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Magnetocaloric Effect in $DyFe_3$ and $GdFe_3$

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Abstract

In this work, we report on the calculation of the temperature dependence of Magnetic moment, total heat capacity and magnetocaloric effect (MCE) of $DyFe_3$ and $GdFe_3$ compounds. The calculation, using the Mean-Field Theory (MFT) of magnetization showed that both $DyFe_3$ and $GdFe_3$ are ferrimagnetic compounds with compensation temperatures around 509 K and 597 K, and Curie temperatures about 624K and 745K for DyFe3 and GdFe3 respectively. The maximum calculated $isothermal\ entropy\ change\ |\Delta S_m(T,\Delta H)|$ are 0.21 and 0.19 J/mol.K and the maximum calculated $adiabatic\ change\ in\ temperature\ |\Delta T_{ad}(T,\Delta H)|$ are 0.92 and 0.82 K at $field\ change = 4\ T$ for $DyFe_3$ and $GdFe_3$ respectively. The relative cooling powers RCP(S) and RCP(T), for a field change of 4T, are 4 and 3.8 J/mol and 19.5 and 24.6 K^2 for $DyFe_3$ and $GdFe_3$. Furthermore, the calculation of the critical exponents supports the suitability of the MFT for handling the systems under study. The type of the magnetic phase transition, at the Curie temperatures, is confirmed from the temperature dependence of the magnetization, heat capacity at different fields and MCE quantities to be a second order one.

Keywords
Magnetocaloric effect, Magnetization, Heat capacity, Critical exponents, Relative cooling power.
Declarations The authors have no relevant financial or non-financial interests to disclose.

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1. Introduction

Studies of MCE have been reported before on rare earth-intermetallic compounds [1]. Magnetic refrigeration technology as an application of MCE is expected to be the following cryogenic technology, environmentally safer and more effective compared to other refrigeration techniques [2]. Sundry studies have been reported on both $DyFe_3$ and $GdFe_3$ compounds e.g., the magnetic properties[3], Debye temperature, low temperature heat capacity[4], magnetic structure and density of states [5].

The rare-earth 3d-transition metals system encompasses a wide spectrum of compounds, either rich in rare-earth or transition elements. The studied properties include a wide range of e.g. magnetic and crystallographic properties, both experimental and theoretical. For example, Simmons et al [6] focuses on the neutron and x-ray diffraction on HoFe3 and YFe3 compounds. In fact, some of the present authors have recently reported on ab initio calculation of the elastic properties and on magnetothermal and magnetocaloric effect in these same compounds [7], also Matsuda et al[8] reported also on the crystallographic properties and on the magnetic moments at 4.2 K only.

The MFT has been used in studies on other rare-earth transition metal compounds e.g. YFe_3 and $HoFe_3$ [7], $TmFe_2$ [9], $R_2Fe_{14}B$ [10], $ErFe_2$ [11], $R_3Co_{11}B_4$ [12] and R_6Fe_{23}[13]. In the present work we present a theoretical study on MCE (ΔS_m , ΔT_{ad}) of DyFe3 and GdFe3 using the MFT. In particular, we calculated the total magnetic moment, the total heat capacity, $|\Delta S_m(T,\Delta H)|$, $|\Delta T_{ad}(T,\Delta H)|$ and the RCP in fields up to 4T at temperature range up to 700K. In addition, we investigated the type order of the phase transition, via the temperature and field dependencies of the magnetothermal and MCE properties. We also calculated both $RCP(S)$ and $RCP(T)$, as figures-of-merit in the field of magnetic refrigeration.

2. Model and Analysis

The exchange fields of rare earth and Fe sub-lattice can be expressed using MFT as follows [3].

$$H_R(T) = H + d[n_{RR} M_R(T) + 3n_{RFe} M_{Fe}(T)] (1)$$
$$H_{Fe}(T) = H + d[n_{RFe} M_R(T) + 3n_{FeFe} M_{Fe}(T)] (2)$$

Where R=D_y or Gd, the symbols in Equations (1) and (2) have their usual meaning and the molecular field coefficients n_{RR}, n_{FeFe} and n_{RFe} are dimensionless.

$M_R(T)$ and $M_{Fe}(T)$ represent the magnetic moments of rare earth and Fe element.

$$M_R(T) = M_R(0) \times B_{J_R}\left[\frac{M_R(0)\, H_R(T)}{k_B T}\right] (3)$$

$$M_{Fe}(T) = M_{Fe}(0) \times B_{J_{Fe}}\left[\frac{M_{Fe}(0)\, H_{Fe}(T)}{k_B T}\right] (4)$$

Where $B_J(y)$ is the Brillouin function and $= \frac{M_J H}{k_B T}$.

The total magnetic moment is:

$$M_{Total}(T) = M_R(T) + 3\ M_{Fe}(T)\ (5)$$

$|\Delta s_m(T, \Delta H)|$, is deduced from Maxwell relation [14].

$$\left(\frac{\partial \Delta S_m(T)}{\partial H}\right)_T = \left(\frac{\partial M(T)}{\partial T}\right)_H (6)$$

$$|\Delta S_m(T, \Delta H)| = \int_{H_0}^{H_f} \frac{\partial M(T)}{\partial T}\, dH\ (7)$$

The total heat capacity is the sum of the magnetic heat capacity C_m (T, H), the lattice heat capacity C_l (T) and the electronic heat capacity C_e (T) [15, 16].

C_m (T, H), is calculated from the first derivative of the magnetic energy:

$$U_m(T, H) = -\frac{1}{2}[n_{RR} M_R^2(T) + n_{FeFe} M_{Fe}^2(T) + 2n_{RFe} M_R(T)\ M_{Fe}(T)\ ] (8)$$

$$C_m(T, H) = \frac{\partial U_m(T, H)}{\partial T} (9)$$

Where $C_l(T)$ in the Debye model as follow $C_l(T) = 9\,R\left(\frac{T}{\Theta_D}\right)^3 \int_0^{\frac{\Theta_D}{T}} \frac{e^x\ x^4}{(e^x-1)^2}\ dx$ (10)

Θ_D is the Debye- temperature and x = Θ_D/ T.

$C_e(T)$is reported by Kittel [17] as follow $C_e(T) = \gamma_e \times T$ (11)

and γ_e represents the electronic heat capacity coefficient.

The adiabatic temperature change$|\Delta T_{ad}(T,\Delta H)|$ [15] is calculated as follow :

$$|\Delta T_{ad}(T,\Delta H)| = -\int_{H_0}^{H_f} \frac{T}{C_{tot}(T,\Delta H)} \frac{\partial M(T)}{\partial T}\, dH \quad (12)$$

3. Results and Discussion

3.1-Magnetization

The calculations of magnetic momenta of both the rare-earth, iron sublattices and the magnetization for $DyFe_3$ and $GdFe_3$ are calculated, in zero field, by using MFT. The magnetic momenta at 0 K, for Dy is (M_{Dy} (0) = $g_{Dy} \times J_{Dy}$ = (4/3) × (15/2) = 10 μ_B/atom), for Gd is (M_{Gd} (0) = $g_{Gd} \times J_{Gd}$= (2) × (7/2) = 7 μ_B/atom). Fig .1[a] displays the magnetic moments of Dy and Fe sublattices, and the total magnetic moment, in zero field and wide temperature range up to the Curie temperature. A ferrimagnetic coupling is evident in this system, has a compensation temperature around 509 K, and a Curie temperature around 624 K.

Fig .1[b] exhibits the corresponding quantities for $GdFe_3$ compound. Its compensation and Curie temperatures are at 597 K and 745 K respectively. The value of magnetic moment of Fe sublattice is evaluated from the experimental data of total magnetic moment and the values of magnetic moments of Dy and Gd sublattices. The percentage difference values between calculated $M_{Total}(0)$ and experimental values [3], is only ≤ % 2 at T=0 K, and also the difference in T_c is ≤ 4.6%. Table 1 displays the total experimental data and calculated results for the total magnetic moment and the Curie temperature for both $DyFe_3$ and $GdFe_3$.

3.2-Total Heat Capacity $C_{tot}(T,\Delta H)$:

First, the magnetic heat capacity $C_m(T, H)$, is dependent on both temperature and field, in contrast to the lattice and electronic contributions which are only temperature-dependent [13, 14]. Figures 2(a, b) show the $C_m(T, H)$, for $DyFe_3$ and $GdFe_3$ respectively in applied magnetic fields in the range 0 to 4 T. It is clear that the magnetic heat capacity increases with increasing temperature, continuously from very low temperatures, and then drops around the Curie temperature. Such behavior is a feature of second order phase transitions. Second, the $C_l(T)$, is calculated from Equation 10, using a Debye temperature of 328 K, for $DyFe_3$, as reported by Narasimhan et al. [4]. Third, the electronic heat capacity$C_e(T)$ is determined from Equation 11, where the γ_e coefficient for $DyFe_3$ is 2.58×10^{-3} J/mol [4].

3.3-Magnetocaloric Effect (ΔS_m and ΔT_{ad})

First, the calculation of $|\Delta s_m(T, \Delta H)|$ for both $DyFe_3$ and $GdFe_3$ compounds was done by Maxwell relation by Equation 7 for $\Delta H = 4\ T$. The results are tabulated in Table 2. Both direct and inverse MCEs are evident, as indicated in Figures 3[a, b]. Two peaks are present: the first around the compensation temperature and the second peak at the Curie temperature. The maximum $|\Delta S_m(T, \Delta H)|$ are 0.21 and 0.19 J/ mol. K , for ΔH=4T, for both $DyFe_3$ and $GdFe_3$ respectively. These values of$|\Delta S_m(T, \Delta H)|$ are comparable to those of YFe3 and HoFe3 [7].

Second, figure 4 (a, b) shows the calculated ($|\Delta T_{ad}(T, \Delta H)|$) for $DyFe_3$ and $GdFe_3$ compounds for field changes ΔH=1, 2, 3 and 4T using equation 12, the data for both systems are shown in table 3. For example, the maximum calculated ($|\Delta T_{ad}(T, \Delta H)|$) is 0.92 K for $DyFe_3$ system at ΔH=4T, so the temperature is decreasing by a rate of 0.23 K/T.

3.4-Relative Cooling Power (RCP)

The RCP is a figure- of- merit in the field of magnetic refrigeration as reported by Franco et al. [18]. The RCP(S) based on isothermal process, is $\Delta S_{max}(T)\times\delta T_{FWHM}$ and it is 4 J/mol, for $DyFe_3$ and 3.8 J/mol for $GdFe_3$ in a field change ΔH=4 T. The RCP(S) for Gd element is 150.7 J/mol at ΔH=5 T [19]. Also, the RCP (T) , based on adiabatic temperature change is

$\Delta T_{max}(T) \times \delta T_{FWHM}$. It has no physical meaning, but it is used for numerical comparison with other MCE materials. The RCP(T) are 19.5 and 24.6 K^2 at ΔH=4 T for $DyFe_3$ and $GdFe_3$ respectively, which are compared with 967 K^2 of Gd element at ΔH=6 T [2].

3.5-Critical Exponents

It would be informative to estimate some of the critical exponents [20,21] and compare with the MFT values. We calculated n, β, δ and ɤ parameters for $DyFe_3$ compound, where n = 1+ (β -1) /(β +ɤ) [22]. The parameter δ has been evaluated from the isothermal magnetization curve, where $M \sim H^{1/\delta}$ [23]. The mean field MFT parameters are: β = 0.5, ɤ =1 and δ=3. From our calculation, the parameter β is 0.48 and ɤ is 1.02, i.e. at most 2.7% and 2.4% off the MFT values respectively. The parameter δ is 2.67, i.e. around 11% off the MFT value. This fair agreement shows that the MFT fairly describes the behavior of the compounds we are reporting on.

4. Conclusions

In this work, we present a study on the magnetic properties and MCE ($|\Delta S_m|$, $|\Delta T_{ad}|$) for $DyFe_3$ and $GdFe_3$ using the MFT. The magnetization calculations showed that $DyFe_3$ and $GdFe_3$ are ferrimagnetic compounds. The compensation temperatures of both compounds are around 509 K and 597K for $DyFe_3$ and $GdFe_3$ respectively. $|\Delta S_m(T, \Delta H)|$ is calculated by Maxwell's relation. The highest ordinary MCE: ($|\Delta S_m|$ and $|\Delta T_{ad}|$) are 0.21 J/mol. K and 0.92 K at ΔH =4T for $DyFe_3$. The MFT proved to be suitable for calculating the temperature dependence of the magnetothermal and magnetocaloric properties of the DyFe3 and $GdFe_3$ compounds. The temperature and field dependences of the aforementioned properties are those of materials with magnetic second order phase transition.

Statement of Novelty

In the present work we present magnetocaloric effect on $DyFe_3$ and $GdFe_3$. There is no available data, up to our knowledge, on the MCE in these systems.

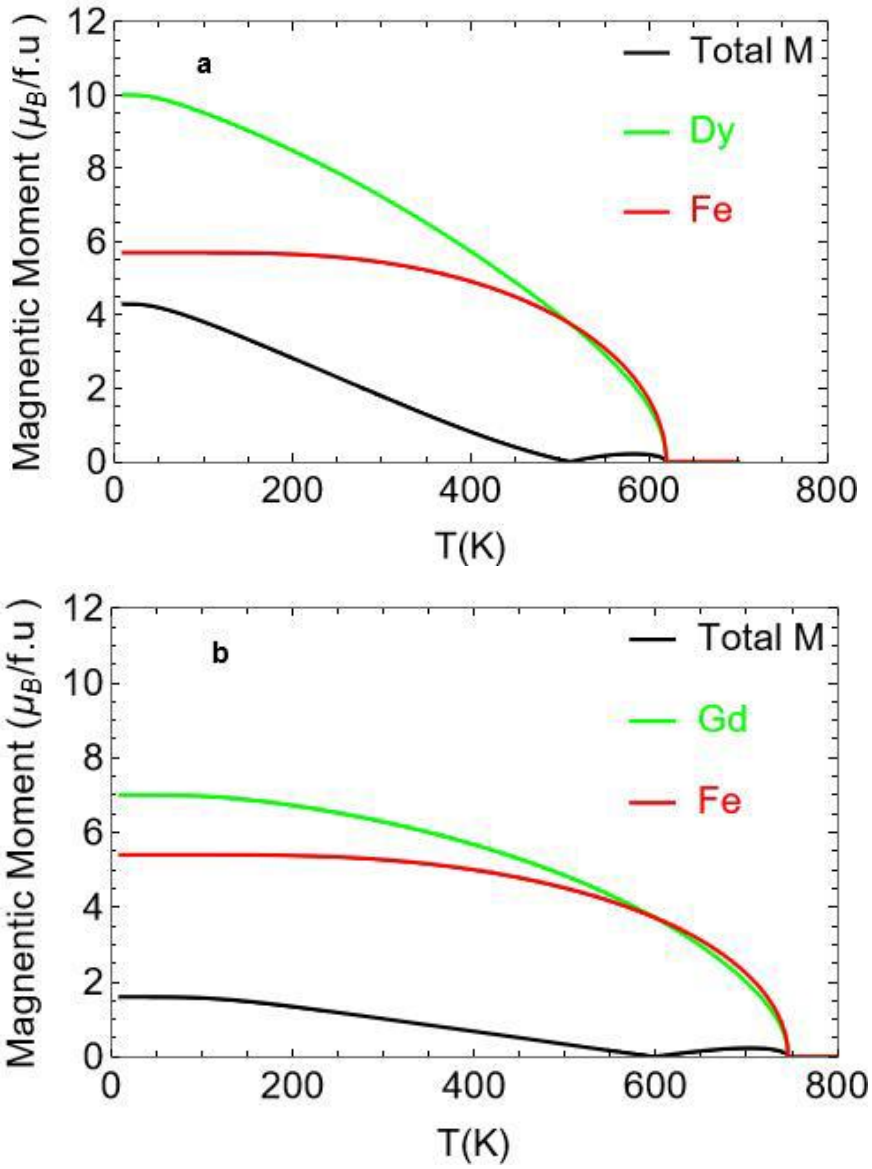

Fig 1. The temperature dependence of magnetization of the total magnetization, R and iron sublattices in zero magnetic field for [a] $DyFe_3$ [b] $GdFe_3$.

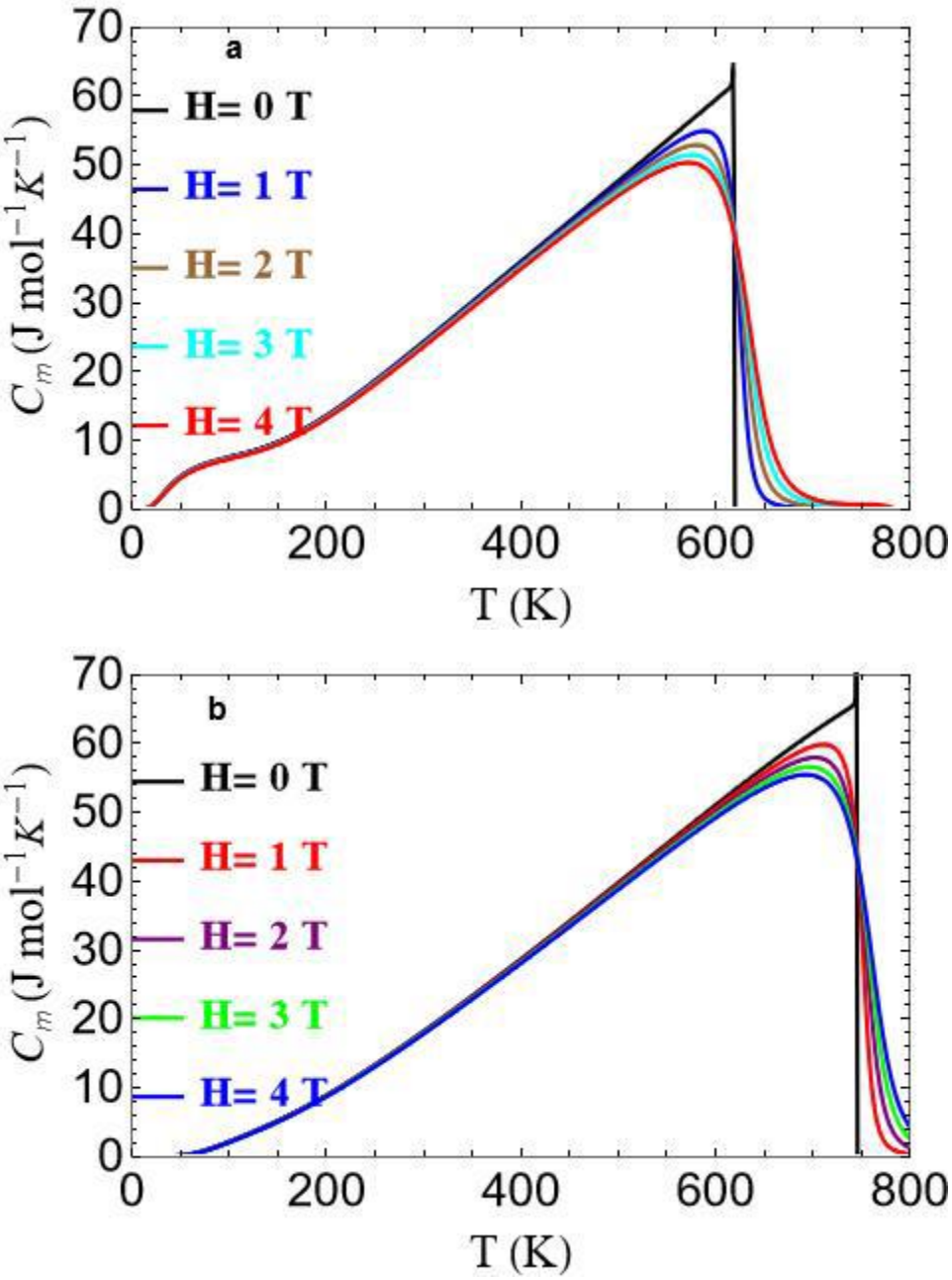

Fig 2. Temperature dependence of magnetic heat capacity for [a] $DyFe_3$ [b] $GdFe_3$ in external fields from 0 to 4T.

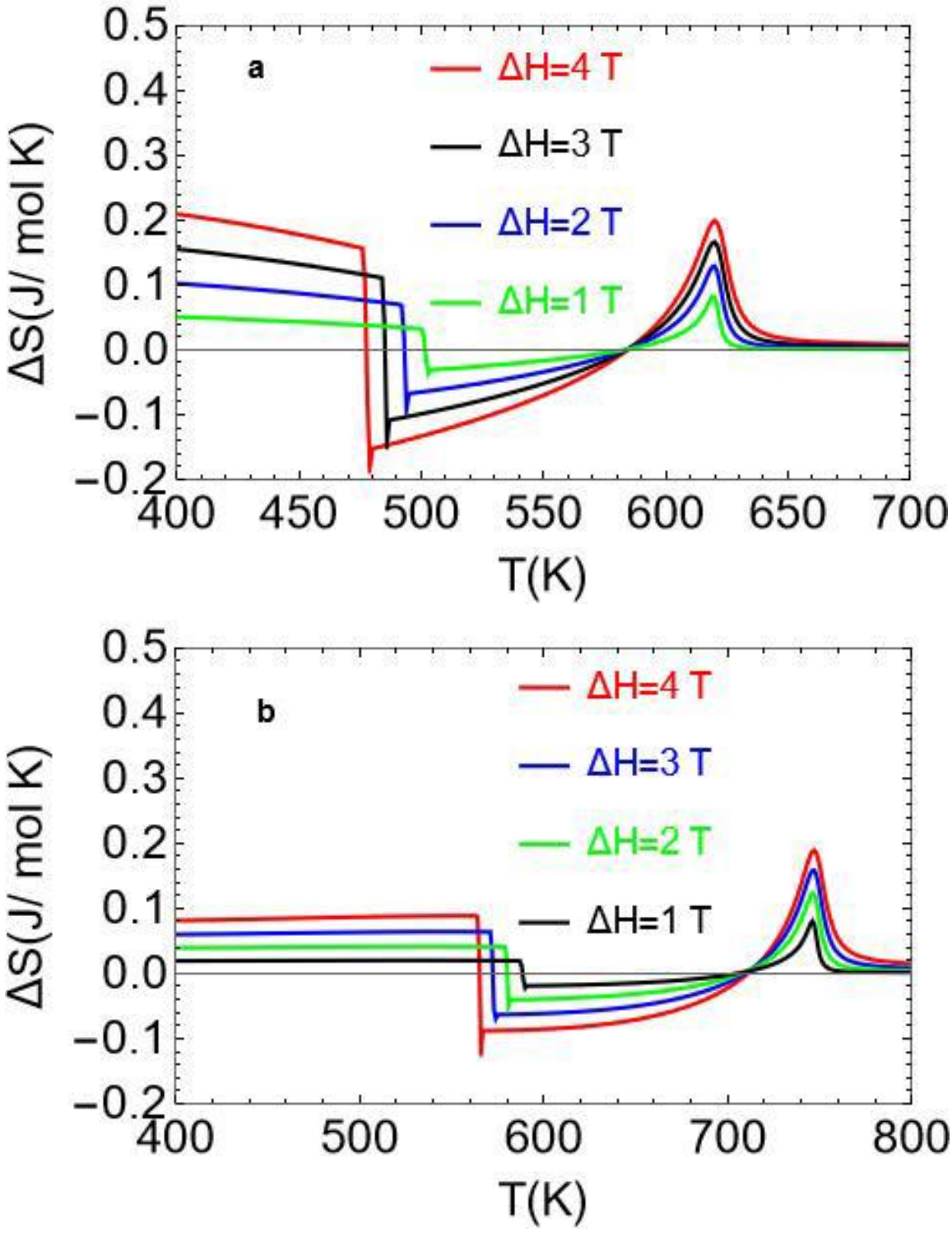

Fig 3. The magnetic entropy change vs. Temperature for [a] $DyFe_3$ [b] $GdFe_3$, for field changes of 1 to 4 T.

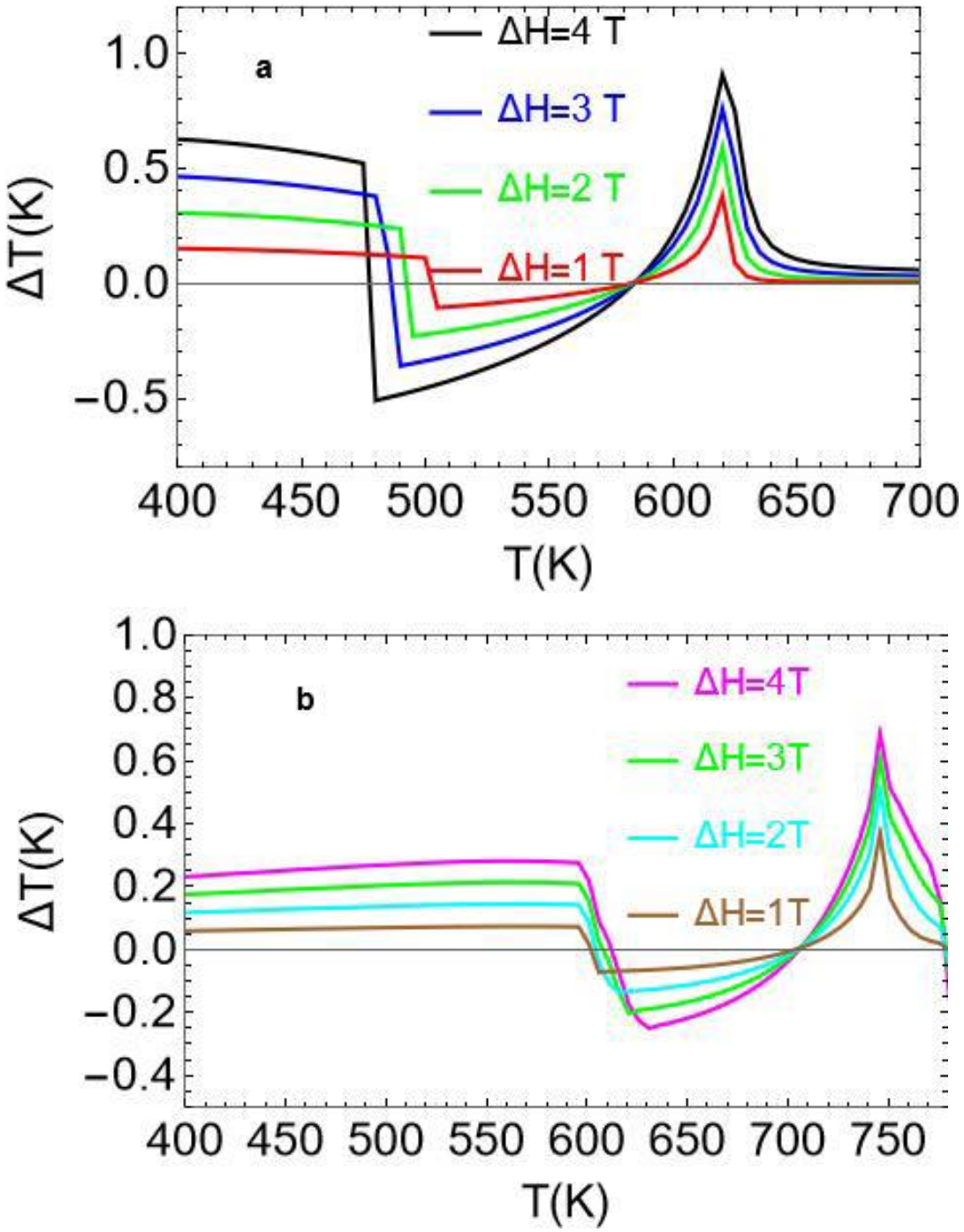

Fig 4. Adiabatic temperature change vs. temperature for [a] $DyFe_3$ [b] $GdFe_3$ for field changes of 1 to 4 T.

Table 1 -The calculated and experimental [3] net magnetic moment, in zero field at very low temperature, and the Curie temperatures for $DyFe_3$ and $GdFe_3$ system.

R	Magnetic moment (μ_B /f. u)		percentage difference	Curie temperature		percentage difference
	Cal.	Exp.		Cal.	Exp.	
Dy	4.2	4.29	2	624	602	3.6
Gd	1.6	1.62	1.2	745	728	2.3

Table 2: The maximum calculated values of ΔS_m for $DyFe_3$ and $GdFe_3$ at ΔH= 1 to 4 T.

	$\lvert\Delta S_m\rvert$ (J/mol. K)			
	ΔH=4 Tesla	ΔH=3 Tesla	ΔH=2 Tesla	ΔH=1 Tesla
$DyFe_3$	0.21	0.172	0.136	0.087
$GdFe_3$	0.19	0.16	0.13	0.08

Table 3: The maximum calculated values of ΔT_{ad} for $DyFe_3$ and $GdFe_3$ at ΔH =1 to 4 T.

	$\lvert\Delta T_{ad}\rvert$ (K)			
	ΔH=4 Tesla	ΔH=3 Tesla	ΔH=2 Tesla	ΔH=1 Tesla
$DyFe_3$	0.921	0.81	0.636	0.421
$GdFe_3$	0.821	0.730	0.616	0.44

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