Investigation of the thermal properties on Dy$_5$Ge$_2$Si$_2$

S. Shanmukharao Samatham$^1$, D. Venkateshwarlu$^1$, Mohan Gangrade$^1$, Swati Pandya$^2$ and V. Ganesan$^1$

$^1$Low Temperature Laboratory, UGC-DAE Consortium for Scientific Research, University Campus, Khandwa Road, Indore-452001, M.P., India
$^2$Currently at Science and Humanities Department, BITS Edu. Campus, Varnama, Vadodara, Gujarat, India

E-mail: vganesan@csr.res.in

Abstract. The calorimetric and thermopower measurements on Dy$_5$Ge$_2$Si$_2$ are presented. The antiferromagnetic ordering resulted in a sharp peak in specific heat and paramagnetic temperature as a shoulder. Magnetic entropy ($S_{\text{mag}}$) is estimated from the magnetic heat capacity, $C_{\text{mag}}$, and is in good agreement with the theoretically calculated value. A small note on correct assessment of $S_{\text{mag}}$ is presented. Thermoelectric power is analysed in line with the specific heat and a temperature region of magnetic correlations is identified. Charge carrier density $n \sim 2.5 \times 10^{23}$ cm$^{-3}$ is calculated using Sommerfeld parameter $\gamma$ and diffusion thermopower constant $\sigma_D$.

1. Introduction
The study of rare-earth based ternary alloys, especially R$_5$T$_4$ (R-rare-earth, T-transition metal), compounds has been paid attention for a decade. Initially, these were studied mainly in the context of magnetic refrigeration usage, for example, Gd$_5$Ge$_2$Si$_2$ [1] for its giant magnetocaloric effect at its magnetic transition temperature 276 K. Later, in the fundamental physics point of view, these are reputed for the first order based kinetics of magnetic glasses and frozen magneto-structural order (Gd$_5$Ge$_4$) [2]. Of the latest years, Dy based alloys are being revisited in the context of existence of Griffiths-like phase. Dy$_5$Ge$_2$Si$_2$ compound exists in Orthorhombic crystal structure with space group Pnma [3]. Though extensive studies have been carried out on these alloys, the physical properties like heat capacity and thermoelectric power are still intriguing and need to be addressed with deeper insight.

This paper presents detailed analysis of calorimetric and thermopower characterizations of the title compound. A small note on the assessment of proper background of specific heat to calculate the magnetic heat capacity/entropy is added. The sensitivity of heat capacity to any kind of magnetic transitions in the title compound by the application of magnetic fields is also highlighted.

2. Experimental Methods
Polycrystalline Dy$_5$Ge$_2$Si$_2$ was prepared by arc-melting the constituent elements in Ar atmosphere using Ti ball as a getter. The elements Dy, Ge and Si are taken in the stoichiometric molar ratio of
The melted ball was flipped many times to ensure the homogeneity. Specific heat, \( C_p(T) \) measurements were carried out by relaxation time calorimetric method using 14 T/2.0 K Physical Property Measurement System (QD, USA) down to 2 K and in magnetic fields up to 1 T. Thermoelectric power measurements were done using home-made setup coupled to 4 K Closed Cycle Refrigerator down to 4 K by differential sandwich method [4].

### 3. Results and discussion

From the magnetic behaviour, \( M(T) \), it was reported that Dy\(_2\)Ge\(_2\)Si\(_2\) behaves as an antiferromagnet (AFM) below 57 K [3]. The employed Curie-Weiss fit to the inverse susceptibility in Ref. [5] resulted in the positive paramagnetic temperature (\( \theta_p = 38 \) K) which is unusual for AFM. Generally, as per Curie-Weiss law, a negative paramagnetic temperature is expected for AFM and a positive value for ferromagnet (FM). Hence, it was speculated that the positive \( \theta_p \) in Dy\(_2\)Ge\(_2\)Si\(_2\) indicates coexistence of the short-range FM and long-range AFM interactions [5].

**Figure 1.** Specific heat \( C_p(T) \) of Dy\(_2\)Ge\(_2\)Si\(_2\) from 2-100 K at 0 T and 1 T. The magnetic transitions at \( T_N \) and \( T_p \) are around 57 K and 40 K, respectively. Upper inset depicts the fit of specific heat equation 1. Down inset shows the temperature derivative of \( C_p \), \( dC_p/dT \) with clearly identifying transition temperatures, \( T_N \& \theta_p \).

In this paper, efforts have been put forward to understand the competing interactions through specific heat and thermoelectric power and also a note on the correct estimation of magnetic entropy of Dy\(_2\)Ge\(_2\)Si\(_2\). Fig.1 presents the specific heat data on Dy\(_2\)Ge\(_2\)Si\(_2\), collected in the absence of magnetic fields, from 2-100 K. The peak at \( T_N = 57 \) K is due to AFM ordering and the specific heat value at peak reduces and smears out in field as evident from the 1 T data. The upper inset to the figure is the fitting of the date to the equation (1) for the low temperature data below 10 K.

\[
C_p(T) = \gamma T + (\beta + \delta)T^3
\]  

(1)

Here, \( \gamma T \) is the electronic heat capacity, \( \beta T^3 \) is the lattice specific heat and \( \delta T^3 \) is for the AFM magnetic contribution. The free fitting parameters are \( \gamma \) and \( \delta \) only as \( \beta \) is directly taken from Y\(_2\)Ge\(_2\)Si\(_2\) (will be discussed later). The obtained Sommerfeld parameter, \( \gamma = 0.15598 \) J. mol\(^{-1}\).K\(^{-2}\) which is unusually high when compared to normal metals [6] and indicates the strong correlation of electrons because of the complex magnetic interactions in the compound. The estimation of magnetic contribution in AFM compounds is not straightforward as it is for other magnetic materials. The complexity arises because of its spin wave spectrum dispersion relation \( \omega_q = a_s(2J/sa^2/h)q \) which is similar to that of phonons [7].

Here, \( J \) is the exchange, \( a \) is lattice parameter and \( 2\pi/q \) is the wave length, \( a_s \) dependent on the crystal structure details and \( s \) is spin quantum number. Using the above relation, \( C_{AFM} \sim T^3 \). Hence, we have adopted Debye temperature of Y\(_2\)Ge\(_2\)Si\(_2\), an isostructural nonmagnetic analogue of Dy\(_2\)Ge\(_2\)Si\(_2\), which is 290 K [8]. \( \beta \) is calculated using \( \theta_D(K) = \frac{\sqrt{3}}{2} \frac{1944 \rho}{\beta} \) where \( \rho \) is the number of atoms in a formula unit.
(p=9 for Dy$_3$Ge$_2$Si$_2$). The calculated β~0.0007173 J.mol$^{-1}$.K$^{-4}$ is a fixed parameter in the equation (1). Now, the estimated magnetic contribution is δ~0.0056427 J.mol$^{-1}$.K$^{-4}$ that is 8 times greater than β indicating the dominant magnetic contribution in Dy$_3$Ge$_2$Si$_2$.

Magnetic entropy has been estimated using the formula $S_{mag} = - \int (C_{mag}/T) dT$. $C_{mag}$ is the magnetic heat capacity assessed by subtracting the sum of $C_{el}$ and $C_{ph}$ from the total specific heat $C_p$, i.e., $C_{mag}=C_p-(C_{el}+C_{ph})$, figure 2a. For estimating the $C_{ph}$, instead of simple $T^3$ dependence, the actual Block Gruniesen function is being used with Debye temperature 290 K of Y$_3$Ge$_2$Si$_2$. $C_{el}$ is $\gamma T$ of Dy$_3$Ge$_2$Si$_2$. Theoretically calculated magnetic entropy for Dy$^{3+}$ is $S_{mag}=R\ln(2J+1)=23.05$ J.mol$^{-1}$.K$^{-1}$ with $J=15/2$ for L (04) $+S(7/2)$. It is evident from the figure 1 that $S_{mag}$ is 21.85 J.mol$^{-1}$.K$^{-1}$ at 100.85 K which essentially meets the theoretical value at 300 K, figure 2b. Hence, the experimentally assessed value is in good agreement with the theoretical value without any reduction whereas the reduction in $S_{mag}$ was shown in Ref. [5]. It is because of the over subtraction of $C_{el}$ by assuming the $C_{ph}$ and $C_{el}$ of Dy$_3$Ge$_2$Si$_2$ are the same as those for Y$_3$Ge$_2$Si$_2$. However, $\gamma$ (1.6758 J.mol$^{-1}$.K$^{-2}$) [8] of Y$_3$Ge$_2$Si$_2$ is one order higher than that for Dy$_3$Ge$_2$Si$_2$ (0.15598 J.mol$^{-1}$.K$^{-2}$). Generally, $C_{mag}$ of magnetic rare-earth based compounds is estimated by subtracting the heat capacity ($C_{el}$+$C_{ph}$) of their non-magnetic counterparts of the same structure (either Y or La based alloys). In this process, at times, $C_{el}$ of non-magnetic structural analogues is not the same as that of magnetic ones. Hence, the problem of over/under estimation of $C_{mag}$ arises because of under/over consideration of $C_{el}$ of nonmagnetic analogues.

![Figure 2a](image1.png)  
**Figure 2a.** Left side: $C_p(T)$. Right side: the estimated $C_{el}$=$\gamma T$ and $C_{ph}$ using $\theta_D$ of Y$_3$Ge$_2$Si$_2$ and with Bloch Gruniesen expression.

![Figure 2b](image2.png)  
**Figure 2b.** Left side: $C_{mag}/T$ as a function of $T$ at 0 T and 1 T. Right side: The calculated $S_{mag}/$Dy$^{3+}$, 21.85 J.mol$^{-1}$.K$^{-1}$ at 100.85 K

Figure 3 shows the thermolectric power, $\sigma(T)$ of Dy$_3$Ge$_2$Si$_2$ down to 8 K from 100 K. Data from 40 K to 80 K is fitted to the linear equation to estimate the diffusion coefficient of thermopower, $\sigma_D$. Sign of $\sigma_D$ is negative, hence indicating the electrons as the charge carries in the sample. The estimated absolute $\sigma_D = 0.02926$ $\mu$V.K$^{-2}$. The value of Fermi energy from the diffusion coefficient of thermopower [9] can be estimated as $E_F = \pi^2 k_B^2 / 2e\sigma_D$ and $E_F$ is found to be at around 1.26 eV. The density of states (DOS) at $E_F$ is calculated using $\gamma = (\pi^2 k_B^2 / 3)N(E_F)$ where $\gamma$ is Sommerfeld coefficient. $N(E_F)$=3.065x10$^{23}$ (eV)$^{-1}$.cm$^{-3}$. The carrier density of charge carries is being estimated using the following formula $n = (2/3)E_F N(E_F)$ and $n$=2.5x10$^{23}$ cm$^{-3}$ which indicates a good metallic behaviour.

The manifestation of FM short-range interactions in the AFM material resulted in the small hump in specific heat in the proximity of $\theta_p$. It is more evident in the thermolectric power as shown in figure 3b. It changes its slope from the linear behaviour at around 42.5 K and low temperature slope change

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is at 31.87 K. This region can, perhaps, be attributed as the region of pronounced FM correlations in Dy$_5$Ge$_2$Si$_2$. The low temperature fall is at around 10 K.

![Figure 3a. Thermopower of Dy$_5$Ge$_2$Si$_2$ down to 8 K. The linear fit is diffusion thermopower and diffusion constant, $\sigma_D=0.02926 \, \mu$V.K$^{-1}$.

Figure 3b. The correlation between the thermopower and specific heat. Pronounced FM correlations region is in the proximity of $\theta_p$.](image)

In conclusion, calorimetric and thermopower measurements on Dy$_5$Ge$_2$Si$_2$ were carried out. The magnetic transitions like antiferromagnetic ($T_N$) and paramagnetic temperature ($\theta_p$) are seen in specific heat. The correctly estimated magnetic entropy by considering $C_{el}$ of Dy$_5$Ge$_2$Si$_2$ and lattice heat capacity of its nonmagnetic isostructural analogue Y$_5$Ge$_2$Si$_2$ is presented. The estimated $S_{mag}$ is in good agreement with the theoretically obtained value. The magnetic correlations in the proximity of paramagnetic temperature are seen in the thermopower and are corroborated with specific heat.

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