T_{comp}/T_C	M_S (A m^2 kg^{-1}) 300 K	M_S (A m^2 kg^{-1}) 173 K
$DyCo_4Ga$	498	403	286	0.5743	5.05	21.13
$DyCo_{3.5}Fe_{0.5}Ga$	568	530	273	0.4806	5.40	17.84
$DyCo_3FeGa$	618		268	0.4337	6.80	16.82
$DyCo_{2.5}Fe_{1.5}Ga$	673		238	0.3536	11.36	12.07

slightly larger than Co as well as the Fe-Fe exchange interactions replacing Co-Co exchange interactions. The isothermal magnetization curves recorded at 173 and 300 K for the $DyCo_{4-x}Fe_xGa$ samples are shown in Figures 5(a) and 5(b), respectively. As shown in Figure 5, the saturation magnetization (M_S) of $DyCo_{4-x}Fe_xGa$ decreases from 20.49 to 11.09 A m^2 kg^{-1} at 173 K but increases from 3.69 to 10.13 A m^2 kg^{-1} at 300 K with increasing Fe content x. This was the result of an increase in the 3*d*-sublattice magnetic moment with increasing iron content, and the magnetic moment of the 3*d* sublattice is antiparallel to that of the dysprosium sublattice (Mayot *et al.*, 2008). The magnetization of the dysprosium (4*f*) sublattice dominates that of the transition metal (3*d*) sublattice at a temperature lower than the compensation temperature T_{comp}, whereas the opposite situation occurs at a temperature higher than T_{comp}. An increase in the 3*d*-sublattice moment by substitution of Fe for Co in $DyCo_{4-x}Fe_xGa$ leads to a decrease in the saturation magnetization recorded at 173 K but an increase in the saturation magnetization at 300 K.

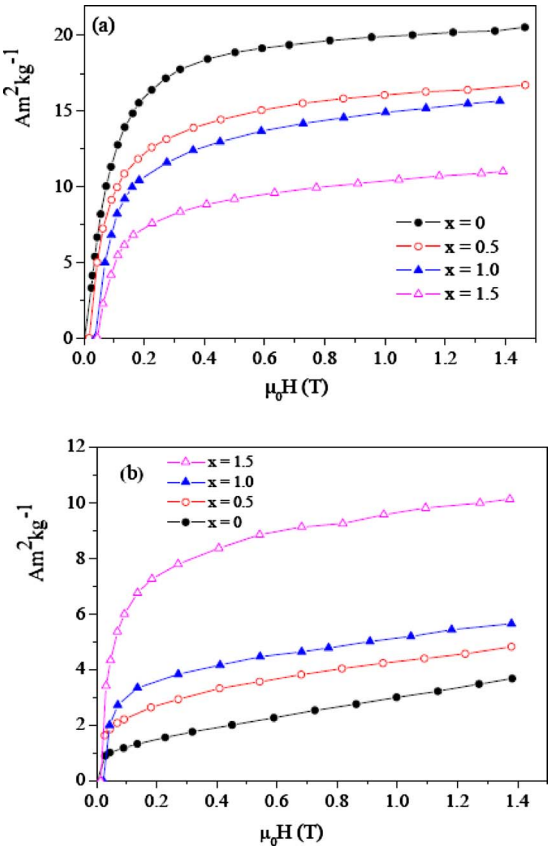

Figure 5. (Color online) Isothermal magnetization curves recorded at 173 K (a) and 300 K (b) for $DyCo_{4-x}Fe_xGa$ with $x=0$, 0.5, 1.0, and 1.5.

IV. CONCLUSION

The crystal structural and magnetic properties of the $DyCo_{4-x}Fe_xGa$ samples with $x=0$, 0.5, 1.0, and 1.5 were studied. The iron solubility limit in $DyCo_4Ga$ was found to be $x<1.5$. The values of the unit-cell parameters *a*, *c*, and *V*, and the 3*d*-sublattice moment of the hexagonal $DyCo_{4-x}Fe_xGa$ increase with increasing Fe content *x*. The increase in the substitution of Fe for Co in $DyCo_{4-x}Fe_xGa$ leads to a decrease in the compensation temperature but increases in the spin-reorientation and Curie temperatures. Our study also show that the value of saturation magnetization at 173 K increases but the value at 300 K decreases with increasing Fe content *x*.

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