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Itinerant electron metamagnetism and magnetocaloric effect in $\text{Dy}(\text{Co},\text{Si})_2$

Niraj K. Singh^{a,*}, K.G. Suresh^a, A.K. Nigam^b

^aDepartment of Physics, Indian Institute of Technology Bombay, Mumbai 400 076, India

^bTata Institute of Fundamental Research, Homi Bhabha Road, Mumbai 400 005, India

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Abstract

Itinerant electron metamagnetism in $\text{Dy}(\text{Co}_{1-x}\text{Si}_x)_2$ compounds was studied in the light of a recent theoretical model based on magnetovolume effect and spin fluctuations. The nature of the magnetic transition in these compounds was analyzed within the framework of this model. The magnetocaloric effect in these compounds has been calculated and correlated with the strength of itinerant electron metamagnetism. The domain wall pinning effect was found to be dominant at low temperatures.

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1. Introduction

Rare earth (R) transition metal (TM) intermetallics show interesting magnetic properties, which make them suitable candidates for fundamental studies as well as for applications [1,2]. Compounds exhibiting first order transitions (FOT) are potential candidates for applications based on magnetocaloric effect (MCE) and magnetoresistance (MR) [2]. Among the various R–TM intermetallics, RCO_2 (R = Dy, Ho and Er) compounds have received considerable attention owing to the presence of FOT at their ordering temperatures (T_C) [3]. It has been found that the FOT in these compounds is due to the onset of itinerant electron metamagnetism (IEM), caused by the exchange field of the rare earth [4]. According to the earlier theories of IEM, the critical parameter that determines the possibility of IEM and thereby the order of transition is the molecular field or the

ordering temperature. However, the second order transitions (SOT) observed in RCO_2 compounds containing rare earths other than Ho, Dy and Er could not be satisfactorily explained using these theories, though they predicted FOT in DyCo_2 , HoCo_2 and ErCo_2 [5]. Recently, these models have been corrected by incorporating the spin fluctuation and magnetovolume effects [5–7]. These refined models have been found to be in good agreement with the experimental results in many compounds [6,7]. In the case of RCO_2 compounds, the model proposed by Khmelevskiy and Mohn [5] appears to be the unified model to describe IEM and the order of transition for both light and heavy rare earths.

In this paper, we report our results on the magnetization and MCE in $\text{Dy}(\text{Co}_{1-x}\text{Si}_x)_2$ ($x = 0, 0.075$ and 0.15) compounds. Since DyCo_2 is a classical IEM system which shows considerable MCE, it is of interest to study IEM and MCE as a function of Si concentration. We try to correlate the variations in the order of transition and MCE in these compounds, within the purview of Khmelevskiy and Mohn model.

* Corresponding author. Tel.: +91-022-257-675-59; fax: +91-022-257-234-80.

E-mail addresses: niraj@phy.iitb.ac.in (N.K. Singh)

2. Experimental details

All the compounds were prepared by arc melting stoichiometric amounts of the constituent elements under argon atmosphere and subsequently annealing the ingots at 950 °C for a week. The samples were characterized by using powder X-ray diffractograms. The magnetization (M) was measured in the temperature range 2–300 K using a Quantum Design SQUID magnetometer/OXFORD vibrating sample magnetometer. The temperature variation of magnetization was carried out both under zero-field cooled (ZFC) and field-cooled (FC) modes. MCE was calculated from the M vs. H plots at various temperatures close to T_C .

3. Results and discussion

Powder X-ray diffraction patterns taken at room temperature revealed that all the compounds have formed in single phase with C15 Cubic Laves phase $MgCu_2$ type structure. Fig. 1 shows the temperature variation of magnetization at 500 Oe under ZFC condition. The ordering temperatures have been calculated from these plots. The variation of lattice parameter, Curie temperature and saturation magnetization (at 2 K) are given in Table 1.

The variation of T_C with Si concentration in this system is similar to that in $ErCo_2$ [8]. Substitution of Si gives rise to magnetovolume effect, chemical effect and magnetic dilution effect. The initial increase in T_C may be due to the predominant magnetovolume effect as a result of the 3d band narrowing following lattice expansion. The subsequent decrease in T_C indicates that there are competing effects from the magnetic dilution and charge transfer between the 3d band of Co and Si. The Co moments (μ_{3d}) have been calculated by taking Dy moments to be $9\mu_B$ and also by assuming antiferromagnetic coupling between Dy and Co moments. It can be seen from Table 1 that there is an increase in μ_{3d} with Si concentration, which reflects the magnetovolume effect.

It can be seen from Fig. 1 that the magnetization changes abruptly at T_C in $DyCo_2$ and the transition smears gradually

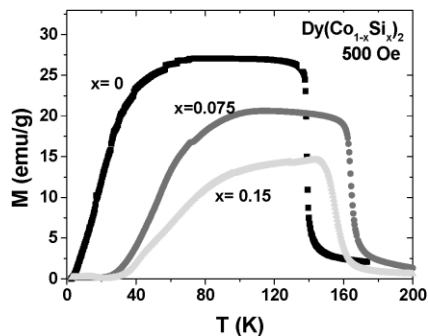


Fig. 1. Temperature variation of magnetization in $Dy(Co_{1-x}Si_x)_2$ compounds at 500 Oe.

Table 1

The values of lattice parameter (a), ordering temperature (T_C), saturation magnetization (M_S) and 3d magnetic moment (μ_{3d}) in $Dy(Co_{1-x}Si_x)_2$ compounds

X	' a ' (Å)	T_C (K)	M_S (μ_B /f.u.)	μ_{3d} (μ_B /atom)
0.0	7.179	139	7.07	0.96
0.075	7.189	164	7.21	0.97
0.15	7.196	154	7.18	1.07

with Si concentration. It has already been reported that $DyCo_2$ shows FOT and this is attributed to the IEM [3,5]. According to the model by Khmelevskiy and Mohn, the lattice parameter, ' a ' of $DyCo_2$ is well within the range $7.05 < a < 7.22$ Å, thereby satisfying the condition for IEM. This is because of the fact that the lattice parameter has to be more than 7.22 Å to enable spontaneous and stable moment formation in the Co sublattice. Therefore, Co sublattice in $DyCo_2$ is nonmagnetic above the ordering temperature. On cooling the sample through the ordering temperature, the Co sublattice becomes magnetic due to the presence of the exchange field of Dy and this is termed as IEM. This moment formation and the subsequent ordering in the Co sublattice are responsible for the FOT. Fig. 2(a) and (b) show the Arrott plots of $DyCo_2$ and $Dy(Co_{0.925}Si_{0.075})_2$, respectively. The onset of IEM in $DyCo_2$ is clearly seen in the S-shaped Arrott plots in Fig. 2(a). If the Co

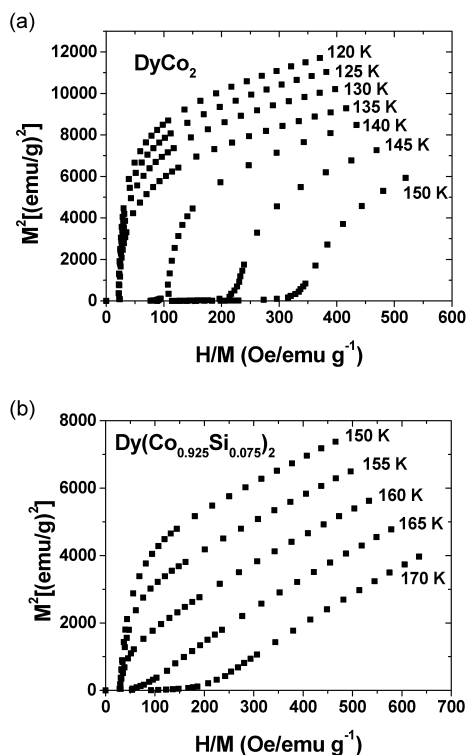


Fig. 2. Arrott plots for (a) $DyCo_2$ and (b) $Dy(Co_{0.925}Si_{0.075})_2$.

sublattice has a permanent moment above the ordering temperature, the Co sublattice would always be spontaneously magnetic and the transition at T_C would be of second order, as seen in many intermetallics. This is the case in RCo_2 compounds containing light rare earths in which the lattice parameters are more than the critical value of 7.22 \AA [5]. It is interesting to see that Duc et al. [9] have reported the critical lattice parameter to be 7.27 \AA for the enhancement of T_C as a result of Al substitution in $\text{R}(\text{Co},\text{Al})_2$ compounds. The increase in T_C in this case has been attributed to the formation of moments in the Co sublattice [9,10]. Therefore, there is a strong correlation between the lattice parameter and Co magnetism in RCo_2 -based compounds. Recent results on MCE and MR seem to favor 7.22 \AA as the critical lattice parameter to observe IEM and FOT in RCo_2 compounds [3].

As mentioned above, there are several experimental results in the literature that are in agreement with the predictions of Khmelevskiy and Mohn model. It has indeed been experimentally observed that YCo_2 undergoes a metamagnetic transition at applied magnetic fields of about 70 T [7]. The appearance of Co moments and the subsequent increase of T_C in Al-substituted $\text{Y}(\text{Lu})\text{Co}_2$ compounds followed by lattice expansion [10] also support this model. The role of lattice parameter in determining the magnetic state of Co is also revealed by the pressure dependence of T_C [6] and also by thermal expansion anomalies in various RCo_2 compounds [8].

However, the magnetic transitions observed in Si-substituted DyCo_2 compounds in the present case are of second order, as revealed by the Arrott plots and also by the lower MCE values (discussed later). Arrott plots for these two compounds are not S-shaped, as can be seen from Fig. 2(b) for $\text{Dy}(\text{Co}_{0.925}\text{Si}_{0.075})_2$. Therefore, it is clear that there is no IEM in these Si-substituted compounds. It has been reported that in $\text{Er}(\text{Co}_{1-x}\text{Si}_x)_2$ [8] and $\text{Ho}(\text{Co}_{1-x}\text{Si}_x)_2$ [11] the transition is FOT for $x \leq 0.075$ and it changes to SOT for $x > 0.075$. A similar variation has been observed in Al-substituted RCo_2 compounds [9,12,13] as well. A common trend seen in both Si and Al substituted compounds is that the critical concentration (of Si or Al) at which FOT changes to SOT is more in Er compounds and it becomes progressively smaller in Dy compounds. It is of interest to note that according to Khmelevskiy and Mohn, the magnetic transitions should be first order in Dy, Ho and Er compounds even for $x = 0.15$ in both Si and Al substitutions, since the lattice parameter is less than the critical value. The reason for this variation can be attributed to spin fluctuations in the 3d sublattice.

Spin fluctuations in these compounds arise due to two reasons. In addition to the usual thermal contribution, the instability of moments in the region $a < a_c$, also contributes to spin fluctuations. Increase in the lattice parameter as a result of Si or Al substitution increases the tendency for the moment formation in the 3d sublattice because of the magnetovolume effect. However, it should be noted that this

moment formation is only local and these moments are not strongly exchange coupled. This gives rise to a weakly ferromagnetic phase with fluctuating moments [9]. From the variation of electronic specific heat coefficient (γ), Wada et al. [10] have established the presence of enhanced spin fluctuations in this region ($a < a_c$). Duc et al. [9] have also reported the presence of larger spin fluctuations in this region compared to that in the region $a > a_c$, based on magnetic and electrical resistivity studies in $\text{R}(\text{Co},\text{Al})_2$ compounds. Since spin fluctuations suppress IEM, there is a trend towards SOT on Si or Al substitution. This is the reason for the change from FOT to SOT in $\text{Er}(\text{Co}_{1-x}\text{M}_x)_2$ and $\text{Ho}(\text{Co}_{1-x}\text{M}_x)_2$ ($\text{M} = \text{Al}, \text{Si}$) for $x > 0.075$. Due to the larger lattice parameters of Dy compounds compared to that of the corresponding Ho and Er compounds, the local Co moment formation is more probable in the former case [13]. This enhances the spin fluctuations in the Co sublattice in Dy compounds and as a result, $\text{Dy}(\text{Co}_{1-x}\text{M}_x)_2$ compounds show SOT at lower 'x' values as compared to the Er and Ho counterparts. A similar trend has been observed in the electrical resistivity of $\text{R}(\text{Co},\text{Al})_2$ compounds with $\text{R} = \text{Er}, \text{Ho}$ and Dy [9]. A few other reports are also available in literature, which suggest the presence of strong spin fluctuations when condition for IEM is nearly satisfied [14,15]. Another reason favoring an early SOT in Dy compounds in the present case may be that the ordering temperatures are higher ($\sim 140 \text{ K}$) than the Er ($\sim 35 \text{ K}$) and Ho ($\sim 75 \text{ K}$) compounds. The spin fluctuation contribution is more at higher temperatures and this also contributes to SOT [6]. Khmelevskiy and Mohn have also reported that higher ordering temperatures lead to SOT, even in compounds where conditions for IEM exist, as in the case of TbCo_2 [5].

Fig. 3 shows M vs. T plots under FC and ZFC conditions for $\text{Dy}(\text{Co}_{0.85}\text{Si}_{0.15})_2$. Similar plots were obtained for the compounds with $x = 0$ and 0.075 as well. The large difference seen between the FC and ZFC magnetization curves, known as thermomagnetic irreversibility, is due to the domain wall pinning effect [16]. In intermetallic compounds possessing large anisotropy and low T_C , width of the domain wall would be comparable to the lattice

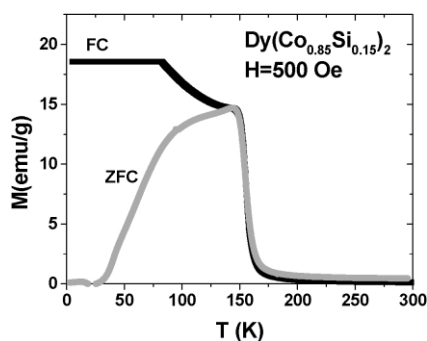


Fig. 3. Temperature variation of magnetization under FC and ZFC conditions in $\text{Dy}(\text{Co}_{0.85}\text{Si}_{0.15})_2$.

spacing and in such systems the magnetization process is quite different as compared to that of normal ferromagnets. The most important characteristics of such narrow domain wall systems are significant FC-ZFC difference, large intrinsic coercivity and remanence at low temperatures [16]. In ZFC, at low temperatures, the domain walls are pinned and with increases of temperature the magnetization increases reaching a maximum around T_C . However, in FC, the presence of the magnetic field during the cooling prevents the pinning of domain walls and therefore, the magnetization increases with the decrease in temperature. The present system, i.e. $\text{Dy}(\text{Co}_{1-x}\text{Si}_x)_2$ can be classified as a narrow domain wall system due to the fact that the ordering temperature is much smaller (compared to DyFe_2). Also, the anisotropy is large due to the magneto-elastic distortions taking place at the T_C , as the sample is cooled from high temperatures [17,18]. Therefore, it is quite possible that the present system exhibits domain wall pinning effect and consequently a large thermomagnetic irreversibility. It has been reported that Al-substituted RCO_2 compounds also show similar behaviour [19].

The MCE in $\text{Dy}(\text{Co}_{1-x}\text{Si}_x)_2$ compounds has been measured as the isothermal magnetic entropy change $\Delta S_M(T, \Delta H)$ for various temperatures and applied magnetic fields. ΔS_M is calculated from magnetic isotherms $M(T_i, H)$, obtained at a sequence of temperatures T_i , using the Maxwell's relation:

$$\Delta S_M(T_{av,i}, H_2) = \int_{H_1=0}^{H_2} \left(\frac{\partial M(T, H)}{\partial T} \right)_{T_{av,i}} dH$$

$$\approx \frac{1}{T_{i+1} - T_i} \int_0^{H_2} [M(T_{i+1}, H) - M(T_i, H)] dH$$

Here, $T_{av,i} = (T_{i+1} + T_i)/2$ and $\Delta T = T_{i+1} - T_i$. ΔS_M for all the compounds for field changes ($\Delta H = H_2 - H_1$) of 1 and 4 T are shown in Fig. 4(a) and (b), respectively. It can be seen that ΔS_M always shows a maximum (ΔS_M^{\max}) close to T_C and has the highest value for DyCo_2 . ΔS_M obtained in DyCo_2 for 1 T in the present case compares well with the recently reported values [12,20]. For $\Delta H = 4$ T, ΔS_M^{\max} was $11.1 \text{ J Kg}^{-1} \text{ K}^{-1}$ for DyCo_2 . The corresponding values for ErCo_2 and HoCo_2 are $38 \text{ J Kg}^{-1} \text{ K}^{-1}$ ($\Delta H = 5$ T) and $22.5 \text{ J Kg}^{-1} \text{ K}^{-1}$ ($\Delta H = 4$ T), respectively [3]. The reason for such large entropy change in these compounds is mainly the FOT at T_C . In addition, the structural transitions associated with the magnetic ordering may also contribute to the MCE. Such field-induced structural transitions are known to cause large MCE in various intermetallics [2]. The relatively lower value of ΔS_M^{\max} in DyCo_2 can be attributed to the presence of spin fluctuations mentioned earlier. It is of interest to note that ΔS_M^{\max} for TbCo_2 , which exhibits SOT is $6.5 \text{ J Kg}^{-1} \text{ K}^{-1}$ ($\Delta H = 5$ T). The fact that this value is not negligible compared to that of DyCo_2 , suggests that the transition in TbCo_2 is predominantly SOT, but has some signature of FOT. MR studies have also shown that maximum MR in TbCo_2 is about 17% whereas it is about

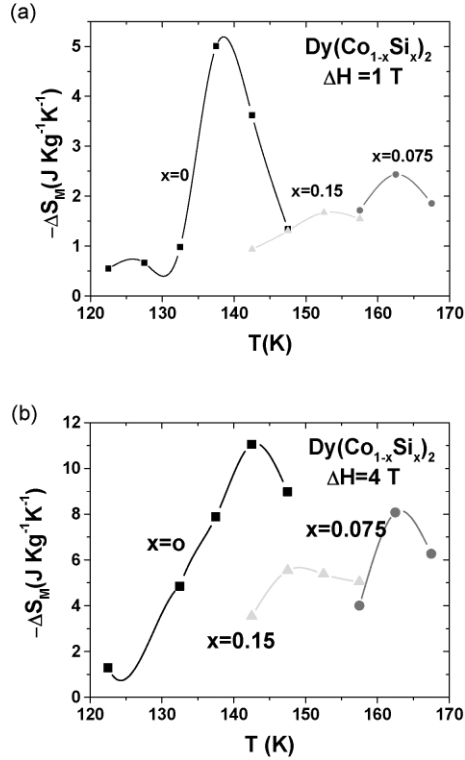


Fig. 4. Isothermal entropy change in $\text{Dy}(\text{Co}_{1-x}\text{Si}_x)_2$ compounds for $\Delta H = 1$ T (a) and 4 T (b).

30% in DyCo_2 and 60% for HoCo_2 [3]. In this context, it is of importance to note that Khmelevskiy and Mohn model predicts conditions favoring IEM in TbCo_2 [5]. Considerable values of MCE and MR in TbCo_2 , therefore, seem to support this model.

It can also be seen from Fig. 4 that ΔS_M^{\max} decreases with Si substitution and this is due to the disappearance of IEM and the subsequent change in the order of transition. ΔS_M^{\max} in $\text{Dy}(\text{Co}_{0.85}\text{Si}_{0.15})_2$ is lower than that of TbCo_2 though both these compounds show SOT. This may be due to the larger contribution from the spin fluctuations in $\text{Dy}(\text{Co}_{0.85}\text{Si}_{0.15})_2$ compared to that in TbCo_2 . Reasonably large values of ΔS_M^{\max} in $\text{Dy}(\text{Co}_{0.925}\text{Si}_{0.075})_2$ along with an increase in T_C of about 25 K, as compared to DyCo_2 , makes this Si-substituted system promising from the point of view of magnetic refrigeration applications around 150 K. Furthermore, in the temperature range 80–250 K where adiabatic cooling is minimal, there is a growing demand for magnetic refrigerant materials possessing considerable low field ΔS_M^{\max} [2].

4. Conclusion

In conclusion, IEM is found to be responsible for FOT in DyCo_2 -based compounds. Spin fluctuations suppress IEM,

thereby making the transitions second order. Low temperature magnetization behaviour in these compounds is governed by domain wall pinning effect.

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