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# Magnetocaloric effect in the rare earth intermetallic compounds RCoNi (R = Gd, Tb, Dy, and Ho)

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Magnetic and magnetocaloric properties of cubic Laves phase RCoNi (R = Gd, Tb, Dy, and Ho) compounds have been studied. The RCoNi (R = Gd, Tb, Dy, and Ho) compounds order ferromagnetically at  $\sim 200$  K,  $\sim 113$  K,  $\sim 68$  K, and  $\sim 42$  K ( $T_C$ ), respectively. Field dependent magnetization data of RCoNi at 5 K in fields up to 7 T reveal saturation behaviour with minimal hysteresis. Magnetocaloric effect in terms of isothermal magnetic entropy change has been calculated. Maximum isothermal magnetic entropy change values of  $\sim -7.2$  J/kg/K,  $\sim -10.1$  J/kg/K,  $\sim -15.5$  J/kg/K, and  $\sim -19.6$  J/kg/K are obtained for RCoNi (R = Gd, Tb, Dy, and Ho) compounds for 7 T field change close to  $T_C$ . Substitution of 50 at. % Ni in Co-site of RCo<sub>2</sub> has led to the reduction of  $T_C$  of the parent compounds by nearly one-half, but broadened the magnetic entropy change vs T curve and hence improved the relative cooling power. The large magnetocaloric effect associated with RCoNi compounds makes them potential candidates for low temperature magnetic refrigeration applications. © 2013 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4798306>]

## INTRODUCTION

Rare earth-based, cubic Laves phase intermetallic compounds, RCo<sub>2</sub> (R = Rare earth metal) have attracted the attention of the researchers over the past few decades due to the diversity and richness in their magnetic properties.<sup>1-3</sup> Compounds with nonmagnetic rare earth, such as YCo<sub>2</sub>, are exchange enhanced Pauli paramagnets and they show field induced magnetic transition in high magnetic fields.<sup>4</sup> The compounds with light rare earths, such as Pr and Nd, show ferromagnetic ordering but those with heavy rare earths Gd, Tb, Dy, Ho, and Er are ferrimagnetically ordered.<sup>5,6</sup> Among these, the magnetic transitions in DyCo<sub>2</sub>, HoCo<sub>2</sub>, and ErCo<sub>2</sub> are first order in nature.<sup>7</sup> In these compounds, Co- possesses a magnetic moment that leads to an interesting metamagnetic transition. High magnetic moment values associated with the rare earth ions in RCo<sub>2</sub> lead to the large changes in isothermal magnetic entropy near their magnetic transition temperatures and hence large magnetocaloric effect (MCE).<sup>6,7</sup> The magnetocaloric effect is the intrinsic property of the magnetic materials where the temperature change and the magnetic entropy change are caused by the application or removal of magnetic field under adiabatic and isothermal conditions, respectively.<sup>8</sup> However, in RNi<sub>2</sub> compounds, Ni is known not to possess magnetic moment and these compounds display strong magnetic anisotropy.<sup>2,9</sup> In the present work, magnetic and magnetocaloric properties of 50 at. % Ni substituted RCo<sub>2</sub> (R = Gd, Tb, Dy, and Ho) compounds are studied. Substitution of Ni at Co-site is expected to alter the *d*-states near Fermi level of RCo<sub>2</sub> compounds<sup>3,10,11</sup> and

hence the magnetic exchange interactions and the associated magnetocaloric effect.

## EXPERIMENTAL DETAILS

Polycrystalline RCoNi (R = Gd, Tb, Dy, and Ho) samples have been prepared by arc melting of stoichiometric amounts of high purity elements in argon atmosphere. The samples were vacuum annealed at 800 °C for 24 h to improve the homogeneity. Powder X-ray diffraction (XRD) patterns were taken at room temperature using PANalytical X'pert Pro powder diffractometer (Cu-K<sub>α</sub>,  $\lambda = 1.5406$  Å). Energy dispersive X-ray analyses (EDAX) were performed to check the stoichiometry. Magnetization measurements were carried out in magnetic fields up to 7 T in the temperature range of 5 K–300 K using SQUID magnetometer (MPMS, Quantum Design). Temperature variation of magnetization was performed under zero-field-cooled (ZFC) and field-cooled (FC) conditions. The data were collected during warming in both cases.

## RESULTS AND DISCUSSION

Room temperature powder XRD data of RCoNi (R = Gd, Tb, Dy, and Ho) compounds confirm that these are in single phase, having MgCu<sub>2</sub> type cubic Laves phase structure as the parent compounds RCo<sub>2</sub> (Space group *Fd* $\bar{3}m$ , No. 227). The EDAX results confirm that the at. % composition of elements R:Co:Ni is close to 1:1:1 ratio in all the samples studied.

Temperature variation of magnetization of RCoNi (R = Gd, Tb, Dy, and Ho) compounds, measured in 0.5 T field in ZFC and FC conditions shows a transition from paramagnetic to ferromagnetic state at  $\sim 200$  K,  $\sim 113$  K,  $\sim 68$  K, and  $\sim 42$  K ( $T_C$ ), respectively [Fig. 1]. The substitution of Ni by 50 at. % at Co-site of RCo<sub>2</sub> compounds reduces the *d*-states

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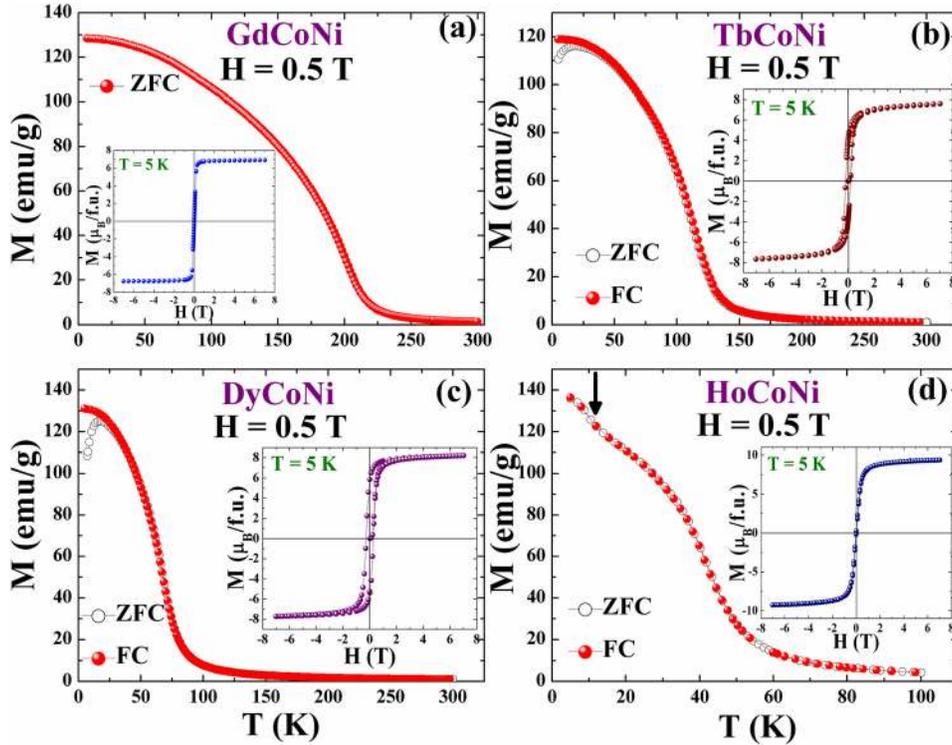


FIG. 1. Magnetization vs temperature of RCoNi (R = Gd, Tb, Dy, and Ho) compounds in applied field of 0.5 T [ZFC—zero-field cooled magnetization and FC—field cooled magnetization]. Inset shows magnetization vs field data.

near  $E_F$  and hence the  $d$ -electron mediated exchange interaction.<sup>2</sup> Accordingly, the magnetic transition temperature of RCoNi compounds is lower and almost one-half of that of the parent compounds. The  $T_C$  values of RCo<sub>2</sub> (R = Gd, Tb, Dy, and Ho) are  $\sim 406$  K, 240 K, 138 K, and 78 K, respectively.<sup>6,7</sup> Such a drastic fall in  $T_C$  was earlier predicted for small Ni-concentrations up to 20% (Ref. 3) and tested in HoCo<sub>2</sub> compound (up to 5% Ni at Co site) by NMR measurements.<sup>10</sup> The sharp fall in  $T_C$  was attributed to the change of shape of Co-density of states near  $E_F$  and the changes in the exchange field acting on  $d$ -ions.

Inverse paramagnetic susceptibility of RCoNi compounds fits to the Curie-Weiss law. The effective magnetic moment ( $\mu_{\text{eff}}$ ) and the paramagnetic Curie temperature ( $\theta_p$ ) values of RCoNi compounds calculated from the Curie-Weiss fit are given in Table I. Positive values of  $\theta_p$  suggest dominant ferromagnetic interactions and the nature of inverse magnetic susceptibility in ordered state indicates

ferromagnetic ordering in the RCoNi compounds. An additional transition has been observed at  $\sim 11$  K within the magnetically ordered state for the compound HoCoNi [shown using an arrow in Fig. 1] and it could be due to spin reorientation.

Considerable magnetic irreversibility between ZFC and FC magnetization is seen in TbCoNi and DyCoNi. This difference could be because of the domain wall pinning and the competition between different interactions. Bifurcation of ZFC and FC curves is absent in GdCoNi and HoCoNi compounds in 0.5 T field.

Magnetization vs field at 5 K shows saturation behavior [Inset in Fig. 1]. No hysteresis is observed for the compounds GdCoNi and HoCoNi, whereas coercivity of  $\sim 0.18$  T and  $\sim 0.28$  T is seen for the compounds TbCoNi and DyCoNi at 5 K. The saturation magnetization moment values are given in Table I. The saturation magnetization values are less than that of the theoretically calculated moment ( $gJ$ ) values assuming collinear ferromagnetic ordering of  $R^{3+}$ , other than for GdCoNi. Antiferromagnetic Co-moment coupling, crystalline electric field, and magnetic anisotropy might be the reasons for the reduction of moment values of the compounds TbCoNi, DyCoNi, and HoCoNi. However, the ordered state moments are closer to the corresponding RNi<sub>2</sub> compounds than RCo<sub>2</sub> compounds, confirming the  $d$  band filling effects.<sup>5,12</sup>

Magnetization vs field data at various temperatures near  $T_C$  were taken and MCE is calculated in terms of isothermal magnetic entropy change ( $\Delta S_m$ ), using the following relation:

$$\Delta S_m = \sum_i \frac{M_{i+1} - M_i}{T_{i+1} - T_i} \Delta H_i,$$

where  $M_i$  and  $M_{i+1}$  are the magnetization values in a magnetic field of strength  $H$  at temperatures  $T_i$  and  $T_{i+1}$ , respectively.<sup>6</sup>

TABLE I. Magnetic properties of RCoNi (R = Gd, Tb, Dy, and Ho) compounds [ $T_C$ —Ferromagnetic ordering temperature,  $\theta_p$ —paramagnetic Curie temperature,  $\mu_{\text{eff}}$ —effective paramagnetic moment,  $M_s$ —saturation magnetization,  $-\Delta S_m^{\text{max}}$ —maximum value of isothermal magnetic entropy change].

Compound name	$T_C$ (K)	$\theta_p$ (K)	$\mu_{\text{eff}}$ ( $\mu_B/\text{f.u.}$ )	$M_s$ ( $\mu_B/\text{f.u.}$ )	$-\Delta S_m^{\text{max}}$ (J/kg/K) ( $\Delta H = 7$ T)
GdCoNi	200	+207	7.4	6.9	7.2
TbCoNi	113	+116	9.1	7.6	10.1
DyCoNi	68	+70	10.3	8.2	15.5
HoCoNi	42	+42	10.6	9.4	19.6

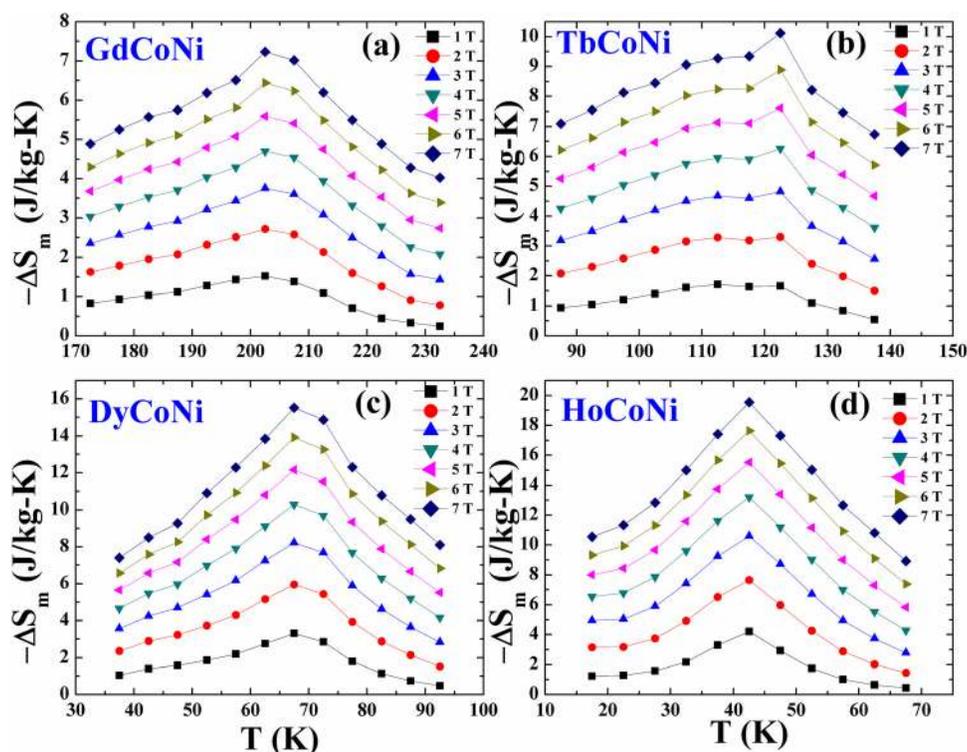


FIG. 2. Isothermal magnetic entropy change vs temperature of RCoNi (R=Gd, Tb, Dy, and Ho) compounds for various magnetic field changes.

The plot of  $\Delta S_m$  vs temperature is shown in Fig. 2. Maximum magnetic entropy change ( $\Delta S_m^{\max}$ ) is centered about  $T_C$ . The value of  $\Delta S_m^{\max}$  of the compounds DyCoNi and HoCoNi is comparable to that of the parent compounds [Table I]. For DyCo<sub>2</sub>,  $\Delta S_m^{\max}$  is  $\sim -11.3$  J/kg/K for  $\Delta H = 5$  T and for HoCo<sub>2</sub> it is  $\sim -23$  J/kg/K for  $\Delta H$  of 5 T.<sup>13</sup> However, DyCo<sub>2</sub> and HoCo<sub>2</sub> are known to exhibit first order magnetic transition at  $T_C$ . The magnetic entropy change vs temperature graphs of RCoNi compounds reflect the second order nature of the magnetic transition. This feature is closer to the behaviour of RNi<sub>2</sub> compounds where broader MCE suitable for Ericsson cycle was evidenced.<sup>9</sup> Since the materials having second order phase transition reduce hysteresis losses during the thermodynamic cycle compared to those materials with first order phase transition, RCoNi compounds will be suitable for magnetic refrigerator applications.<sup>8</sup> Magnetic field dependences of maximum isothermal magnetic entropy change of RCoNi compounds varies as  $H^n$ , with  $n$  values ranging from 0.76 to 0.91 for RCoNi (R = Gd, Tb, Dy, and Ho), whereas the mean field value of  $n$  is 2/3. This deviation could possibly be addressed by considering RCoNi compounds as spatially inhomogeneous ferromagnets where Ni atoms statistically occupy Co-sites.<sup>14</sup> Thus, substitution of Ni in Co-site of RCo<sub>2</sub> by 50 at. % leads to  $d$ -band filling effects and drives the system from ferrimagnetic ground state to the ferromagnetic state, drastically reducing the  $T_C$ . The high MCE values as well as second order magnetic phase transition in RCoNi compounds make them suitable for the magnetic refrigeration application at low temperatures.

## CONCLUSIONS

The rare earth intermetallic compounds RCoNi (R = Gd, Tb, Dy, and Ho) order ferromagnetically with their magnetic transition temperatures close to one-half of that of parent compounds RCo<sub>2</sub>. The isothermal magnetic entropy changes near  $T_C$  are considerable and comparable to that in RCo<sub>2</sub>. The second order nature of the ferromagnetic transition in RCoNi leads to broader peak in  $-\Delta S_m$  vs  $T$  plot near  $T_C$ , and larger relative cooling power compared to that in RCo<sub>2</sub> compounds.

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