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Structural and magnetic properties of $Dy_{1-x}Nd_xCo_4Ga$ compounds

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ABSTRACT

The structural and magnetic properties of $Dy_{1-x}Nd_xCo_4Ga$ compounds with $x = 0$, 0.2, 0.4, 0.6, 0.8 and 1.0, have been investigated by X-ray diffraction and magnetic measurements. Powder X-ray diffraction analysis revealed that the $Dy_{1-x}Nd_xCo_4Ga$ compounds form in single phase with a hexagonal $CaCu_5$-type structure (space group $P6/mmm$) for all the composition range. The substitution of Dy by Nd in the compound increases its lattice parameters a, c and cell volume V, but decreases the rare earth 4f-sublattice moment and reduces the 3d–3d exchange interaction. As result, the Curie temperatures of $Dy_{1-x}Nd_xCo_4Ga$ decreases from 498 K for $x = 0$ to 410 K for $x = 1.0$. The compensation temperatures T_{comp} decrease from 286 K for $x = 0$ to 178 K for $x = 0.2$, and even lower than 100 K for the samples with $x = 0.4$ to $x = 1$. The spin-reorientation transitions decreases from 403 K for $x = 0$ to 303 K for $x = 1.0$. The maximum magnetic entropy change $(-\Delta S_M)$ are 0.91 J kg^{-1} K^{-1} at 301 K for the spin-reorientation (SR) transition and 0.62 J kg^{-1} K^{-1} at 405 K for FM–PM transition in the compound $NdCo_4Ga$ in the magnetic field change of 1.5 T.

1. Introduction

Rare earth-transition metal (R-T) intermetallics represent an important group of compounds with interesting magnetic properties [1]. Their technological importance as well as interesting properties resulted in a continuous experimental and theoretical research [1,2] over the last several decades. Among the R-T intermetallics, hexagonal Haucke compounds ($CaCu_5$-type structure, space group of $P6/mmm$) of the RCo_5 composition are one of the most interesting subclasses, which were widely studied from a fundamental viewpoint but also for their possible applications as permanent magnets [3]. The compound $DyCo_5$ is high temperature phase which decomposes into Dy_2Co_7 and Dy_2Co_{17} by eutectoid reaction at about 1130 °C [4]. Substitution of Ga for Dy in this compound can stabilize its $CaCu_5$-type structure at lower temperature [5]. The investigations of the structural and magnetic properties for $DyCo_4M$ (M = Al, Ga) [6], $DyCo_{5-x}Cu_x$ [7] and $Dy_{1-x}Y_xCo_5$ [8] compounds indicate that the substitutions of non-magnetic atoms, Al, Ga and Cu for Co, or rare earth Y for Dy have remarkable influences on both crystal structure and magnetic properties of the compound, such as the Curie temperatures (T_C), compensation temperatures T_{comp}, spin-reorientation transitions T_{SR} and magnetization. In this work, we study the effects of the substitution of Nd for Dy on both crystal structural and magnetic properties of $DyCo_5$ in a wide composition range which has not been studied before. The compounds $Dy_{1-x}Nd_xCo_4Ga$ show two successive magnetic transitions: spin-reorientation (SR) transition near room temperature (300–400 K) and transition from ferromagnetic (FM) to paramagnetic (PM) states at 400–500 K. In this work, we investigated the magnetocaloric effect (MCE) due to the contribution from the SR and FM–PM transitions for possible magnetic refrigeration application near room temperature. The magnetocaloric effect with a SR is receiving more attention nowadays [9].

2. Experimental details

The polycrystalline $Dy_{1-x}Nd_xCo_4Ga$ compounds with $x = 0$, 0.2, 0.4, 0.6, 0.8 and 1.0 were prepared by arc melting using a non-consumable tungsten electrode and a water-cooled copper tray in an atmosphere of pure argon. The alloy samples, each 2 g in total weight, were prepared from Dy (99.9 wt.%), Nd (99.9 wt.%), Co (99.95 wt.%) and Ga (99.99 wt.%). The alloy buttons were re-melted at least three times to ensure homogeneity. No composition analysis was carried out since the weight loss of the sample was less than 1% during the preparation. The alloy buttons were sealed in evacuated quartz tubes and annealed at 950 °C for 1 week, and then furnace cooled to room temperature. X-ray powder diffraction (XRD) data were collected by a Bruker D8 Advance SS/18 kW diffractometer with Cu Kα radiation. JADE 5.0 and Topas 3.0 software were used for phase analysis and structure determination. The temperature dependence and field dependence of the magnetization were measured using a vibrating sample magnetometer (Nanjing University VSM-HH20). The Curie temperatures were identified as the minimum of the first derivative of the magnetization with respect to temperature. The magnetocaloric effect can be characterized by the isothermal magnetic entropy change $\Delta S_M(T, \Delta H)$ upon application of a magnetic field H. The value of $\Delta S_M(T, \Delta H)$ can be determined using the thermodynamic Maxwell relation [10,11]:

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

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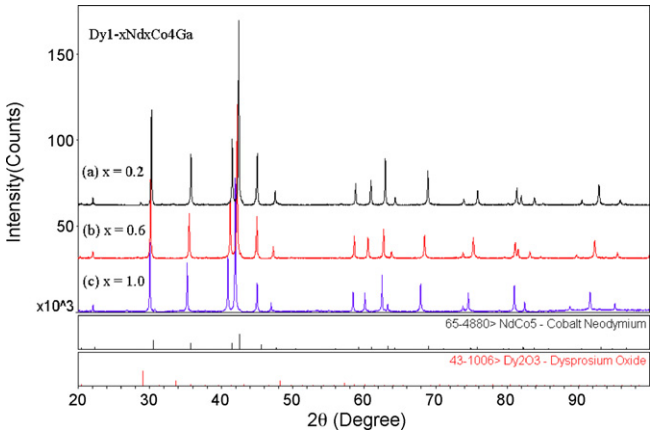

Fig. 1. XRD patterns for $Dy_{1-x}Nd_xCo_4Ga$ with (a) $x = 0.2$ (b) $x = 0.6$ and (c) $x = 1.0$.

3. Results and discussion

3.1. Crystal structure

The powder X-ray diffraction patterns of the $Dy_{1-x}Nd_xCo_4Ga$ alloys, shown in Fig. 1 with $x = 0.2$, 0.6 and 1.0 as representative, revealed that they form in single phase with a hexagonal $CaCu_5$-type structure (space group *P6/mmm*) for all the composition range. A very small amount of oxide Dy_2O_3 appears in some samples. The XRD patterns of the $CaCu_5$-type phase in the samples $Dy_{1-x}Nd_xCo_4Ga$ move to the smaller 2θ as increasing Nd content x obviously, indicating the expansion of the lattice as the substitution of Nd for Dy in $DyCo_4Ga$. The representative Rietveld refinement results for $Dy_{0.8}Nd_{0.2}Co_4Ga$ using the Topas 3.0 program are shown in Fig. 2. The refinement results show the samples $Dy_{1-x}Nd_xCo_4Ga$ contain the single phase with a hexagonal $CaCu_5$-type structure mainly, together with about 1 wt. % Dy_2O_3. The very small amount of the oxide Dy_2O_3 may be occurred during sample preparation which does not much affect the investigation of structural and magnetic properties for the $Dy_{1-x}Nd_xCo_4Ga$. The rare earth Dy and Nd atoms occupy 1a (0, 0, 0) sites, two Co atoms occupy 2c (1/3, 2/3, 0) and 3 g (1/2, 0, 1/2) sites, and the Ga atoms occupy the 3 g sites in the $CaCu_5$ structure. The refinement parameters obtained by Rietveld refinement for $Dy_{1-x}Nd_xCo_4Ga$ are given in Table 1. The compositional dependence of lattice parameters a, c, and unit cell volume V for $Dy_{1-x}Nd_xCo_4Ga$ are shown in Fig. 3(a) and (b). Both the lattice parameters a and c increase on the lower substitution of Nd for Dy from $x = 0$ to 0.6, but a increases more quickly while c decreases for high substitution from $x = 0.6$ to 1.0 (Fig. 3(a)). However, the unit cell V keep increase near linearly in all composition range due to the larger atomic radius of Nd (Fig. 3(b)). The expansion of the unit cell lattice may be responsible for the magnetic properties of the compound $Dy_{1-x}Nd_xCo_4Ga$.

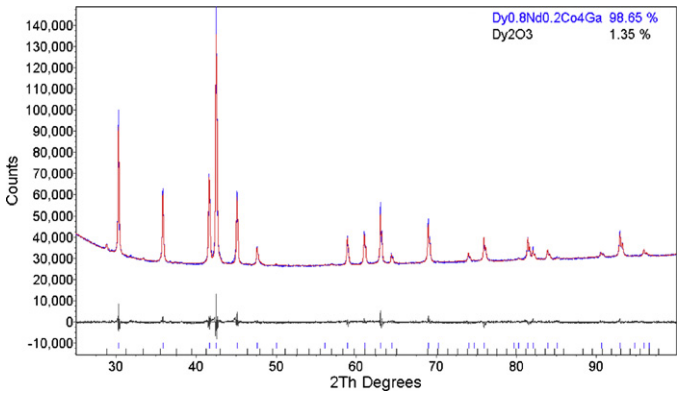

Fig. 2. Rietveld refinement for the XRD patterns of the compound $Dy_{0.8}Nd_{0.2}Co_4Ga$.

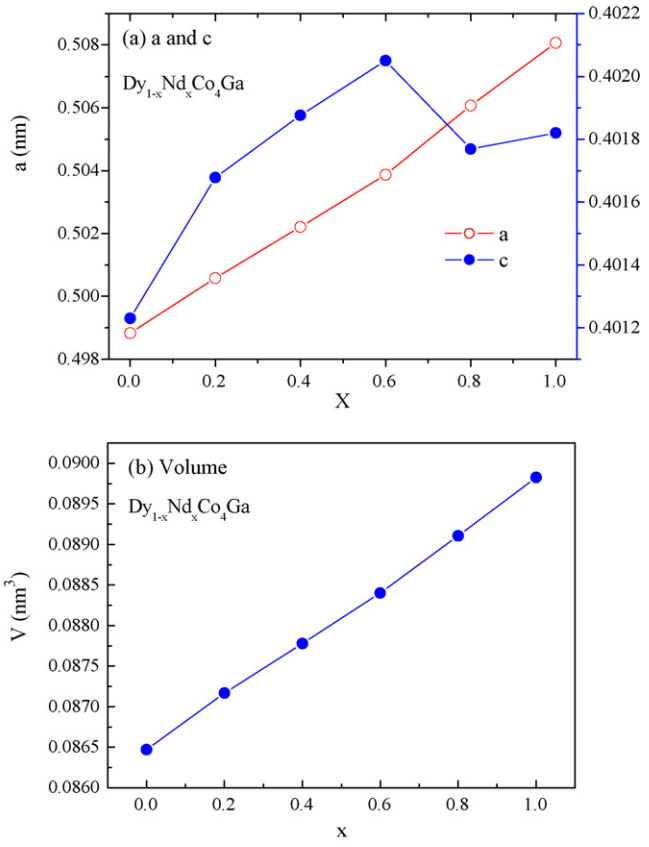

Fig. 3. Compositional dependence of (a) the lattice parameters a, c and (b) the unit volume V for the $Dy_{1-x}Nd_xCo_4Ga$ compounds.

3.2. Magnetic properties

Fig. 4 shows the temperature dependence of the magnetization (M–T curves) for the $Dy_{1-x}Nd_xCo_4Ga$ compounds with $x = 0$, 0.2, 0.4, 0.6, 0.8 and 1.0 measured in the applied field of 0.1 T and the temperature range from 80 to 700 K. All the $Dy_{1-x}Nd_xCo_4Ga$ samples have magnetic ordering, which show the same magnetic

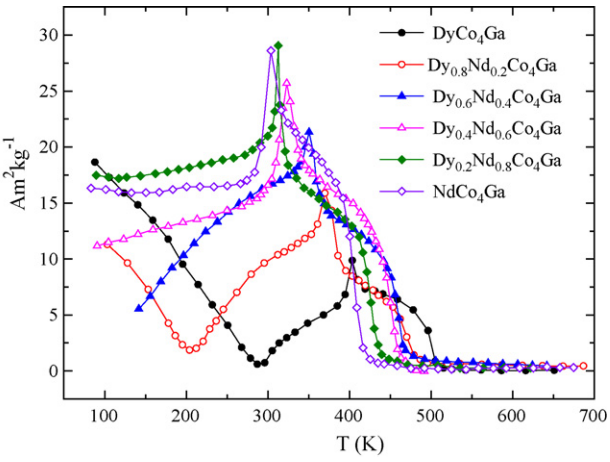

Fig. 4. Temperature dependence of the magnetization (M–T curves) for the $Dy_{1-x}Nd_xCo_4Ga$ compounds with $x = 0$, 0.2, 0.4, 0.6, 0.8 and 1.0 measured in the applied field of 0.1 T and the temperature range from 80 to 700 K.

Table 1
Structural and magnetic properties of $Dy_{1-x}Nd_xCo_4Ga$ compounds with $x = 0$, 0.2, 0.4, 0.6, 0.8 and 1.0.

Compound	a (nm)	c (nm)	V (nm^3)	T_C (K)	T_{SR} (K)	T_{comp} (K)
$DyCo_4Ga$	0.49887 (4)	0.40129 (3)	0.08649 (2)	498	403	287
$Dy_{0.8}Nd_{0.2}Co_4Ga$	0.50058 (1)	0.40168 (1)	0.08717 (2)	470	370	204
$Dy_{0.6}Nd_{0.4}Co_4Ga$	0.50221 (2)	0.40188 (1)	0.08778 (6)	461	350	
$Dy_{0.4}Nd_{0.6}Co_4Ga$	0.50387 (1)	0.40206 (2)	0.08840 (3)	450	323	
$Dy_{0.2}Nd_{0.8}Co_4Ga$	0.50606 (4)	0.40177 (6)	0.08911 (2)	433	313	
$NdCo_4Ga$	0.50807 (3)	0.40181 (1)	0.08983 (4)	410	303	

behavior with that of the compound $DyCo_4Ga$ reported in Ref. [6]. The compensation transition and the spin-reorientation transition are found in the compound $DyCo_4Ga$ in this work at $T_{comp} = 287$ K and $T_{SR} = 403$ K, respectively, which is in good agreement with those reported in Ref. [6]. The previous analysis of powder neutron diffraction for $DyCo_4Ga$ indicated that the Dy-sublattice magnetization is anti-parallel to the Co-sublattice magnetization in this compound and much more temperature dependence than that of Co-sublattice in this compound [6]. Almost cancellation of Dy- and Co-sublattice magnetization occurs at its compensation temperature T_{comp}. The compensation temperature T_{comp} decreases with Nd concentration from 287 K for $x = 0$ to 204 K for $x = 0.2$, and even lower than 100 K for higher Nd concentration x due to the decrease of rare earth 4f-sublattice moment by the substitution of Nd for Dy in this compound. The spin-reorientation transition occurs when the magnetic moments rotate continuously with temperature near temperature T_{SR} originated from the competition between axial Co (3d) and plannar rare earth (4f) magnetocrystalline anisotropic in this compound [6]. The spin-reorientation transitions appear in the $Dy_{1-x}Nd_xCo_4Ga$ compounds with $x = 0$, 0.2, 0.4, 0.6, 0.8 and 1.0 are also listed in Table 1 and shown in Fig. 5. We can see from Table 1 and Fig. 5 that the spin-reorientation transitions temperature decrease as Nd concentration increase from 403 K for $x = 0$ to 303 K for $x = 1.0$ since the weakening of the 4f-sublattice moment by the substitution of Nd for Dy in this compound. The Curie temperature T_C of $Dy_{1-x}Nd_xCo_4Ga$ decreases upon Nd substitution from 498 K for $x = 0$ to 410 K for $x = 1.0$ The Curie temperature is mainly determined by the 3d–3d exchange interaction [6]. Here its decrease may be due to the substitution of the larger atomic radius of Nd atom for smaller Dy atom, which leads to expansion of the unit cell and thus reduces the 3d–3d exchange interaction in this compound. The composition dependences of the compensation temperature T_{comp}, the spin-reorientation temperature T_{SR} and the Curie temperature T_C for the $Dy_{1-x}Nd_xCo_4Ga$ compounds are shown in Fig. 5. The structural and magnetic parameters are summarized in Table 1.

The compounds $Dy_{1-x}Nd_xCo_4Ga$ show two successive magnetic transitions: spin-reorientation (SR) transition near room temperature (300–400 K) and transition from ferromagnetic (FM) to paramagnetic (PM) states at 400–500 K. The magnetocaloric effect (MCE) of $NdCo_4Ca$, as a representative, due to the contribution from the SR and FM–PM transitions for possible magnetic refrigeration application near room temperature was investigated in this work. Fig. 6(a) and (b) shows the isothermal magnetization curves of $NdCo_4Ca$ measured in the applied magnetic field up to 1.5 T in a wide temperature range with an intervening temperature 3 K over the spin-reorientation transition temperature and 5 K over the Curie temperature. From the isotherm magnetization curves and Eq. (1), we calculated the magnetic entropy change ΔS_M (T,

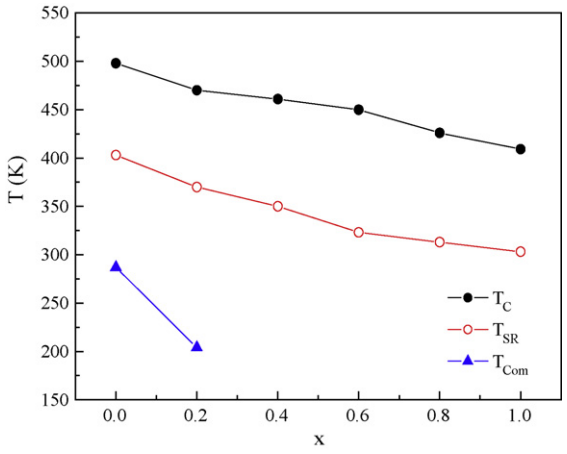

Fig. 5. Composition dependences of the compensation temperature T_{comp}, the spin-reorientation temperature T_{SR} and the Curie temperature T_C for the $Dy_{1-x}Nd_xCo_4Ga$ compounds.

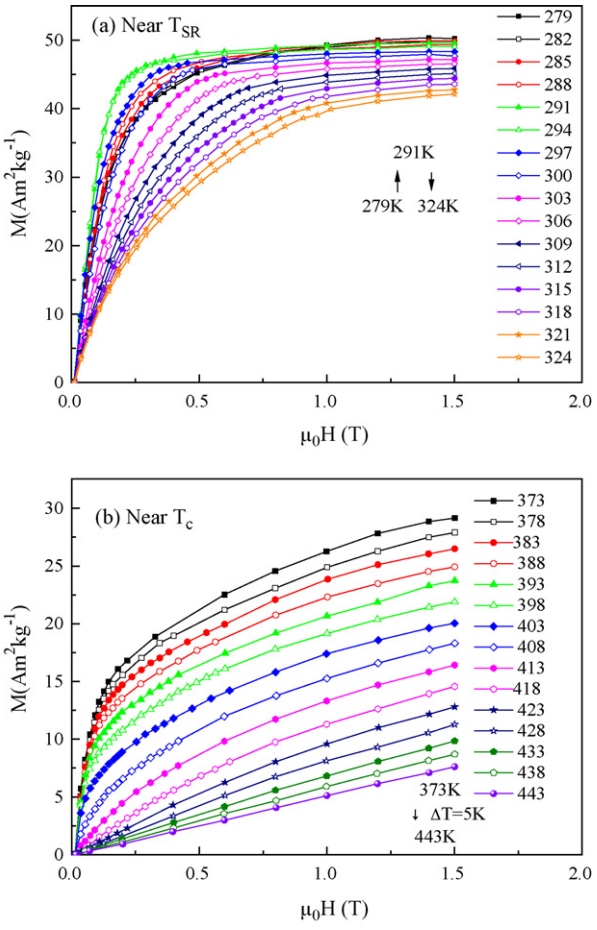

Fig. 6. Magnetization isotherms of $NdCo_4Ga$ in a wide temperature range with an intervening temperature 3 K over the spin-reorientation transition temperature (282–324 K) and 5 K over the Curie temperature (373–443 K) in the magnetic field up to 1.5 T.

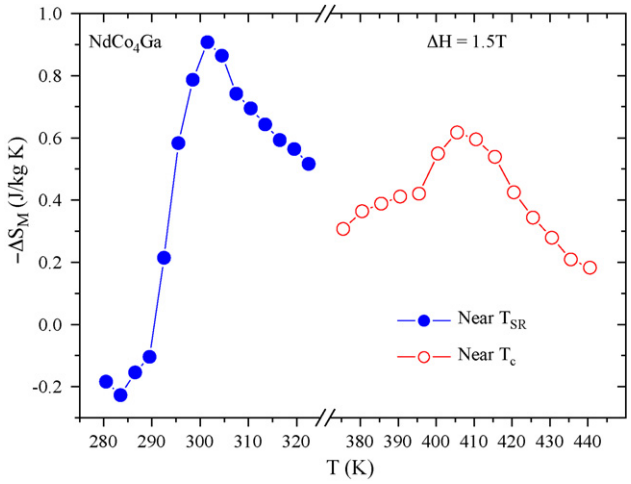

Fig. 7. Temperature dependence of the magnetic entropy changes ΔS_M in $NdCo_4Ga$ in a magnetic field change of 1.5 T for its SR FM–PM transitions.

H) as a function of temperature on the magnetic field change of 1.5 T and plotted in Fig. 7 ($-\Delta S$ (T, H) vs. T plot). The magnetic entropy change ($-\Delta S(T,H)$) reaches maximum of 0.91 J kg^{-1} K^{-1} at 301 K for the spin-reorientation (SR) transition and 0.62 J kg^{-1} K^{-1} at 405 K for FM–PM transition in the compound $NdCo_4Ca$. A small $-\Delta S_M$ of not more than 1.8 J kg^{-1} K^{-1} in $ThFe_{11}C_x$ compounds for a field change of 4.5 T at the spin-reorientation temperature T_{SR} have been reported [12]. The maximum $-\Delta S_M$ values are 6.3 and 11.2 J kg^{-1} K^{-1} at T_{SR} of 32 K and T_C of 85 K, respectively, for a field change of 5 T in the compound Ho_2In [9]. The magnetocaloric effect of the compound $NdCo_4Ca$ for its spin-reorientation FM–PM transitions is small for practical application even though the transitions are near room temperature.

4. Conclusion

We studied the structural and magnetic properties of $Dy_{1-x}Nd_xCo_4Ga$ compounds with $x = 0$, 0.2, 0.4, 0.6, 0.8 and 1.0. The substitution of Dy by Nd in the compound keeps its hexagonal $CaCu_5$-type structure, increases its lattice parameters a, c and cell volume V, but reduces its rare earth 4f-sublattice moment and its 3d–3d exchange interaction. It leads to decreases its compensation, spin-reorientation and Curie temperatures. The maximum magnetic entropy change ($-\Delta S_M$) are 0.91 J kg^{-1} K^{-1} at 301 K for SR transition and 0.62 J kg^{-1} K^{-1} at 405 K for FM–PM transition in the compound $NdCo_4Ga$ in the magnetic field change of 1.5 T.

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