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Heat capacity and magnetocaloric studies of RPd_2Si ($\text{R} = \text{Gd}, \text{Tb}$ and Dy)

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Abstract

Heat capacity and magnetocaloric studies on the compounds RPd_2Si ($\text{R} = \text{Dy}, \text{Tb}$ and Gd) are presented. The zero-field heat capacity shows a clear peak around the magnetic transition temperature. The magnetic entropy change across the transition indicates a doublet ground state for TbPd_2Si and a quartet ground state for DyPd_2Si . For GdPd_2Si an excess contribution to heat capacity well above the magnetic ordering temperature (for $T > 2T_N$) has been observed, which might be attributable to Pd ions. The magnetocaloric effect (MCE) in the compound DyPd_2Si around 10 K is comparable to other large MCE materials in this temperature range, whereas in the case of TbPd_2Si the MCE is small due to the presence of strong crystalline electric field and two well separated magnetic transitions.

1. Introduction

The physical properties of rare earth intermetallic compounds exhibit a wide range of different ground state properties including magnetism, superconductivity and intermediate valency. The understanding of rare earth intermetallic compounds is of interest not only from a fundamental point of view but also has technological importance. One such application is magnetic refrigeration, where compounds with large magnetocaloric effect (MCE) are required [1]. MCE is defined as an adiabatic temperature change or isothermal entropy change with the application of magnetic field. The realization that the MCE could be used for refrigeration even up to room temperature has spurred great interest in this field [2]. The success of magnetic refrigeration depends on the discovery of new materials with large MCE in the temperature range of interest. Rare-earth intermetallic compounds are particularly suited for this purpose as they have large magnetic moment. Also, their magnetic ordering temperature varies from room temperature to a few Kelvin, which is the temperature range of interest for magnetic refrigeration. Indeed

some of the materials with highest MCE known currently are the rare earth intermetallic compounds [1, 3, 4].

With a motivation to find new materials with large MCE we studied the compound GdPd₂Si earlier and observed a large MCE around 15 K in this system [5]. The compound GdPd₂Si is a member of the RPd₂Si system (R = Gd, Tb, Dy, Ho and Er) which crystallizes in Fe₃C-type orthorhombic structure [6]. Out of these only Gd, Tb and Dy compounds have magnetic ordering temperatures above 4 K, which is the temperature range of our interest. The magnetic properties of these compounds result from indirect exchange interaction between rare earth moments through conduction electron and crystalline electric field effects acting on rare earth ions [7]. In the case of the Gd compound crystal field effects are not expected. Therefore, the study of Dy and Tb compounds can throw light on the role of the crystal field effect in this series. In this report the infield heat capacity and magnetocaloric studies on the compounds DyPd₂Si and TbPd₂Si are presented and compared with the magnetocaloric properties of GdPd₂Si. The heat capacity study of the non-magnetic LuPd₂Si is also carried out to obtain the magnetic contribution to heat capacity in these compounds.

2. Experimental details

The polycrystalline sample of the compounds RPd₂Si (R = Gd, Tb, Dy and Lu) were prepared by arc melting the constituent elements (purity better than 99.9%) in high purity argon atmosphere. As-prepared samples were characterized by the powder x-ray diffraction technique. All the compounds are found to have Fe₃C type orthorhombic crystal structure with a space group of *Pnma*. All the lines in the XRD pattern were identified with the above space group, indicating that compounds are single phase in nature. Structural refinement for all the compounds was carried out using the Rietveld refinement method (DBWS) [8]. The lattice parameters are found to be in agreement with earlier reports [6] and are listed in table 1. The

Table 1. Lattice parameters *a*, *b* and *c*, magnetic ordering temperature (T_{ord}) and magnetic entropy changes ΔS_{mag} at 3 K above the high temperature magnetic transition along with theoretical maxima for the compounds RPd₂Si (R = Gd, Tb, Dy and Lu). Also listed are some of the magnetocaloric effect parameters for a magnetic field change ΔH : maximum adiabatic temperature change ($\Delta T_{\text{ad,max}}$) and maximum isothermal entropy change (ΔS_{max}).

	Lattice parameter (Å)	T_{ord} (K)	ΔS_{mag} (J mol ⁻¹ K ⁻¹)		MCE		
			At $T_{\text{ord}} + 3$ K	$R \ln(2J + 1)$	ΔH (T)	$\Delta T_{\text{ad,max}}$ (K)	ΔS_{max} (J mol ⁻¹ K ⁻¹)
LuPd ₂ Si	<i>a</i> = 7.1396 <i>b</i> = 6.9307 <i>c</i> = 5.4282	—	—	—	—	—	—
DyPd ₂ Si	<i>a</i> = 7.2874 <i>b</i> = 6.9139 <i>c</i> = 5.4929	$T_{\text{C}} = 7.8$	10.9	23.03	1 2 5	1.7 3.4 7.2	1.8 3.1 5.3
TbPd ₂ Si	<i>a</i> = 7.3241 <i>b</i> = 6.9102 <i>c</i> = 5.5120	$T_{\text{N}} = 18.7$ ($T_{\text{R}} = 9$)	5.6	21.28	1 2 5	0.4 1.5 4.3	0.2 0.8 2.4
GdPd ₂ Si	<i>a</i> = 7.3625 <i>b</i> = 6.9075 <i>c</i> = 5.5418	$T_{\text{N}} = 16.8$ ($T_{\text{R}} = 12.5$)	16.5	17.28	1 2 5	0.9 3.2 8.5	0.4 1.8 6.0

heat capacity (C) measurements at various constant magnetic fields (up to 5 T) were performed using a home made semi-adiabatic heat pulse calorimeter [9]. The magnetocaloric effect is calculated from the measured zero-field and in-field heat capacity data.

3. Results and discussion

The temperature dependence of heat capacity (C) in the presence of various constant magnetic fields is shown in figure 1(a) for the compound DyPd_2Si . The zero-field C curve of the compound LuPd_2Si is also shown in the same figure. As expected the C behaviour of LuPd_2Si is typical of a non-magnetic metal. The coefficient of electronic contribution to the heat capacity and Debye temperature is found to be $2.5 \text{ mJ mol}^{-1} \text{ K}^{-2}$ and 182 K respectively for this compound. The heat capacity of LuPd_2Si is here taken as a lattice and electronic

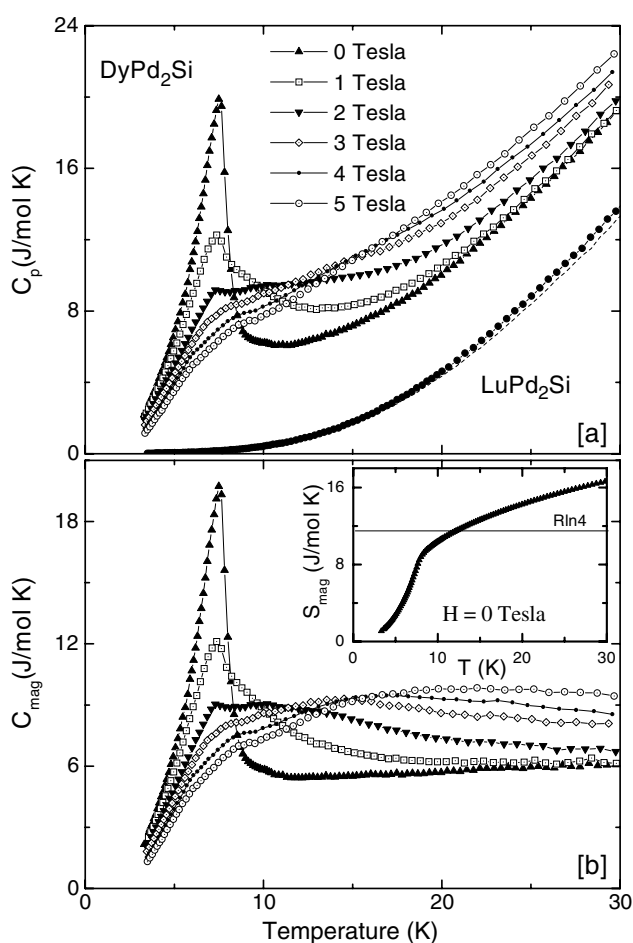


Figure 1. (a) Temperature dependence of heat capacity for the compound LuPd_2Si at zero magnetic field and for DyPd_2Si at 0, 1, 2, 3, 4 and 5 T magnetic field. The dashed line shows the heat capacity of LuPd_2Si normalized for DyPd_2Si (C_{nm}). (b) Magnetic contribution to heat capacity (C_{mag}) obtained by subtracting C_{nm} from measured C data of DyPd_2Si . The inset shows the temperature dependence of the zero-field magnetic entropy. The lines through the data points are guides to the eye.

contribution to heat capacity for the compounds RPd_2Si . The magnetic contribution to heat capacity (C_{mag}) is obtained by subtracting the heat capacity of LuPd_2Si with the proper normalization factor (to take in to account of different masses of Lu and R ions [10]) from the total heat capacity of respective compounds.

The zero-field heat capacity of the compound DyPd_2Si (figure 1(a)) shows a sharp peak at 7.5 K, which is slightly lower than the ferromagnetic ordering temperature (9 K) reported by Gignoux *et al* [7] from their magnetization measurements. The ferromagnetic transition temperature (T_C) from the heat capacity data, which is taken as the inflection point above the heat capacity peak, is found to be 7.8 K. With the application of magnetic field the peak height decreases and becomes broader. Besides this peak, the infield heat capacity curve also shows a shallow hump-like feature just above the magnetic ordering peak. This feature is more prominent in the C_{mag} data (see figure 1(b)), which is obtained by subtracting the normalized heat capacity of LuPd_2Si from the measured C data of DyPd_2Si . This hump in the C_{mag} curves appears to shift to higher temperature with increasing magnetic field. The appearance of this feature could be due to the complex magnetic nature of the compound and/or the strong crystalline electric field effect. However, the modification of the above mentioned feature even for a modest amount of magnetic field suggests complex magnetic ordering rather than crystal electric field effects as its origin. The magnetic entropy S_{mag} , which is obtained by numerically integrating the area under the C_{mag}/T versus T curve for zero-field data is shown in the inset. S_{mag} increases rapidly up to the magnetic transition temperature. The magnetic entropy change up to 11 K, which is the minimum of the heat capacity curve, is about $11 \text{ J mol}^{-1} \text{ K}^{-1}$. This is quite small compared to the expected $R \ln 16$ value ($=23 \text{ J mol}^{-1} \text{ K}^{-1}$) for free Dy^{3+} ion, which indicates the presence of a strong crystalline electric field effect. This value, $11 \text{ J mol}^{-1} \text{ K}^{-1}$ ($\sim R \ln 4$), of S_{mag} also indicates the quartet ground state for this compound.

For the compound TbPd_2Si two peaks are observed in the heat capacity data (figure 2(a)), indicating two transitions in this compound. This is in agreement with the magnetization measurements reported by Gignoux *et al* [7], where this compound is reported to order antiferromagnetically around 21 K and shows another spin reorientation transition around 8.5 K. The transition temperatures obtained from the inflection point of our C data (18.7 and 9 K) are listed in table 1 and are in close agreement with the earlier report [7]. With the application of magnetic field the heat capacity peaks are drastically modified. The peak at 8.5 K vanishes even for 1 T magnetic field and the peak at 21 K becomes very broad. Upon further increase in the magnetic field up to 5 T, C increases monotonically with increasing temperature. As in the case of DyPd_2Si , large magnetic heat capacity C_{mag} (see figure 2(b)) even well above magnetic transition temperatures is observed for the TbPd_2Si compound also. The magnetic entropy change (inset of figure 2(b)) just above the magnetic ordering temperature is about $5 \text{ J mol}^{-1} \text{ K}^{-1}$ ($\sim R \ln 2$), which suggests that ground state is a doublet for this compound. The entropy change is much smaller compared to the maximum theoretically possible entropy change for the Tb^{3+} ion ($R \ln 13$ for $J = 6$). The crystal field effects are much stronger in this compound compared to DyPd_2Si . This is evident from the larger C_{mag} observed for TbPd_2Si , which shows an increase with increasing temperature even at 40 K. The near symmetry and narrow width of the low temperature (9 K) peak (full width at half maximum $\sim 0.6 \text{ K}$) suggest this is a first order phase transition. The entropy change associated with this spin reorientation transition is calculated by fitting C data above and below the peak with a polynomial. This fitted curve is taken as background to obtain the heat capacity and entropy associated with this transition. The spin reorientation entropy thus calculated is found to be $0.4 \text{ J mol}^{-1} \text{ K}^{-1}$, which is about 8% of the total magnetic entropy change across the 21 K transition.

Figure 3 shows C_{mag} and S_{mag} curves for the compound GdPd_2Si . The zero-field heat capacity data of this compound and non-magnetic LuPd_2Si are shown in the inset; these are

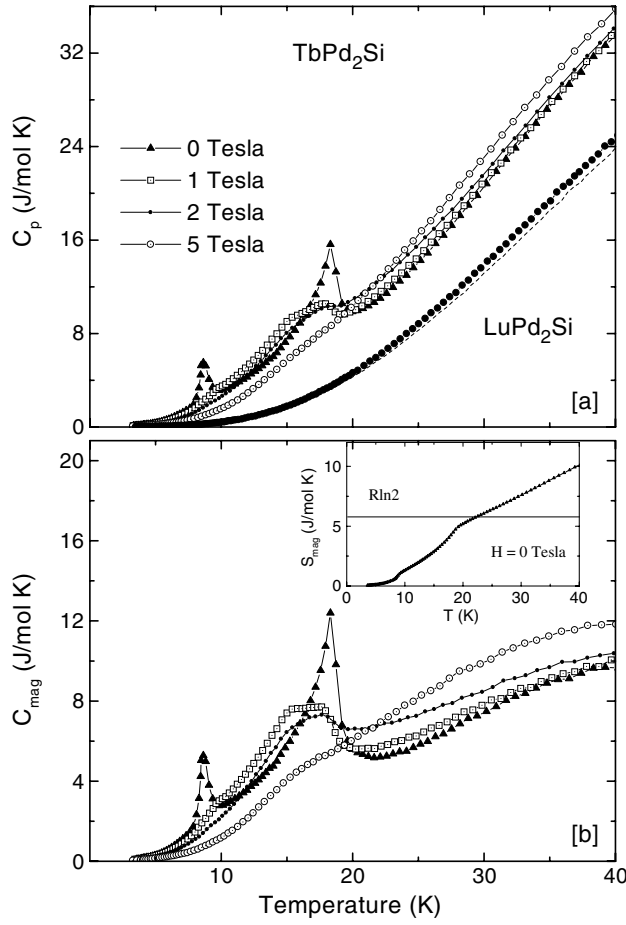


Figure 2. (a) Temperature dependence of heat capacity for the compound LuPd_2Si at zero magnetic field and for TbPd_2Si at 0, 1, 2 and 5 T magnetic field. The dashed line shows the heat capacity of LuPd_2Si normalized for TbPd_2Si (C_{nm}). (b) The magnetic contribution to heat capacity (C_{mag}) obtained by subtracting C_{nm} from measured C data of TbPd_2Si . Inset shows the temperature dependence of magnetic entropy. Lines through the data points are guide to eyes.

used for obtaining the C_{mag} curve of GdPd_2Si . The heat capacity and magnetocaloric studies of the compound GdPd_2Si was reported by us earlier [5]; however, the magnetic contribution to heat capacity C_{mag} is presented for the first time. As can be seen in figure 3, the jump around the 17 K transition is about $12 \text{ J mol}^{-1} \text{ K}^{-1}$ high. It has been shown by Blanco *et al* [11] that in the mean-field approximation the heat capacity jump at the magnetic transition for the amplitude modulated system is given by

$$\Delta C_{AM} = \frac{10}{3} \frac{J(J+1)}{2J^2 + 2J + 1} R \quad (1)$$

and that for the equal moment system

$$\Delta C_{EM} = 5 \frac{J(J+1)}{2J^2 + 2J + 1} R \quad (2)$$

where J is the total orbital angular moment. These equations could be applied as such to Gd compounds, as the crystal field effects are not expected and therefore J is a good quantum

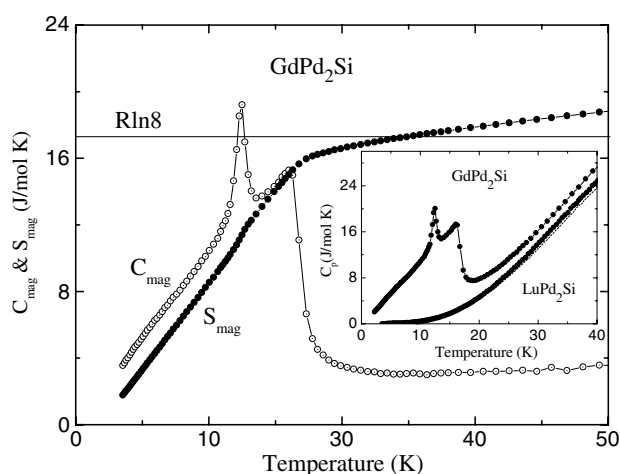


Figure 3. Temperature dependence of the magnetic contribution to the heat capacity and magnetic entropy for the compound GdPd_2Si . The inset shows the measured heat capacity for the compound GdPd_2Si and LuPd_2Si . The dashed line in the inset shows the heat capacity of LuPd_2Si normalized for GdPd_2Si (C_{nm}). Lines through the data points are guides to the eyes.

number, whereas in the case of other compounds J will no longer be a good quantum number due to the presence of the crystal field effect as discussed above. Therefore for the Gd system ($J = 7/2$) the discontinuity in C_{mag} at T_N should be $\sim 20 \text{ J mol}^{-1} \text{ K}^{-1}$ for an equal moment system, whereas for an amplitude modulated system it is expected to be two-thirds of that for the equal moment system i.e. $13.4 \text{ J mol}^{-1} \text{ K}^{-1}$. In the GdPd_2Si compound the heat capacity jump around the 17 K transition is about $12 \text{ J mol}^{-1} \text{ K}^{-1}$, which indicates that this compound orders into an amplitude modulated structure around this temperature. The sharp peak observed at 13.5 K indicates a first order phase transition associated with some spin reorientation transition [5]. The spin reorientation entropy change associated with this transition is found to be about $0.55 \text{ J mol}^{-1} \text{ K}^{-1}$.

A new and interesting result, which is observed in the present study, is that C_{mag} is significant up to 40 K, which is much higher than the magnetic ordering temperature. This is an unusual result because unlike the other two compounds the crystal field effects are expected to be absent in this compound as Gd is an S ion ($J = S = 7/2$, $L = 0$). The magnetic entropy change across the magnetic transition temperature reaches the $R \ln 8$ value (the theoretical maximum for Gd system) by 24 K, which indicates that short-range magnetic correlation vanishes by this temperature. Here it will be interesting to point out that we have observed a minimum in zero-field resistivity of this compound around 22 K [5]. This minimum, above the magnetic ordering temperature, is speculated to be due to short-range correlation present in the system [5]. This is in agreement with the present magnetic entropy analysis, which reaches the full $R \ln 8$ value around 24 K, well above the magnetic ordering temperature. C_{mag} is nearly constant, $\sim 3.5 \text{ J mol}^{-1} \text{ K}^{-1}$, beyond 24 K up to the highest measured temperature. Since the magnetic entropy change associated with the magnetic transition approaches the theoretical maximum for the Gd ion ($\sim 17 \text{ J mol}^{-1} \text{ K}^{-1}$) by 24 K, this extra contribution cannot be attributed to magnetic precursor effects. Besides this, magnetic precursor effects if present are expected to vanish by $2T_N$ [10, 12], whereas in the present case C_{mag} is significant even at 40 K ($> 2T_N$). Similar heat capacity behaviour has been observed for the compound GdPd_2In by Parson *et al* [13]. This compound is also found to

order in an amplitude modulated structure around 9 K and magnetic heat capacity even at 30 K is found to be more than $4 \text{ J mol}^{-1} \text{ K}^{-1}$. They speculated that the excess entropy even well above the magnetic ordering temperature arises from a conduction electron contribution associated with the Pd site and/or the coupling of lattice and magnetic degrees of freedom. Moreover, for the compound GdCu_2In , which is isostructural to GdPd_2In , C_{mag} is found to be zero above the magnetic transition temperature [13]. Therefore, the extra contribution to specific heat may be attributed to Pd ions. We have observed large magnetoresistance following negative H^2 dependence even well above the magnetic ordering temperature (at 40 K) in the compound GdPd_2Si [5], which indicates strong spin fluctuations in this compound. From these observations, we speculate that excess C_{mag} may be arising from the spin fluctuation of induced magnetic moments of Pd ions. If so then it may also be contributing to C_{mag} of Dy and Tb compounds besides the crystal field effect. However, in the absence of crystal field effect parameters, it is difficult to verify and distinguish the role of these two effects.

From the heat capacity data at zero and various constant magnetic fields the magnetocaloric effect is calculated for both the compounds TbPd_2Si and DyPd_2Si . Due to irreversibility in the field dependence of magnetization for TbPd_2Si [7], caution is needed in the interpretation of the obtained MCE of this compound. However, in the case of DyPd_2Si , the field dependence of magnetization is found to be reversible, therefore no such complication arises in the calculated MCE. The results for the compound TbPd_2Si are not shown as MCE is found to be quite small in this compound ($< 1 \text{ K T}^{-1}$). However, important parameters are given in table 1. The small MCE is expected, as the entropy change across the magnetic transition for this compound is found to be only about $5.5 \text{ J mol}^{-1} \text{ K}^{-1}$. The MCE behaviour at 1 T shows a positive maximum along with a negative minimum around the 20 K transition, which is in accordance with the antiferromagnetic ground state [7] of this compound. At 5 T magnetic field the MCE is positive in the entire temperature range, which is consistent with the reported metamagnetic transition around 1 T magnetic field.

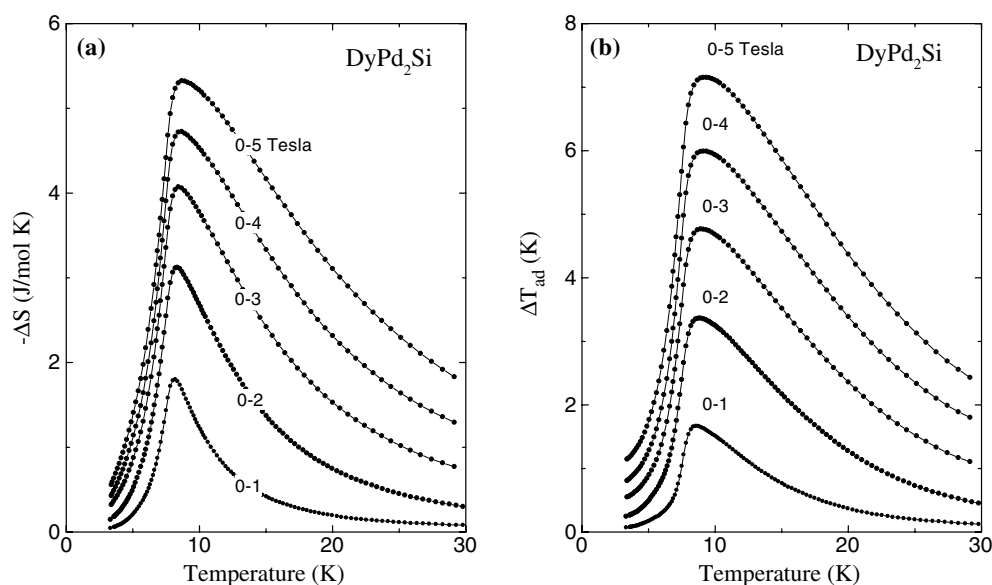


Figure 4. (a) Isothermal entropy change (ΔS) and (b) adiabatic temperature change (ΔT_{ad}) as a function of temperature for 1, 2, 3, 4 and 5 T magnetic field change. Lines through the data points are guides to the eyes.

The adiabatic temperature change (ΔT_{ad}) and isothermal entropy change (ΔS) for the compound DyPd_2Si are shown in figure 4 for 1, 2, 3, 4 and 5 T magnetic field change. The MCE is positive in the entire temperature range for all the field values, indicating a ferromagnetic ground state for this compound. The peak value of ΔT_{ad} is more than 7 K for 5 T magnetic field change. Compared to GdPd_2Si , which shows a large magnetocaloric effect around this region [5], the magnetocaloric effect for 5 T magnetic field change is smaller and narrower in the compound DyPd_2Si . However, for small magnetic field change the MCE for the DyPd_2Si is significantly higher. The magnetocaloric effect of these compounds is comparable to some of the compounds which show the largest magnetocaloric effect in this range. For example, ΔT_{ad} for 5 T magnetic field change is around 9, 7 and 6 K respectively for ErAl_2 , $\text{Gd}_{0.2}\text{Er}_{0.8}\text{NiAl}$ and ErNiAl [1, 14, 15].

The field dependence of ΔT_{ad} and ΔS peak values for all three compounds is shown in figure 5. The field dependence of the peak value of the MCE is typical of a ferromagnet for DyPd_2Si with monotonically decreasing slope whereas for Tb and Gd compounds it is similar to an antiferromagnetic system with metamagnetic transitions [16]. For a ferromagnet the molecular field model gives $H^{2/3}$ dependence for ΔS at Curie temperature (T_C) and is given by the following relation [1, 17]:

$$-\Delta S = 1.07R(g\mu_B JH/kT_C)^{2/3} \quad (3)$$

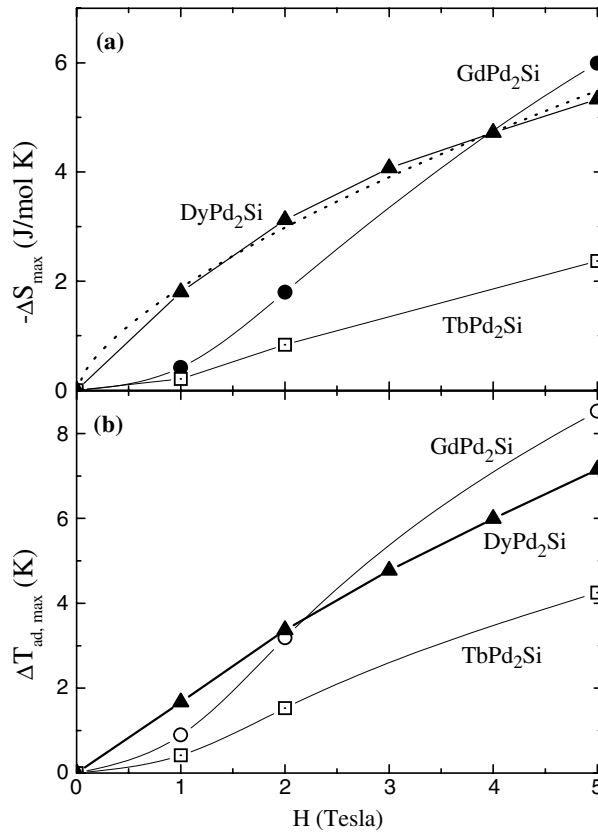


Figure 5. Maximum value of (a) $-\Delta S$ and (b) ΔT_{ad} as a function of magnetic field change for RPd_2Si ($R = \text{Gd}, \text{Tb}$ and Dy). The dotted line shows the fitted curve using equation (3) for DyPd_2Si . Solid lines through the data points are guides to the eyes.

where T_C is the magnetic ordering temperature and other symbols have their usual meaning. The data for the ferromagnetic compound DyPd_2Si is fitted with the above equation and the best fit to the data is shown by the dotted line in figure 5(b). There is a good agreement between the experimental data and the fitted curve. However, the calculated J value from fitting parameters is found to be around 0.9, which is much smaller compared to the 7.5 expected for free Dy^{3+} ions. The difference can be attributed to crystal field effects, as the model used in deriving equation (3) does not take into account the crystal field effect explicitly. In the presence of the crystal field effect J is no longer a good quantum number, and therefore, even though the entropy change across the transition indicates a quartet ground state, J values may not be taken as $3/2$. Equation (3) is not applicable for the other two compounds as both the compounds order in the antiferromagnetic ground state and show metamagnetic transitions for magnetic field less than 1 T [5, 7].

4. Conclusions

The compounds RPd_2Si ($R = \text{Gd}, \text{Tb}, \text{Dy}$ and Lu) are investigated using in-field heat capacity measurement. The magnetic entropy change across the magnetic transition indicates doublet and quartet ground states for Tb and Dy compounds respectively. Magnetic heat capacity data for the Gd compound show that this compound orders in an amplitude modulated structure around 17 K and short-range magnetic correlation persists up to 24 K. An excess heat capacity is found for this compound even well above the magnetic ordering temperature (up to 40 K) and it may be attributed to spin fluctuation of induced magnetic moment of Pd ions. The calculated magnetocaloric effect for the compound TbPd_2Si is found to be very small, whereas for the compound DyPd_2Si the MCE is significant and is even better than GdPd_2Si at low field. Therefore, this compound could be useful for low field application in magnetic cooling.

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