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**LETTER TO THE EDITOR**

# Magnetocaloric and magnetoresistance studies of $GdPd_2Si$

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**Abstract**

The compound $GdPd_2Si$, which is reported to order antiferromagnetically at 13 K, has been investigated by heat capacity and electrical resistivity measurement in the presence of external magnetic fields. In contrast to an earlier report, the zero-field heat capacity and resistivity data indicate two magnetic transitions at 13 and 17 K. The external magnetic field substantially influences the resistivity and heat capacity of the compound around the magnetic ordering temperature. The magnetocaloric effect, which is calculated from in-field heat capacity data, is quite large around the magnetic transition temperature. The magnetoresistance is also large near the magnetic ordering temperature. The metamagnetic transition is observed for 10 kOe magnetic field both in magnetocaloric and in magnetoresistance data. The metamagnetic transition strongly influences the magnetocaloric effect and magnetoresistance, which is large in this compound.

## 1. Introduction

The magnetocaloric effect (MCE) is the change in temperature ($\Delta T_{ad}$) of magnetic materials in adiabatic conditions under the influence of an external magnetic field ($H$) [1]. With the realization that the MCE can have substantial technological interest in the area of efficient cooling [2], studies related to this effect have appeared to gain momentum recently [3, 4]. Its technological success depends substantially on the discovery of new materials with large MCEs at the temperature of interest. As a continuation of our ongoing programme of searching for materials with large MCEs [5], we have prepared and studied the intermetallic compound $GdPd_2Si$. The compound $GdPd_2Si$ is known to crystallize in the orthorhombic crystal structure [6] and orders antiferromagnetically below 13.5 K [7]. The positive paramagnetic curie temperature ($\theta_P = 14$ K) and antiferromagnetic ordering in this compound indicate strong competition between antiferromagnetic and ferromagnetic interactions [7]. With the application of a reasonably small external magnetic field, a metamagnetic transition is expected in this compound due to such competing interactions. The modification of the magnetic structure may influence strongly the MCE and magnetoresistance (MR). With the motivation of wishing to verify the above-mentioned expectation and to look for systems with large magnetocaloric effects, we have studied the compound $GdPd_2Si$. Interestingly, in this compound two magnetic transitions have been observed and the nature of the transition is substantially influenced by the external magnetic field. It also gives rise to a large magnetocaloric effect and magnetoresistance around the magnetic ordering temperature.

## 2. Experimental methods

The polycrystalline sample of $GdPd_2Si$ was prepared by arc melting of constituent elements (purity better than 99.9 wt.%) in an argon atmosphere. The sample was characterized by x-ray diffraction of a powder sample and was found to be single phase. The heat capacity ($C$) measurements were performed by the semi-adiabatic heat pulse method with absolute accuracy ~0.5% in the presence of fields of 0, 10, 20, 50 and 80 kOe. The absolute accuracy for the few 80 kOe data is limited to 1.5% due to the larger fluctuations in the data. The resistivity ($\rho$) measurements were performed by the conventional four-probe method in the presence of helium exchange gas. The measurements of the longitudinal magnetoresistance ($\Delta\rho/\rho = \{\rho(H) - \rho(0)\}/\rho(0)$) at 3, 6, 10, 20, 30 and 40 K were carried out up to 80 kOe magnetic field.

## 3. Results and discussion

The temperature dependence of $C$ at various constant magnetic fields is plotted in figure 1. The zero-field $C$-data show two peaks indicating two phase transitions at 17 and 13 K in this compound. With the application of a small external magnetic field (10 kOe), both of the peaks are shifted to lower temperatures indicating the antiferromagnetic nature of both of the transitions. The observation of two magnetic phase transitions is in contrast to that of only one magnetic phase transition by Gignoux *et al* [7], at 13.5 K, in their magnetization measurements. It may be mentioned that the large anomaly in the zero-field heat capacity data around 17 K cannot be explained by considering the very small amount of impurity phase—if any—which is undetectable by means of x-ray diffraction. Blanco *et al* [8] showed that the associated $C$-discontinuity for the transition from paramagnetic to equal-moment (EM) magnetic structure ($\Delta C_{EM}$) for a Gd compound is about 20 J mol$^{-1}$ K$^{-1}$. For amplitude-modulated (AM) structure, the jump in heat capacity ($\Delta C_{AM}$) reduces strongly. According to their calculations, $\Delta C_{AM} = (2/3)\Delta C_{EM}$. From the zero-field $C$-data, it appears that $GdPd_2Si$ orders magnetically with amplitude-modulated structure at 17 K.

We have obtained the MCE ($\Delta T_{ad}$ and $-\Delta S$) from the total entropy ($S_{total}$), which was calculated from the experimental $C$-data (2–40 K) at various constant magnetic fields. Due to the significant contribution of the magnetic heat capacity in the temperature range 2–6 K, no good fit was obtained using physical models. Hence to calculate the entropy contribution for temperature lower than 2 K, we assumed that $C$ is positive and that, below 6 K, $C$ decreases smoothly with decreasing temperature and goes to zero at 0 K. With these assumptions, the heat capacity data were fitted to a polynomial in the temperature region 2–6 K and extrapolated down to 0 K. $\Delta T_{ad}$ is obtained as the difference in temperature required for moving iso-entropically from the zero-field to the in-field data in the plot of $S_{total}$ with respect to temperature [9]. It was shown earlier by Dan'kov *et al* [10] that the $\Delta T_{ad}$ obtained by this indirect method is essentially same as that obtained by the direct method. $-\Delta S$ is obtained similarly to $\Delta T_{ad}$ from the same

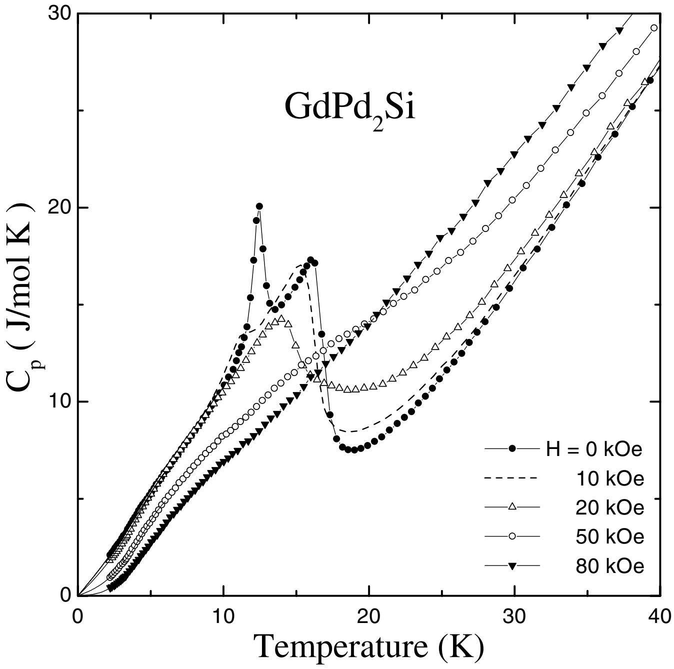


**Figure 1.** The heat capacity ($C$) as a function of temperature in the presence of magnetic fields ($H$) for the compound $GdPd_2Si$. The lines through the data points serve as a guide to the eyes. The continuous lines from 0 to 2 K are the extrapolated curves, obtained by fitting the respective $C$ versus $T$ data in the temperature range 2–6 K to a polynomial equation.

plot; the only difference is that one has to move isothermally. For simple ferromagnetic ordering, the plot of $\Delta T_{ad}$ as a function of temperature is expected to be of caret-like shape, with its maximum at the ordering temperature ($T_c$). And for simple antiferromagnetic material, $\Delta T_{ad}$ is negative and its temperature dependence is believed to be of reverse-caret-like shape with a minimum around $T_N$ [11].

The plots of $\Delta T_{ad}$ and $-\Delta S$ as functions of temperature for 10, 20, 50 and 80 kOe field changes are shown in figures 2(a) and 2(b) respectively. The $\Delta T_{ad}$ for 0–10 kOe is positive and increases with decreasing temperature from 40 K to 17 K. This could be due to the increased magnetization with decreasing temperature in the paramagnetic state. Below 17 K, possibly due to the dominance of antiferromagnetic interactions, $\Delta T_{ad}$ decreases. A further decrease in $\Delta T_{ad}$ with decreasing temperature occurs around 13 K. It may be noted that 17 K and 13 K are the antiferromagnetic ordering temperatures of the compound taken from zero-field heat capacity data. The negative $\Delta T_{ad}$ around 12 K is consistent with antiferromagnetic ordering. For higher fields, the magnetic moment becomes more and more oriented along the field direction, which results in positive and larger $\Delta T_{ad}$. The absence of the negative $\Delta T_{ad}$ and the minimum around 12 K in the 0–20 kOe data indicate a metamagnetic transition around 10 kOe magnetic field. The most interesting observation is that the value of $\Delta T_{ad}$ around 15 K for higher magnetic field changes is significantly large, about 12 K for 0–80 kOe magnetic field change. It should be noted here that the constituent elements of the compound $GdPd_2Si$ were commercially purchased, with purity about 99.9 wt.%. Considering that even a small amount of impurity generally reduces the MCE [12] of a material, we can expect the MCE observed in $GdPd_2Si$ to be enhanced further if the sample is prepared from higher-purity constituent

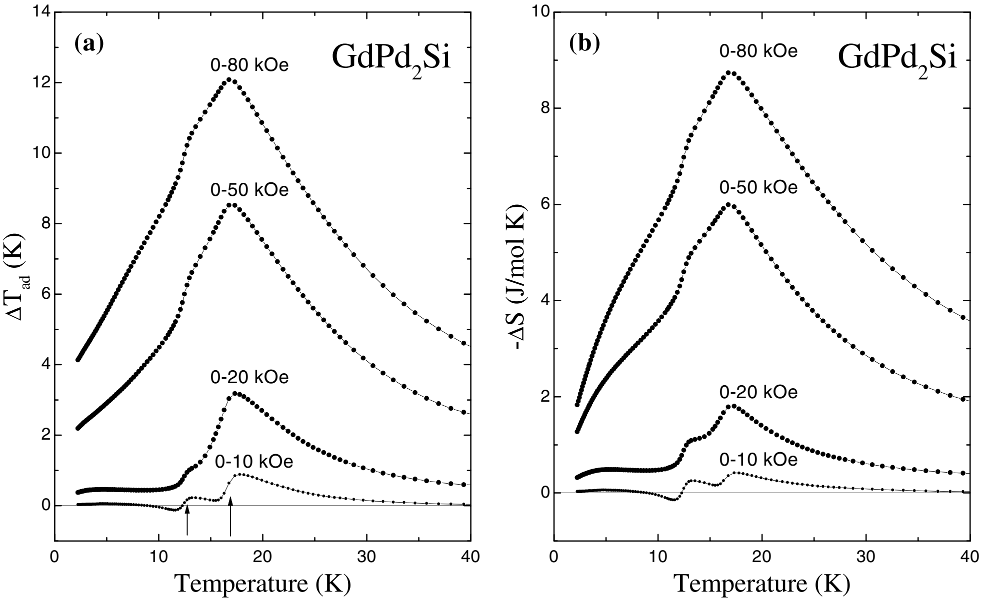


**Figure 2.** The temperature dependence of the magnetocaloric effect, (a) $\Delta T_{ad}$ and (b) $-\Delta S$, calculated with respect to zero field for $GdPd_2Si$ at various magnetic fields. The vertical upward arrows in (a) indicate the magnetic ordering temperature obtained from the zero-field heat capacity data. The continuous lines drawn through the data points are guides to the eyes.

elements. The various features in the temperature dependence of $-\Delta S$ (figure 2(b)) are similar to those of $\Delta T_{ad}$ (figure 2(a)).

Figure 3 shows the peak value of $\Delta T_{ad}$, taken from figure 2(a), as a function of magnetic field change $\Delta H$. The signature of a metamagnetic transition can be clearly observed in this plot. At 10 kOe, the slope of the $\Delta T_{ad,peak}$ versus $\Delta H$ curve increases and above 20 kOe the slope decreases monotonically. The monotonic decrease in the slope above 20 kOe is similar to that observed for ferromagnetic compounds, where the MCE tends to saturate for higher magnetic field changes [10, 13]. The plot indicates the changeover of the magnetic structure in $GdPd_2Si$ at low temperature from predominantly antiferromagnetic to ferromagnetic for field values higher than 10 kOe.

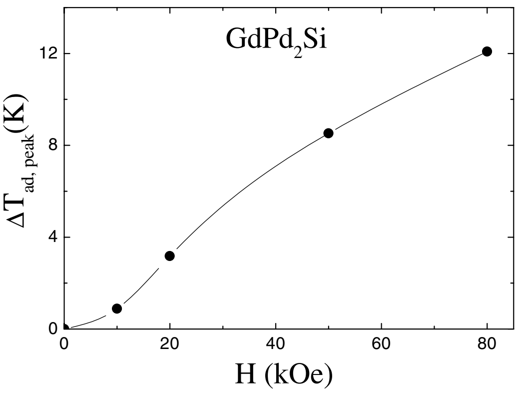


**Figure 3.** The peak value of $\Delta T_{ad}$, taken from figure 2(a), as a function of the magnetic field change $\Delta H$ for the compound $GdPd_2Si$. The continuous lines drawn through the data points are guides to the eyes.

Recently we have reported [14] that the temperature dependences of $-\Delta\rho$ $(=\rho(0)-\rho(H))$ and $\Delta T_{ad}$ are expected to be similar where the change in carrier concentration is not dominant. A large MCE implies a significant change in magnetic moment configuration in response to an external magnetic field. The scattering of conduction electrons from the localized magnetic moment is expected to be modified substantially with the change in localized magnetic moment configuration. As a result, one expects reasonably large magnetoresistances in systems with large MCEs. However, the large MR, which can also originate due to a change in carrier concentration, need not give rise to a large $\Delta T_{ad}$. Since we have observed a significant $\Delta T_{ad}$ for $GdPd_2Si$ at low temperature, an enhanced MR was expected in this compound. To verify our expectation and also to see the clear signature of a metamagnetic transition (which was observed in the MCE), $\rho$ and MR measurements were carried out.

The various features of $\rho$ at low temperature are highlighted in figure 4. Two distinct drops in $\rho$, corresponding to magnetic ordering temperatures obtained from zero-field $C$-data, are indicated by the vertical arrows. Interestingly, $\rho$ shows a minimum at 22 K, which is highlighted in figure 4, inset (a). In the case of Ce-based intermetallic compounds, the rise in resistivity with decreasing temperature is generally attributed to the Kondo effect. But in the case of Gd compounds this cannot be attributed to the Kondo effect, as the 4f electrons of Gd ions are well localized. Such resistivity minima well above the ordering temperature for some Gd-based intermetallic compounds were observed earlier [15, 16] and attributed to short-range magnetic ordering of Gd ions or spin fluctuations of transition metal ions. The temperature dependence of the MR $(=\{\rho(80\text{ kOe}) - \rho(0\text{ kOe})\}/\rho(0\text{ kOe}))$, which is shown as inset (b), was calculated from the $\rho$-data plotted in figure 4. It indicates that the magnetoresistance is

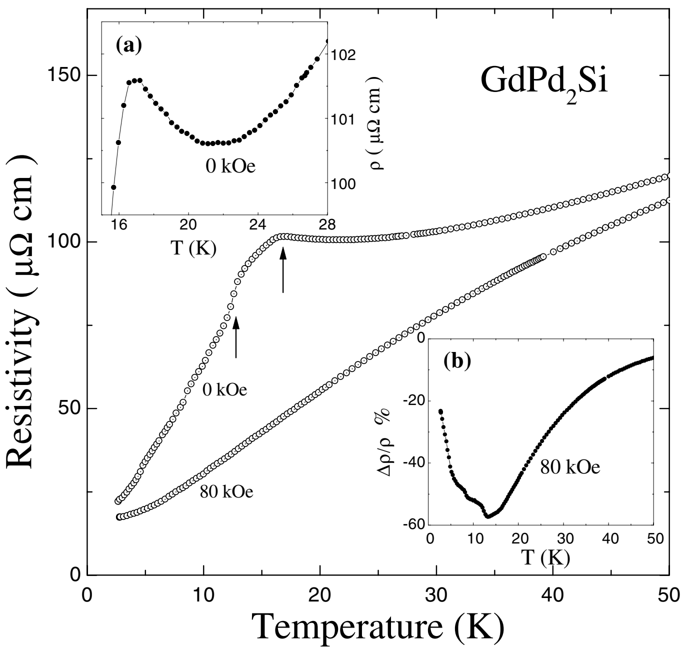


**Figure 4.** The electrical resistivity ($\rho$) versus temperature at zero and 80 kOe magnetic field for $GdPd_2Si$. The vertical upward arrows indicate the magnetic ordering temperature obtained from the zero-field heat capacity data. Inset (a) highlights the minimum around 22 K in the zero-field $\rho$-data. Inset (b) shows the magnetoresistance versus temperature obtained from 0 kOe and 80 kOe $\rho$-data. The continuous lines through the data points are guides to the eyes.

more than 55% around 15 K in this compound. Moreover, the MR is quite large (>10%) even at 40 K (>$2T_N$), indicating strong spin fluctuations in this compound well above the ordering temperature.

The field dependence of the MR at various temperatures is plotted in figure 5. At 3, 6 and 10 K, the MR is positive and increases approximately as $H^2$ for magnetic fields up to 10 kOe. This is expected for an antiferromagnetic system. For field values higher than 10 kOe, the MR decreases and its field dependences in this region are typical of ferromagnetic materials [17]. There is a clear signature of a metamagnetic transition around 10 kOe, which was observable even in our MCE data. The metamagnetic transition at 1.5 K for 10 kOe magnetic field was observed earlier by Gignoux *et al* [7] in their magnetization measurements. At 20 and 30 K the MR shows deviations from the $-H^2$ behaviour at higher fields, indicating the magnetic correlation for higher magnetic fields in this temperature range. The most interesting point is well above $2T_N$ (e.g. at 40 K): the magnetoresistance is reasonably large, negative and varies approximately as $H^2$. This indicates that strong spin fluctuations exist well above the magnetic ordering temperature. The metamagnetic transition and spin fluctuation, which were observed clearly in the MR, contribute even to the MCE.

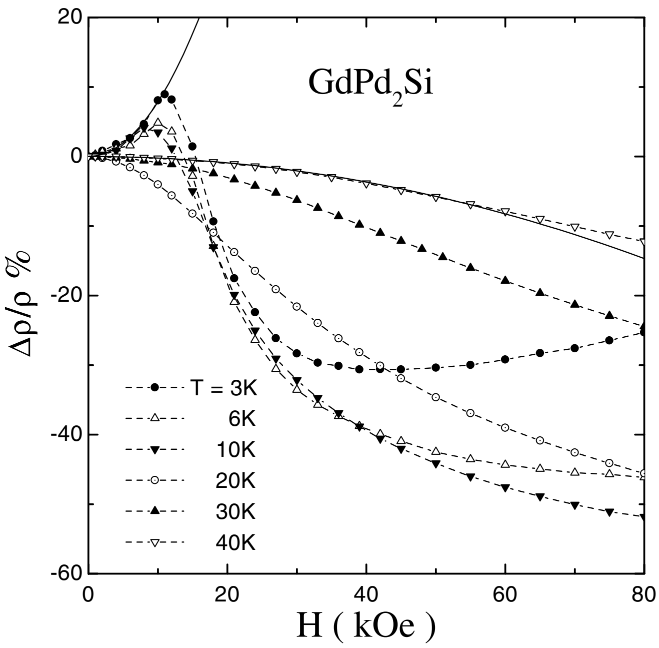


**Figure 5.** The isothermal magnetoresistance as a function of magnetic field for $GdPd_2Si$. The dashed lines through the data points serve as a guide to the eyes. The $H^2$-fit in the range 0–10 kOe for the 3 K data is shown by a continuous line extrapolated up to 15 kOe. The 40 K data are fitted to a $-H^2$ dependence in the range 0–60 kOe shown by the continuous line and extrapolated up to 80 kOe.

## 4. Conclusions

Two magnetic transitions were observed at 17 and 13 K for the compound $GdPd_2Si$, in contrast to the earlier report [7]. Both magnetic transitions are antiferromagnetic in nature and substantially influenced by the external magnetic field. The 17 K transition appears to be a transition from paramagnetic to amplitude-modulated magnetic structure. The MCE for this compound is quite large for higher magnetic fields around the magnetic ordering temperature. The low-field MCE indicates the metamagnetic transition around 10 kOe magnetic field. Besides showing the signature of two magnetic transitions, $\rho$ also shows a minimum around 22 K. The increase in resistivity with decreasing temperature indicates the possibility of short-range correlation of Gd ions well above the magnetic ordering temperature and/or enhanced spin fluctuation of the transition metal. As expected from the observation of the large MCE in this compound, a large negative MR was also observed around the magnetic ordering temperature. The strong influence of the metamagnetic transition can be observed both in MCE and in MR data.

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