Evidence for the formation of the spin-glass state in U_2PdSi_3

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(Received 30 December 1996; revised manuscript received 24 November 1997)

Results of dc magnetization, magnetic relaxation, specific heat, and electrical resistivity measurements on a well-annealed polycrystalline U_2PdSi_3 sample are reported. The temperature dependence of the dc magnetization exhibits a cusp at a characteristic temperature T_f that strongly depends on the applied magnetic field. Below T_f, the magnetic relaxation measurements reveal a decay of the isothermal remanent magnetization vs time that is drastically slower than above T_f. No anomalies around T_f are observed in the specific heat and electrical resistivity data, which rules out the existence of usual long-range spatial magnetic order. These results can be considered as clear evidence for the formation of a spin-glass state in U_2PdSi_3 with a freezing temperature $T_f = 13.5$ K. The necessary randomness in the U-U magnetic exchange interactions arises from a statistical distribution of Pd and Si atoms on a crystallographic site of the U_2PdSi_3 crystal lattice. [S0163-1829(98)04914-5]

I. INTRODUCTION

Anomalous crystallographic and magnetic properties observed in the ternary uranium intermetallics U_2XSi_3 (X = transition metal element) have attracted much attention in recent years.[1–5] Most members of these compounds crystallize in a disordered derivative of the hexagonal AlB_2-type structure, where X and Si atoms are randomly distributed into the trigonal prisms of a primitive hexagonal array of uranium atoms.[1,4] Exceptions are U_2RuSi_3 and U_2OsSi_3, where Ru or Os and Si atoms appear to be ordered in a two-dimensional network.[5] Because the hybridization between $5f(U)$ and $d(X)$ electronic states is considered to strongly influence magnetic interactions of U_2XSi_3 compounds,[6] the random distribution of transition-metal elements and silicon can be expected to cause some anomalous magnetic properties. This has indeed been confirmed by first experimental results reported for U_2XSi_3 compounds: ac susceptibility data[4] suggest spin-glass behavior at low temperatures for the samples with X = Co, Ni, Cu, and Pd. U_2PtSi_3 with a remanent magnetization and enhanced specific heat has been classified as a spin glass[7] and as a weak itinerant ferromagnet.[3] However, to clarify the mechanism of magnetic interactions more complete systematic experimental data on U_2XSi_3 compounds are necessary. In this work, we present the results of dc magnetization, magnetic relaxation, specific heat, and electrical resistivity on a well-annealed polycrystalline U_2PdSi_3 sample.

II. EXPERIMENTAL DETAILS

A polycrystalline U_2PdSi_3 sample was synthesized by arc melting the pure elements (U: $3N$; Pd: $4N$; Si: $6N$) with stoichiometric starting composition in an argon atmosphere and was annealed at 800 °C for 72 h in high vacuum. The x-ray-diffraction pattern of the annealed U_2PdSi_3 sample can be completely indexed with the hexagonal AlB_2-type structure with room-temperature lattice constants $a = 4.083$ Å and $c = 3.932$ Å. The dc magnetization and magnetic relaxation were measured between 2 and 40 K in magnetic fields up to 1 T using a Quantum Design superconducting quantum interference device magnetometer. Specific-heat experiments were performed between 1.6 and 40 K in magnetic fields of 0 and 0.1 T by an adiabatic heat pulse method. Electrical resistivity measurements were performed between 0.5 and 300 K by the conventional four-terminal dc method.

III. RESULTS

The temperature variation of the zero-field-cooled (ZFC) magnetization M_{ZFC}, divided by the applied dc magnetic field H, of U_2PdSi_3 is displayed in Fig. 1. For small fields the M_{ZFC}/H curve exhibits a well defined peak at a temperature $T_f = 13.5$ K ($H = 0.005$ T). With increasing magnetic field, the peak loses intensity, broadens and the position shifts to lower temperatures ending up in a rounded maximum at about 5.2 K ($H = 1$ T). Figure 2 compares the temperature variation of the M_{ZFC}/H and M_{FC}/H curves for U_2PdSi_3 measured in the zero-field cooling mode and the field-cooling (FC) mode in an applied field $H = 0.01$ T. At temperatures above T_f typical paramagnetic behavior is observed with no difference between ZFC and FC magnetization. For a constant field H the M_{FC} curve is reversible and traces the same path independent on how the temperature is approached and independent of the time of the measurement.

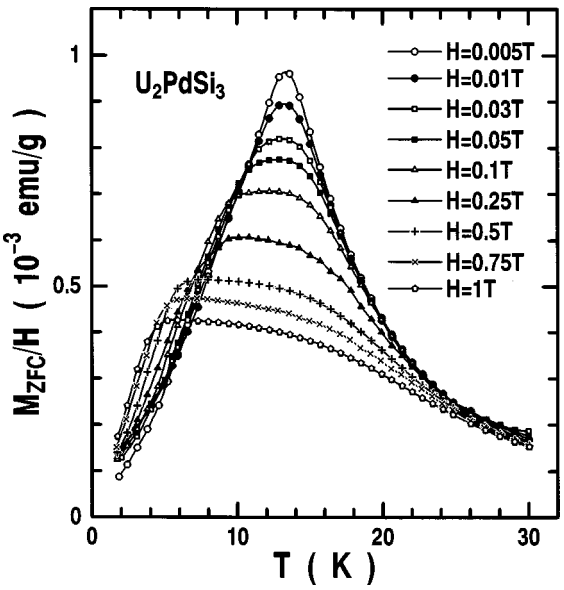

FIG. 1. The temperature dependence of M_{ZFC}/H of U_2PdSi_3 measured for various external dc magnetic fields.

In contrast, a characteristic cusplike maximum at T_f is observed for the M_{ZFC} curve, which below T_f is considerably smaller than the M_{FC} curve and time dependent. For the measurement of the isothermal remanent magnetization M_{IRM} as a function of time t the U_2PdSi_3 sample was first zero-field cooled from a temperature much higher than T_f. Then a magnetic field of 0.5 T was applied for 5 min and switched off (at $t=0$). At 14 K the magnetization M_{IRM} drops to zero within minutes, whereas for temperatures below T_f a nonzero remanent magnetization M_{IRM} could still be detected after 3 h (see Fig. 3). This indicates that applying a magnetic field below T_f creates the metastable and irreversible states in U_2PdSi_3. As shown by solid lines in Fig. 3 the observed time dependence of M_{IRM} could be nicely reproduced by a fit using the expression

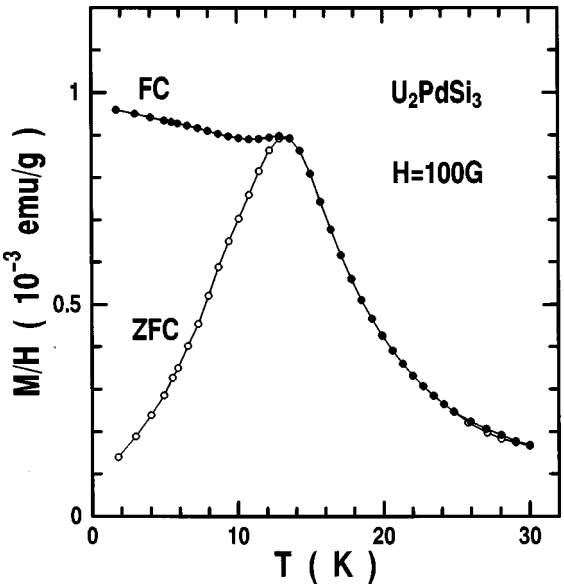

FIG. 2. Magnetic susceptibility data M/H vs temperature for U_2PdSi_3 measured in the zero-field cooling (ZFC) and in the field cooling (FC) mode in an applied external field $H=0.01$ T.

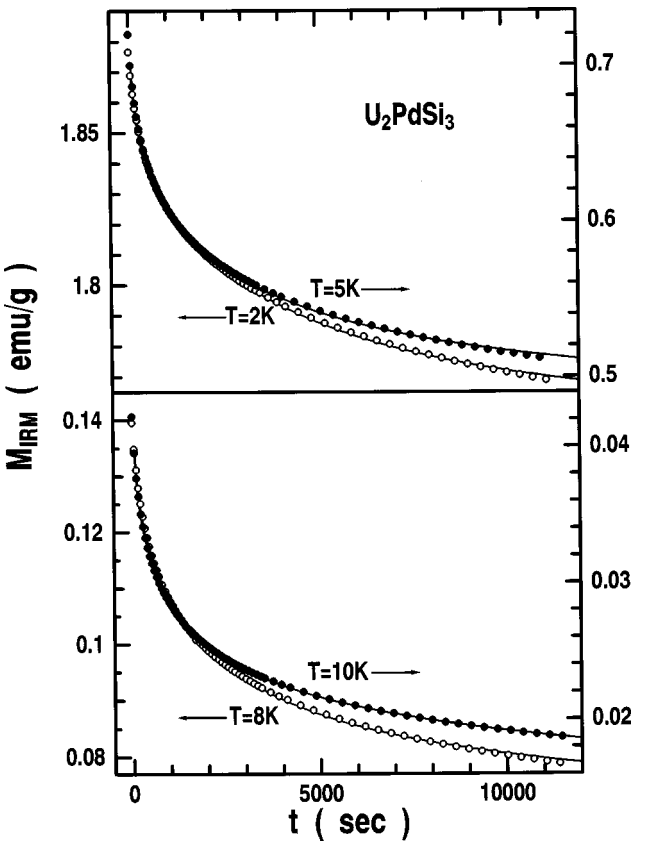

FIG. 3. Time dependence of the isothermal remanent magnetization $M_{IRM}(T,t)$ of U_2PdSi_3 measured at different temperatures below T_f. The solid lines represent ''least-squares'' fits using Eq. (1).

$$M_{IRM}(T,t)=M_0(T)+\alpha(T)\ln t+\beta(T)\exp[-t/\tau(T)], \tag{1}$$

with the values for the temperature-dependent fitting parameters $M_0(T)$, $\alpha(T)$, $\beta(T)$, and $\tau(T)$ given in Table I. Figure 4 displays the hysteresis loop of the magnetization of U_2PdSi_3 at 5 K with a remanent magnetization of about $0.04\,\mu_B$ per U atom. The specific heat $C(T)$ curves of U_2PdSi_3 measured in external magnetic fields $H=0$ and 0.1 T are almost identical (see Fig. 5). The measurements of the electrical resistivity $\rho(T)$ on several pieces cut from different sides of the large button of our U_2PdSi_3 sample yield $\rho(T)$ curves similar to the one shown in Fig. 6. For both, $C(T)$ and $\rho(T)$, no anomalies are observed at $T_f=13.5$ K.

IV. DISCUSSION

The experimental results on U_2PdSi_3 presented in Sec. III: (i) the well-defined peak at $T_f=13.5$ K in the low-field

TABLE I. Results of a fit of Eq. (1) to the isothermal remanent magnetization $M_{IRM}(t)$ of U_2PdSi_3.

T (K)	M_0 (emu/g)	α (emu/g)	β (emu/g)	τ ($\times 10^3$ s)
2	1.894	−0.014	−0.033	3.891
5	0.779	−0.028	−0.041	2.606
8	0.157	−0.008	−0.013	2.199
10	0.050	−0.003	−0.003	1.411

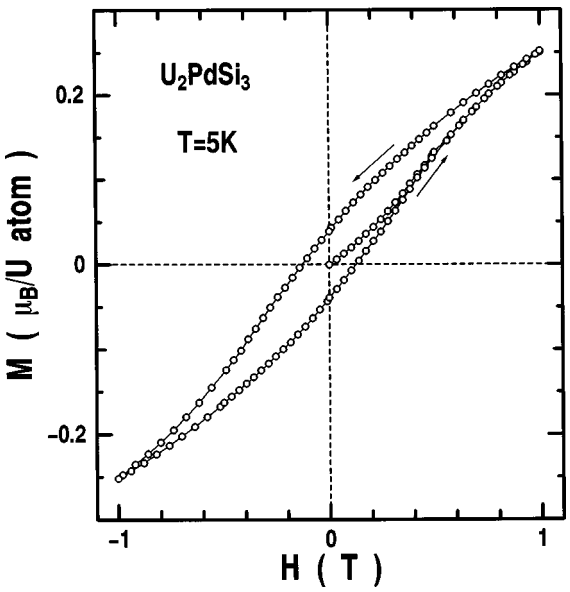

FIG. 4. Hysteresis loop of the magnetization of U_2PdSi_3 at 5 K.

susceptibility M_{ZFC}/H and its particular field dependence shown in Fig. 1; (ii) the difference between the temperature variation of M_{ZFC} and M_{FC} curves below T_f; (iii) the decay of the isothermal remanent magnetization $M_{IRM}(T,t)$ vs time, which is drastically slower below T_f than above T_f; (iv) the magnetization showing a hysteresis loop with a nonzero remanent magnetization below T_f can be considered as clear evidence for the formation of a spin-glass state in U_2PdSi_3 with a freezing temperature $T_f = 13.5$ K. Furthermore, the absence of anomalies around T_f in specific heat and electrical resistivity prove that usual long-range spatial magnetic order does not occur at T_f.

For AuFe with 8 at. % Fe,[8] a typical spin glass, the time dependence of the isothermal magnetic relaxation $M_{IRM}(T,t)$ was successfully reproduced by using only the first two terms of Eq. (1) with the two fitting parameters

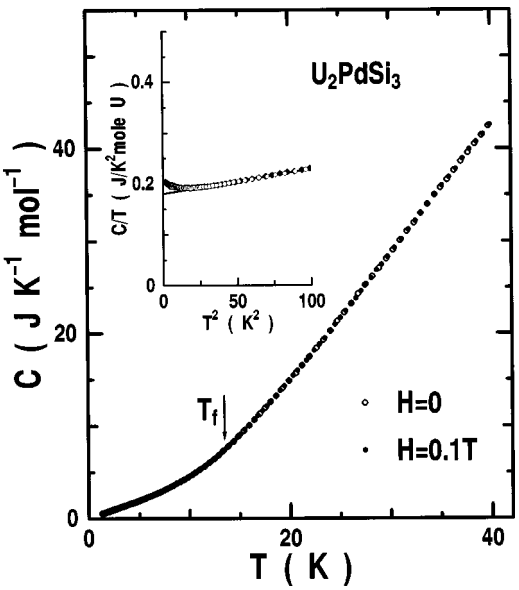

FIG. 5. Temperature dependence of specific heat $C(T)$ of U_2PdSi_3 in magnetic fields of 0 and 0.1 T. A C/T vs T^2 plot is shown in the inset.

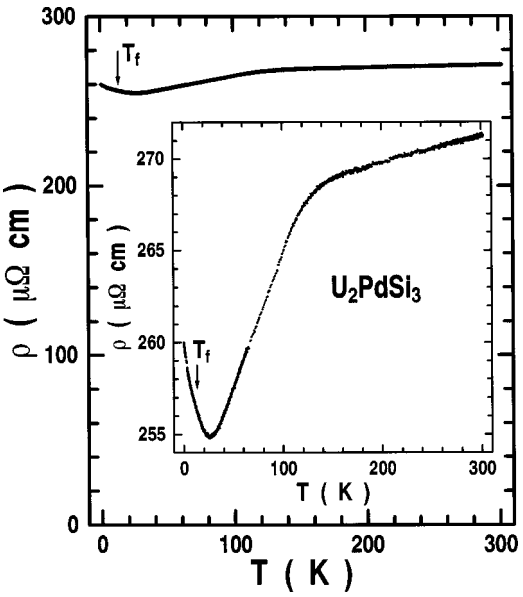

FIG. 6. Temperature dependence of electrical resistivity $\rho(T)$ of U_2PdSi_3 between 0.5 and 300 K. The inset displays the $\rho(T)$ data in an expanded scale.

$M_0(T)$ and $\alpha(T)$. The latter was called magnetic viscosity. A similar fit to our U_2PdSi_3 data can well describe the long-time behavior ($t > 400$ s) of M_{IRM} but is very poor for shorter time. Thus, for U_2PdSi_3, it was necessary to add the third term of Eq. (1), an exponential term, which for increasing time rapidly approaches zero. For example at $T = 10$ K and $t = 1000$ s the contribution from the second term turns out to be about 15 times larger than that of the third term. So far a lot of experimental data on the magnetic relaxation behavior of spin-glass systems are available and in literature various equations have been used to fit the data for the different samples.[9] Thus, not all spin-glass properties seem to be universal and the glasslike structure might vary in its details for the different systems. The remanent magnetization of the hysteresis loop of U_2PdSi_3 shown in Fig. 5 may originate from an anisotropy of the spin-glass state.[9,10]

The specific heat $C(T) = C_p + C_e + C_m$ of U_2PdSi_3 contains contributions from a phonon part C_p (proportional to T^3), from an electronic part C_e (linear in T) and from a magnetic part C_m (in the case of a spin glass: linear in T for $T < T_f$). The C/T vs T^2 plot shown in the inset of Fig. 5 yields for $T \to 0$ K a rather large value for the specific-heat coefficient of T-linear term, $\gamma = \gamma_e + \gamma_m = C/T \approx 180$ mJ (mole U)$^{-1}$ K^{-2}. Based on our experimental data it is impossible to accurately separate the electronic part (γ_e) and the magnetic part (γ_m). Recent systematic specific-heat experiments[11] revealed large γ values for all the compounds U_2XSi_3 (X = Fe,Co,Ni,Cu,Ru,Rh,Ir,Pt,Au), in particular $\gamma \approx 115$ mJ (mole U)$^{-1}$ K^{-2} for U_2RuSi_3 with paramagnetism down to 1.6 K and no spin-glass behavior. Thus we point out the possibility that future more detailed experiments might confirm that U_2PdSi_3 is a heavy fermion spin glass. A coexistence of heavy fermion behavior and spin-glass freezing has been reported for URh_2Ge_2 (Ref. 12) ($\gamma = 130$ mJ (mole U)$^{-1}$ K^{-2}) and for amorphous $(U_{0.25}Pt_{0.75})_{1-x}Si_x$ alloys[13] [γ values of 250–350 mJ (mole U)$^{-1}$ K^{-2}].

The electrical resistivity $\rho(T)$ of our U_2PdSi_3 sample is

large and as shown in Fig. 6 there is only a very weak temperature dependence resulting in a small residual resistivity ratio $\rho(T=300\ \mathrm{K})/\rho(T=0.5\ \mathrm{K}) \approx 1.04$. $\rho(T)$ is dominated by a temperature-independent contribution of the order of $\rho \approx 255\ \mu\Omega$ cm that can be attributed to scattering at structural disorder. Thus, for our U_2PdSi_3 sample the degree of disorder of Pd and Si atoms in the crystal lattice seems to be high and homogeneous [similar $\rho(T)$ curves for different pieces of our sample]. Such an interpretation is supported by a recent investigation[4] of the crystal structure of U_2PdSi_3 by x-ray and electron diffraction, which found that the U atoms are perfectly ordered on one site of the AlB_2-type structure, whereas Pd and Si atoms are statistically distributed on the other site. The temperature dependence of the electrical resistivity of U_2PdSi_3 shown in an expanded scale in the inset of Fig. 6 exhibits a decrease from 271 $\mu\Omega$ cm at 300 K to 255 $\mu\Omega$ cm at 26 K and at lower temperature a slight increase of $\rho(T)$ from 255 $\mu\Omega$ cm at 26 K to 260 $\mu\Omega$ cm at 0.5 K. A minimum of $\rho(T)$ like in U_2PdSi_3 at 26 K ($\approx 2T_f$) has not been observed down to 1.6 K (Ref. 11) in the isostructural spin-glass system U_2CoSi_3. For disordered systems different mechanisms determine the electrical behavior that cannot easily be separated. But obviously the temperature variation of $\rho(T)$ in U_2PdSi_3 at low temperatures is different from the T^2 dependence[14] or the $T^{3/2}$ dependence[15] observed for $T \ll T_f$ in diluted metallic spin glasses.

Because U_2PdSi_3 is neither a diluted nor an amorphous sample the mechanism of the formation of a spin-glass state is interesting. To get a spin glass one needs two ingredients:[9] (1) There must be a competition between ferromagnetic and antiferromagnetic interactions so that no single configuration of the spins is uniquely favored by all the interactions. This is commonly called frustration. (2) These interactions must be at least partially random. Thus, for U_2PdSi_3 the disorder of Pd and Si atoms in the crystal lattice seems to introduce the randomly frustrated U-U exchange interactions necessary for the occurrence of the spin-glass state. A similar mechanism exists in URh_2Ge_2,[12] where the spin-glass behavior was attributed to structural disorder of Rh and Ge atoms. The hexagonal compounds UNi_4B (Ref. 16) and CePdAl (Ref. 17) are examples, for which geometrical frustration leads to a coexistence of magnetically ordered and disordered spins. For UNi_4B the U moments in the easy basal plane have triangular symmetry with antiferromagnetic interactions. Below $T_N = 20$ K, only two out of every three U moments order in vortexlike arrangements around the third paramagnetic spin. In CePdAl magnetic Ce atoms on site $3f$ form a Kagomé-lattice like arrangement in the magnetically hard basal plane. Below $T_N = 2.7$ K, magnetically ordered moments at Ce(1) and Ce(3) coexist with frustrated disordered moments at Ce(2). The experimentally determined magnetic structure of CePdAl is in agreement with group theoretical symmetry analysis considerations, which confirm that for Ce(2) an ordered moment parallel to the magnetically easy c axis is forbidden by symmetry. On one hand, both systems, UNi_4B and CePdAl, exhibit no spin-glass behavior because of the absence of random magnetic interactions. On the other hand, long-range magnetic order may appear in randomly frustrated systems if the amount of randomness is small enough. Hence, randomness and frustration are necessary but may not be sufficient to obtain spin-glass behavior.

In conclusion, our results of dc magnetization, magnetic relaxation, specific heat, and electrical resistivity measurements on a well-annealed polycrystalline U_2PdSi_3 sample can be considered as clear evidence for the formation of a spin-glass state with a freezing temperature $T_f = 13.5$ K. The statistical distribution of Pd and Si atoms on one site of the U_2PdSi_3 crystal lattice seems to introduce the randomly frustrated U-U exchange interactions necessary for the occurrence of the spin-glass state. For a more detailed interpretation of the observed large γ value in the specific heat and of the electric resistivity curve, further theoretical and experimental work on U_2XSi_3 samples is necessary. Especially, it will be interesting to measure transport and magnetic properties of U_2PdSi_3 single crystals once they become available.

ACKNOWLEDGMENT

We would like to thank Professor A. V. Andreev for helpful discussions.

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