Re-entrant spin glass behaviour and large magnetocaloric effect in Er$_2$PtSi$_3$

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Abstract. We present the magnetic properties and magnetocaloric effect of ternary intermetallic compound Er$_2$PtSi$_3$ with the orthorhombic Ba$_2$LiSi$_3$-type structure. Dc magnetization, ac susceptibility, magnetic relaxation, electrical resistivity and specific heat measurements indicate that this system undergoes two magnetic phase transitions from a paramagnetic state sequentially to an antiferromagnetic state at $T_N=5.4$ K and then to a random spin freezing state at $T_f=2.4$ K. In addition, the large magnetocaloric effect is also observed for the Er$_2$PtSi$_3$ alloy. Near its Néel temperature $T_N$, the maximum magnetic entropy change, relative cooling power and maximum adiabatic temperature change are estimated to be 16.1 Jkg$^{-1}$K$^{-1}$, 290 Jkg$^{-1}$ and 7.7 K, respectively, for a field change of 5 T. These results suggest that Er$_2$PtSi$_3$ should be classified as a re-entrant spin-glass system and can be considered as a potential low-temperature magnetic refrigeration material.

1. Introduction

Ternary silicides with the composition $R_2$PtSi$_3$ ($R$=rare earth or uranium) constitute an interesting series of the 2:1:3 nonmagnetic atom disorder (NMAD) intermetallic compounds. They are reported to crystallize in an AlB$_2$-derived hexagonal structure, and a doubling of the unit-cell parameter $c$ occurs for $R$=Gd and Y, but not for $R$=La, Ce, Pr and Nd [1]. Magnetic measurements reveal that compounds $R_2$PtSi$_3$ with $R$ = Ce, Nd, and Gd show ferromagnetic (FM) phase transition at Curie temperature $T_C=5$, 18, and 24 K, respectively [1], while complex magnetic properties are observed for the Pr, Tb and Dy compounds [1-3]. Moreover, our study suggests that more or less Pt and Si atoms in $R_2$PtSi$_3$ randomly distribute on the Pt-Si superstructure, and strong or weak spin-glass (SG)-like effects exhibit in these compounds [2]. In addition, 5f electronic compound U$_2$PtSi$_3$ crystallizing in the AlB$_2$-type NMAD structure, shows the simple SG behavior without long-range magnetic order [4]. In order to fully observe and understand the magnetic properties of this series of compounds, we have prepared a polycrystalline Er$_2$PtSi$_3$, another member of the $R_2$PtSi$_3$ family, and undertaken a systemic measurement on its magnetic and magnetocaloric properties. In this paper, we present the detailed experimental results including ac susceptibility $\chi_{ac}(T)$, dc magnetization $M(H)$, magnetic relaxation $M(t)$, electrical resistivity $\rho(T)$ and specific heat $C(T)$ on a well-annealed Er$_2$PtSi$_3$ sample.

2. Experimental
Polycrystalline sample of Er$_2$PtSi$_3$ was prepared by arc melting high-purity raw metals (Er: 3N; Pt: 4N; Si: 6N) in an arc furnace under a purified argon atmosphere. The button was flipped and remelted four times to ensure homogeneity, and then wrapped into tantalum foil and annealed in evacuated silica tube at 900 °C for 23 days. The quality of the obtained sample was checked by x-ray powder diffraction at room temperature with Cu$Kα$ radiation, and the result indicates that the annealed sample is almost single-phased with negligible impurity phases. The observed diffraction pattern can be indexed based on the orthorhombic Ba$_2$LiSi$_3$-type structure model (space group $Fddd$), an ordered superstructure derivative of the hexagonal AlB$_2$-type. There are five different crystallographic positions in this structure, two of them are occupied by Er atoms, and mixed positions of Pt and Si atoms are distributed on the other three non-equivalent sites as recently determined for another 2:1:3 system, Yb$_2$AuSi$_3$ [5].

The dc magnetization, ac susceptibility and magnetic relaxation were measured between 2 and 300 K in magnetic fields up to 7 T using a SQUID magnetometer. The thermal-relaxation technique was employed for specific heat measurement in the temperature range between 2 and 30 K by using a physical properties measurement system (PPMS, Quantum Design). Electrical resistivity measurements were performed between 0.5 and 285 K using a standard four-terminal DC method.

3. Results and discussion

Figure 1 shows the low temperature dc susceptibility $\chi$ (=M/H) of Er$_2$PtSi$_3$ between 2 and 7 K measured in magnetic fields of $H=10$ and 100 Oe under zero field-cooled (ZFC) and field-cooled (FC) conditions. It is clear from this figure that both $\chi_{ZFC}(T)$ and $\chi_{FC}(T)$ curves show an evident peak at $T_N=5.4$ K and no difference between them around $T_N$ indicating an antiferromagnetic (AFM) phase transition in Er$_2$PtSi$_3$ at $T_N$. As the temperature is further decreased to ~4 K, the $\chi$ value increases again, while $\chi_{ZFC}(T)$ and $\chi_{FC}(T)$ curves clearly separate from each other below $T_f$~2.4 K. Such an irreversible magnetic behaviour suggests the occurrence of some kind of magnetic phase transition, that is, the system re-enters a SG-like metastable magnetic state at the temperature $T_f$ (below $T_N$). Above about 20 K, $\chi(T)$ follows a Curie-Weiss behaviour $\chi(T) = \mu^2_{\text{eff}}/8(T - \theta_p)$. The least-squares fitting (solid line in Fig. 2) yields a small paramagnetic Curie temperature of $\theta_p=3.3$ K, and an effective magnetic moment of $\mu^2_{\text{eff}}=9.6 \mu_B$/Er, close to the value of 9.58 $\mu_B$ expected for free Er$^{3+}$ ion in the $J=15/2$ Hund’s rule ground state indicating that the 4f electrons are almost localized within the Er atoms.

Figure 1. Temperature dependence of the dc susceptibility (M/H) of Er$_2$PtSi$_3$ measured in magnetic fields of 10 and 100 Oe under FC (○) and ZFC (●) conditions.

Figure 2. Temperature dependence of the reciprocal dc susceptibility (H/M$\text{FC}$) of Er$_2$PtSi$_3$ measured in a field of 100 Oe under FC condition.
In order to confirm the low-temperature SG effect, we performed an ac susceptibility measurement on the Er$_2$PtSi$_3$ sample at frequency range $0.1 \text{ Hz} \leq \omega/2\pi \leq 1000 \text{ Hz}$. Figure 3 shows the in-phase component $\chi'_{ac}(T, \omega)$ and out-of-phase component $\chi''_{ac}(T, \omega)$ of the ac susceptibility between 2 and 8 K. It is clear from this figure that $\chi'_{ac}$ exhibits an evident peak at $T_N=5.4 \text{ K}$ with the amplitude and position independent of the frequency. This is the typical feature of long-range order magnetic phase transition. Moreover, further reducing the temperature, $\chi'_{ac}(T, \omega)$ shows another characteristic maximum near $T_f=2.4 \text{ K}$ with the amplitude and position strongly depending on the frequency $\omega$ of the applied ac magnetic field. As $\omega$ increases, $T_f$ in $\chi'_{ac}(T, \omega)$ shifts to higher temperatures. For example, at $\omega/2\pi=0.1 \text{ Hz}$, the peak in $\chi'_{ac}(T, \omega)$ appears at 2.4 K, which shifts to 3.3 K at $\omega/2\pi=1000 \text{ Hz}$. This is a typical behaviour characteristic of SG materials [5]. Moreover, the initial frequency shift of $T_f$, which is usually defined as $\delta T_f = \Delta T_f/(\Delta T_f/\Delta \log \omega)$ and is used to distinguish a canonical SG from a SG-like material [5], is 0.08 for Er$_2$PtSi$_3$ comparable to the typical values for spin glasses (from a few thousandths to a few hundredths). These results can be considered as important evidence for the re-entrant SG state in Er$_2$PtSi$_3$ below $T_f$.

On the other hand, it is interesting to note that the out-of-phase component $\chi''_{ac}(T, \omega)$, which has rather small magnitude (roughly one order of magnitude smaller than $\chi'_{ac}$), shows a significant increase and strong frequency dependence at the temperatures near $T_f$ suggesting the influence of SG effect. However, there is no distinct peak in $\chi''_{ac}(T, \omega)$ curve around $T_N=5.4 \text{ K}$, where $\chi'_{ac}(T, \omega)$ as well as dc susceptibility shows a significant peak. This is an exemplary feature characterizing the AFM phase transition. In this paper, the temperature $T_N=5.4 \text{ K}$ and $T_f=2.4 \text{ K}$ observed in $\chi'_{ac}(T, \omega)$ at $\omega=0.1 \text{ Hz}$ is defined as Néel temperature and spin freezing temperature, respectively, for Er$_2$PtSi$_3$.

It is well known that remanence and long-time magnetic relaxation effect, relating to the activated processes between the metastable magnetic states, are also the characteristic features of spin glasses [5, 6]. These phenomena have also been observed for the Er$_2$PtSi$_3$ sample at the temperatures below $T_f$. Figure 4 illustrates the field variation of the magnetization $M(H)$ measured at 2 K ($<T_f$) up to 5.5 T for Er$_2$PtSi$_3$ after cooling the sample in zero field from room temperature. The inset shows the low field part in an expanded scale. As increasing $H$, $M(H)$ increases relatively quickly up to ~1 T, then rises slowly and reaches a value of 5.7 $\mu_B$ per Er atom at 5.5 T. This value is much smaller than 9 $\mu_B$/Er, the expected saturation value for Er$_2$PtSi$_3$. When $H$ is returned from 5.5 T, weak hysteresis effect appears at about 0.2 T, and a small remanent magnetization of about 0.02 $\mu_B$ per Er atom is detected at zero field (inset of Fig. 4). From a careful measurement of the hysteresis loop we determine the coercive field $H_C$ of Er$_2$PtSi$_3$ to be 23 Oe at 2 K.

Figure 3. Temperature dependences of real component (a) and imaginary component (b) of the ac susceptibility of Er$_2$PtSi$_3$ measured at various frequencies with an excitation field of $H_{ac}=1 \text{ Oe}$.
To measure magnetic relaxation effect in a field, the sample was first cooled in zero field from 50 K to 2 K, then a magnetic field of 50 Oe (much larger than $H_{\text{c}}$=23 Oe) was applied and the recording started immediately just as the field stabilized ($t=0$) [Fig. 5(a)]. Furthermore, to measure the relaxation behaviour in zero field, we first cooled the sample in zero field from 50 K to 2 K, then, a field of 5000 Oe was applied for about 5 min before switching it off ($t=0$) [Fig. 5(b)]. As seen from Fig. 5, in both cases the decay of $M(t)$ is remarkably slow. After waiting for one hour both nonsaturation magnetization at 50 Oe and nonzero remanence in zero field are still far from saturation. Such a long-time magnetic relaxation feature in Er$_2$PtSi$_3$ could be contributed to the SG effect. Using a logarithmic function, $M(t)=M_0+St$[$t+t_0$], the obtained relaxation behaviour can be fitted very well over the full time range studied. The best fitting results obtained by using the least-squares method are shown by the solid lines in Fig. 5, which yields following values of fitting parameters for Er$_2$PtSi$_3$: $M_0$=0.7446 emu/g and $S$=0.0069 emu/g for $H$=50 Oe [inset of Fig. 5(a)], and $M_0$=0.6182 emu/g and $S$=−0.0444 emu/g for $H$=0 [inset of Fig. 5(b)]. Note that similar logarithmic function had also been used to describe the relaxation behaviour for many other SG systems such as for Gd$_{2-\epsilon}$Y$_{\epsilon}$PdSi$_3$ ($\epsilon=0$, 0.4, 1.0 and 1.6) [7]. Where $M_0$ and $S$, called as initial zero-field magnetization and magnetic viscosity, respectively, are the fitting parameters depending on the temperature. The parameter $t_0$ depends on the measuring conditions and has only limited physical relevance.

The electric resistivity and specific heat measurements give further evidence for the formation of re-entrant SG state in Er$_2$PtSi$_3$. It is clear from Fig. 6 that the temperature dependence of electrical resistivity, $\rho(T)$, shows an upturn as the temperature is lowered near $T_N$. After passing through a maximum value at about 4 K, $\rho(T)$ decreases smoothly down to 0.5 K. This behaviour is often observed in rare-earth compounds and explained as the decrease of carrier density due to the formation of magnetic Brillouin-zone boundary gaps [8]. Note that no anomaly (peak or rapid decrease) can be detected around $T_f$ (=2.4 K). At high temperatures, $\rho(T)$ shows metallic conductivity and downward bending between 50 and 250 K, which may be resulted from crystal field interaction and/or $s$-$d$ interband scattering of conduction electrons [9].

The experimental results of temperature dependence specific heat $C(T)$ of Er$_2$PtSi$_3$ measured in fields of 0 and 5 T are illustrated in Fig. 7. In zero field, a large peak is observed at 5 K just below $T_N$, due to the AFM ordering. It is interesting to note that, at the spin freezing temperature $T_f$ where ac susceptibility shows an evident frequency dependent maximum, no anomaly can be detected in the $C(T)$ curve. Experimentally, it is not easy to determine the magnetic contribution $C_m$ to the total specific heat accurately, since the total specific heat consists of vibrational, electronic and magnetic parts. However,
at low temperature, the vibrational part is smaller and electronic contribution is proportional to $T$. Thus the absence of dramatic change in $C(T)$ at $T_f$ means the magnetic part $C_m(T)$ do not behaves anomaly at this temperature. This result excludes the possibility of a long-range magnetic order phase transition at $T_f$ in Er$_2$PtSi$_3$. The anomalous magnetic properties around $T_f$ in ac and dc susceptibilities can only be originated from the formation of SG state. Using the data between 12 and 22 K, the $\gamma$ value (specific heat coefficient of $T$-linear term) estimated from the $C/T$ vs. $T^2$ plots to be 400 mJ(mole-Er)$^{-1}$K$^{-3}$ much larger than that of a normal metal. Random distribution of Pt and Si atoms may be responsible for this larger $\gamma$ value as usually observed in NMAD compounds [10]. Note that the larger specific heat peak observed in zero field is almost completely smoothed out in a field of 5 T. These data are also used to calculate the magnetic entropy change as described below.

It is very significant to compare the experimental results mentioned above to those observed for other 2:1:3 NMAD intermetallic compound. Among them, long-range magnetic ordering occurs in some systems with strong magnetic exchange interactions such as in ferromagnets Nd$_3$PtSi$_3$ [11] and Nd$_3$RhSi$_3$ [12] and in antiferromagnets Tb$_2$RhSi$_3$ [12] and Tb$_2$AgIn$_3$ [13]. In contrast, in some systems with weak magnetic coupling SG state may dominate the magnetic properties such as in Ce$_2$AgIn$_3$ [14], Ce$_2$CuSi$_3$ [12] and some U$_2$M$_2$Si$_3$ compounds [15]. For Er$_2$PtSi$_3$, we found the coexistence of long-range magnetic ordering and SG state. Such a reentrant SG behaviour has also been observed in some other 2:1:3 compounds such as in Tb$_2$CuIn$_3$ [16], Nd$_2$CuSi$_3$ [17], Tb$_2$PdSi$_3$ and Dy$_2$PdSi$_3$ [18]. It seems that in these reentrant SG systems a part of spins could exist as random individual spins or finite-size granules with net magnetic moments (magnetic clusters) due to the NMAD structure and don’t participate in long-range magnetic ordering. In the present case, Er atoms in Er$_2$PtSi$_3$ occupy two different crystallographic positions, and mixed positions of Pt and Si atoms are distributed on three non-equivalent sites. This characteristic crystal structure may result in the formation of randomly distributed individual spins or magnetic clusters, which could weakly interact with each other at low temperatures mediated by the conduction electrons and frustrated magnetic moments could be formed. As the temperature is decreased crossing the critical point $T_f$, magnetic moments of these individual spins or clusters would be frozen in disorderly directions forming metastable SG state similar to what happen in amorphous or diluted metallic SG materials. In fact, magnetic clusters have been confirmed to form in similar 2:1:3 NMAD compounds U$_2$PdGa$_3$ and U$_3$PtGa with dimension 120–150 Å based on the neutron powder diffraction measurements [19]. For Er$_2$PtSi$_3$, however, since there is no detailed experimental data on the magnetic structure, we cannot give convincing information about the amount of individual spins and the

**Figure 6.** Temperature dependence of electrical resistivity of Er$_2$PtSi$_3$ between 0.5 and 285 K. The inset shows the low temperature data.

**Figure 7.** Temperature dependence of specific heat of Er$_2$PtSi$_3$ measured in $H$=0 and 5 T between 2 and 30 K. The inset shows the data plotted as $C/T$ vs. $T^2$. 
dimension of magnetic cluster based on the present work. In this sense, further experimental works including neutron powder diffraction measurement on Er$_2$PtSi$_3$ are necessary.

On the other hand, in order to obtain more comprehensive information on the magnetic properties of Er$_2$PtSi$_3$, magnetocaloric effect (MCE) of this compound is also studied by measuring $M(H)$ isotherms up to 7 T at the temperatures around $T_N$ with increments of 1.5-3.0 K. The measurements are shown in Fig. 8. In general, MCE is characterized by magnetic entropy change $\Delta S_m$ caused by a field change. Using the Maxwell relation, $\Delta S_m(T, H) = \int_0^H [\partial M(T, H)/\partial T]_H dH$, magnetic entropy change $\Delta S_m$ can be calculated from the $M(H)$ data. In the present case, the calculated results of $\Delta S_m$ are displayed in Fig. 9 for Er$_2$PtSi$_3$. Magnetic hysteresis effect was ignored in this calculation, since almost no magnetic hysteresis can be observed in the $M(H)$ curves at the temperatures near $T_N$. The negative values of $\Delta S_m$ (positive MCE) are observed even in small magnetic field changes. It is clear that at temperature just above $T_N$, $\Delta S_m$ shows a maximum value, $\Delta S_m^{\text{max}}$, which increases with the magnetic field change ($\Delta H$) and reaches a value of $-\Delta S_m^{\text{max}}=16.1$ Jkg$^{-1}$K$^{-1}$ for $\Delta H=5$ T.

![Figure 8](image8.jpg)  
**Figure 8.** Magnetization of Er$_2$PtSi$_3$ as a function of magnetic field measured at different constant temperatures.

![Figure 9](image9.jpg)  
**Figure 9.** Magnetic entropy change of Er$_2$PtSi$_3$ as a function of temperature determined from the magnetization and specific heat measurements.

![Figure 10](image10.jpg)  
**Figure 10.** Magnetic field dependence of the relative cooling power of Er$_2$PtSi$_3$.

![Figure 11](image11.jpg)  
**Figure 11.** Adiabatic temperature change of Er$_2$PtSi$_3$ calculated from the specific heat data for $\Delta H=5$ T.
In order to verify the accuracy of the magnetic entropy change estimated based on the Maxwell relation, $\Delta S_m$ of Er$_2$PtSi$_3$ was also calculated based on the specific heat data measured in zero and 5 T (see Fig. 7) using the expression $\Delta S_m=\Delta S=8(H,T)-S(0,T)$, where $S(H,T)=\int_0^T[C(H,T)/T]dT$. The calculating results are also displayed in Fig. 9 together with the data calculated by the magnetic method. It is found that the calorimetric and magnetic methods yield the similar results in the temperature range measured, even though the $\Delta S_m$ value estimated from $C(H,T)$ is slightly larger than that estimated from $M(H,T)$.

It is well known that relative cooling power (RCP) and adiabatic temperature change ($\Delta T_{ad}$) are also important parameters for evaluating the usefulness of a magnetic refrigerant material, and are usually defined as $RCP=|\Delta S_m|/\Delta T_{FWHM}$ [20, 21] and $\Delta T_{ad}(\Delta H, T)=[T(S)_H-T(S)_0]\Delta S$ [22], respectively. Where $\Delta T_{FWHM}$ is the full width at half maximum of the $-\Delta S_m$ vs $T$ plot. Figure 10 shows the calculated results for Er$_2$PtSi$_3$. The RCP value increases linearly with increasing $\Delta H$ and reaches a value of $RCP=290$ Jkg$^{-1}$ for $\Delta H=5$ T, while $\Delta T_{ad}$ increases with $T$, reaches a maximum at the temperature slightly higher than $T_N$, and then decreases with further lowering the temperature. The maximum $\Delta T_{ad}$ is observed at ~6 K with a larger value of $\Delta T_{ad}^{max}=7.7$ K for $\Delta H=5$ T.

In conclusion, we have investigated the magnetic properties and MCE of polycrystalline Er$_2$PtSi$_3$ by both magnetic and calorimetric techniques. X-ray diffraction result suggests that the annealed sample crystallizes in the orthorhombic Ba$_2$LiSi$_3$-type structure (space group Fdd2), an ordered superstructure derivative of the hexagonal AlB$_2$-type. With decreasing the temperature, this system undergoes a magnetic phase transition from PM to AFM state at $T_N=5.4$ K, and then reenters the SG state at $T_F=2.4$ K. The clear peak near $T_N$ and lack of anomaly around $T_J$ in both $C(T)$ and $\rho(T)$ curves, the frequency independent peak at $T_N$ and strongly frequency related maximum at $T_J$ observed in $\chi_{ac}(T,\omega)$ (shift of $T_J$ with increasing $\omega$), the long-time magnetic relaxation effect and the irreversible magnetism observed below $T_J$ can be considered as the evidence for the re-entrant SG behaviour. Similar to other NMAD SG systems, random distribution of Pt and Si atoms on the three different crystallographic positions may be the main origin of the low temperature SG state in Er$_2$PtSi$_3$. On the other hand, both magnetic and calorimetric measurements reveal a large MCE for the Er$_2$PtSi$_3$ compound with the maximum magnetic entropy change $-\Delta S_m^{max}=16.1$ Jkg$^{-1}$K$^{-1}$, the relative cooling power $RCP=290$ Jkg$^{-1}$ and the maximum adiabatic temperature change $\Delta T_{ad}^{max}=7.7$ K for $\Delta H=5$ T at the temperature near $T_N=5.4$ K. These data are comparable with those shown in the literatures for some other rare earth based refrigerant materials with similar working temperatures, such as ErRu$_2$Si$_3$ [23] and ErNi$_3$ [24]. Thus, re-entrant SG compound Er$_2$PtSi$_3$ could also be considered as a promising candidate for use as a magnetic refrigerant at low temperatures.

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