Mass enhancement and spin-glass behavior in Pr_2CuSi_3

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We report magnetic-susceptibility, specific-heat, and electrical resistivity measurements of Pr_2CuSi_3. This compound exhibits ferromagnetism at $T_c = 10$ K and upon further cooling shows spin-glass properties below about $T_f = 8$ K. The coefficient of the term linear in temperature in the specific heat γ of Pr_2CuSi_3 is 0.505 J mol^{-1}K^{-2} which is much larger than that of normal metals. This compound might be classified as a nonmagnetic atom-disorder spin glass. [S0163-1829(97)00642-5]

I. INTRODUCTION

Spin-glass magnetism could result in a possible enlargement of specific heat.[1,2] As an example, the γ value of $CePd_3B_{0.3}$ is 0.240 J mol^{-1}Ce K^{-2}; so Gschneidner *et al.*[3] suggested that the enhancement of γ is due to a presence of atomic site disorder. In $CePd_3B_{0.3}$ the B atoms randomly occupy the body-center site of this antiperovskite crystal, which introduces a varying electronic environment around Ce ions and thus causes a variation in the Ruderman-Kittel-Kasuya-Yosida mediated exchange interaction between the Ce ions. The interaction depends upon the boron occupation in the vicinity of Ce ions. It is this random Ce-Ce exchange interaction which gives rise to the spin-glass behavior and this accounts for the large observed γ value, where γ is the coefficient of the term linear in temperature in the specific heat. Gschneidner *et al.* called this phenomena nonmagnetic atom-disorder spin glasses (NMAD spin glasses).

The NMAD spin glasses U_2TSi_3 (T = Fe,Co,Ni,Ru,Rh, Pd,Os,Ir,Pt,Au) which crystallize in the hexagonal AlB_2-type structure, were reported by Kaczorowski and Noel.[4] The low-temperature spin-glass behavior in U_2TSi_3 results from the statistical distribution of T and Si atoms at crystallographically equivalent lattice site, and gives some randomness in U-U exchange interactions.

An additional AlB_2-type NMAD spin glass $CeCuSi_3$ was reported by Hwang, Lin, and Tien.[5] The electric specific heat indicated a γ of 0.076 J mol^{-1} K^{-2} Ce. The enhancement of γ could be due to the B site being occupied randomly by Si and Cu. If this argument is correct, we might also observe the spin-glass behaviors with the enhancement of γ in other RE_2CuSi_3 compounds. In this paper, we discuss the enhancement of γ in Pr_2CuSi_3 .

II. EXPERIMENTAL RESULTS

Polycrystalline samples of Pr_2CuSi_3 and La_2CuSi_3 were prepared by the arc melting of the pure elements in their stoichiometric ratio in an atmosphere of purified argon gas. The button was flipped over and remelted a number of times to achieve good homogeneity. The overall weight loss during the melting was less than 0.1%. X-ray measurements of the sample were carried out at room temperature and showed only a single phase. Figure 1 shows the x-ray-diffraction patterns of Pr_2CuSi_3 and La_2CuSi_3 . The structure is consistent with the hexagonal AlB_2 type. The lattice parameters are $a = 4.052$ Å, $c = 4.255$ Å for Pr_2CuSi_3, and $a = 4.084$ Å, $c = 4.395$ Å for La_2CuSi_3.

The magnetization studies were performed in a superconducting quantum-interference device (SQUID) magnetometer. The inset of Fig. 2 is the temperature dependence of the inverse of molar susceptibility $1/\chi$ for Pr_2CuSi_3 at 50 G. The magnetic susceptibility of La_2CuSi_3 is roughly three orders of magnitude smaller than that of Pr_2CuSi_3. As shown in the inset of Fig. 2, the susceptibility of Pr_2CuSi_3 follows Curie-Weiss law above 15 K. Below this temperature, a negative deviation appears. The effective moment deduced from the paramagnetic region is $3.54\mu_B$ which is in agreement with the theoretical value of Pr^{3+} free atom at $^3H_4$ state. Below 10 K, Pr_2CuSi_3 is ferromagnetic. Figure 2 is the susceptibilities

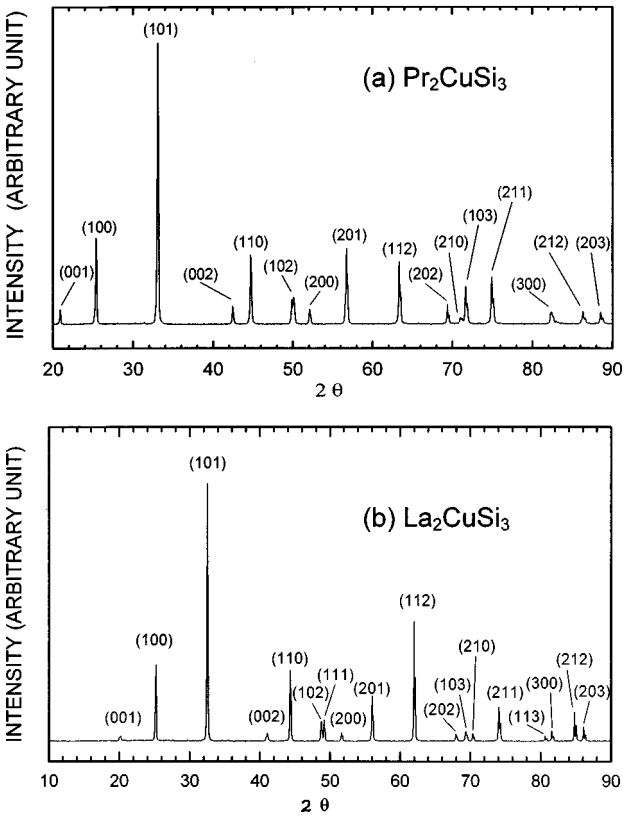

FIG. 1. The x-ray-diffraction patterns of Pr_2CuSi_3 and La_2CuSi_3.

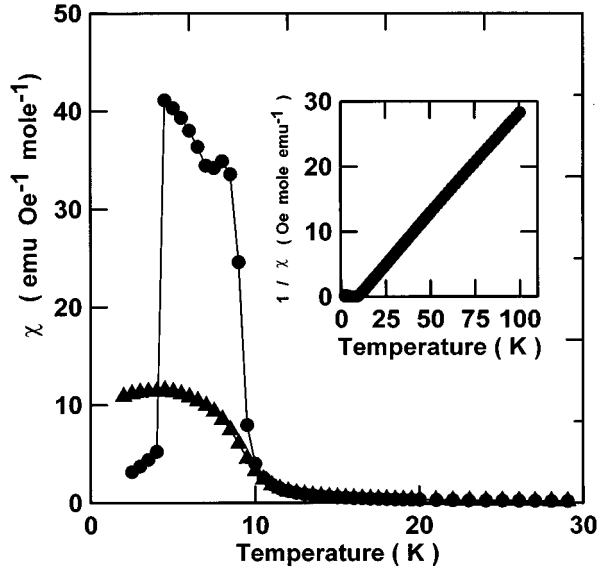

FIG. 2. The susceptibilities of Pr_2CuSi_3 between 2 and 30 K in 50 G (●) and 1000 G (▲). The inset is the temperature dependence of the inverse of molar susceptibility $1/\chi$ for Pr_2CuSi_3 at 50 G.

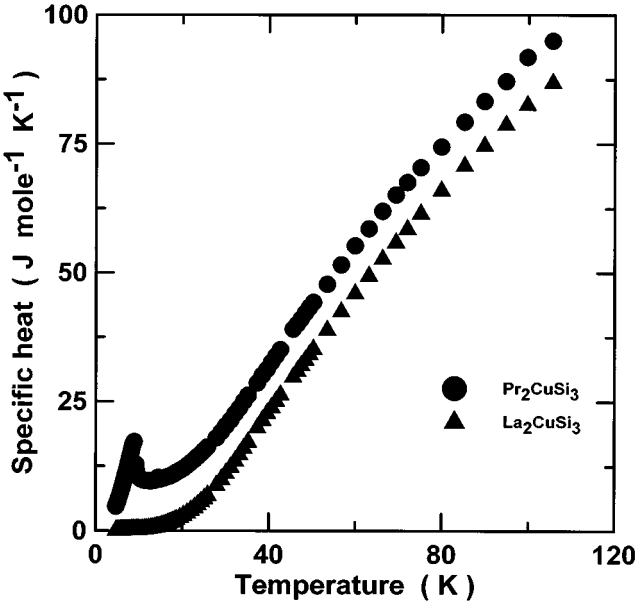

FIG. 4. The specific heat versus temperature $C(T)$ of Pr_2CuSi_3 and La_2CuSi_3.

of Pr_2CuSi_3 between 2 and 30 K in 50 and 1000 G. The method to measure the susceptibility is the zero-field-cooling (ZFC). We cooled the sample from 300 to 2 K in the zero field and applied the field at 2 K. Then we heated the sample while measuring the magnetization M within the constant field. In 50 G, there is a ferromagnetic transition at 10 K but the magnetization at 2 K is much smaller than that at 8 K. A small peak was observed at 8.5 K. A similar behavior was observed in U_2NiSi_3.[6] This 8.5 K peak will be smeared out in 1000 G. However, even in 1000 G, the magnetization at 2 K in a zero-field-cooling process is still smaller than that at 8 K. The field dependencies of the magnetization $M(H)$ of Pr_2CuSi_3 at 20, 10, 8, and 2 K are shown in Fig. 3. Below 10 K, the magnetization curves clearly deviate from a linear relationship between M and H. As shown in Fig. 3, there is no hysteresis or remanent magnetization at 20, 10, and 8 K. However, as shown in Fig. 3, the $M(H)$ at 6 and 2 K show remanent magnetization and hysteresis.

The specific-heat measurements were performed in an adiabatic calorimeter by a modified heat-pulse method.[7] Figure 4 gives the specific heat versus temperature $C(T)$ of Pr_2CuSi_3 and La_2CuSi_3. The peak of $C(T)$ indicates a phase transition in Pr_2CuSi_3 near 8 K. Below 40 K the $C(T)$ of La_2CuSi_3 can be described by $C(T)=\gamma_1 T+\beta_1 T^3$ with $\beta_1=0.344\times10^{-3}$ J mol^{-1} K^{-4} and $\gamma_1=5.61\times10^{-3}$ J mol^{-1} K^{-2}. Between 20 and 40 K, the $C(T)$ of Pr_2CuSi_3 can be fitted by $C(T)=\gamma_2 T+\beta_2 T^3$ with $\beta_2=0.184\times10^{-3}$ J mol^{-1} K^{-4} and $\gamma_2=0.509$ J mol^{-1} K^{-2}. The magnetic specific heat is defined here as $C_m(T)=C(Pr_2CuSi_3)$

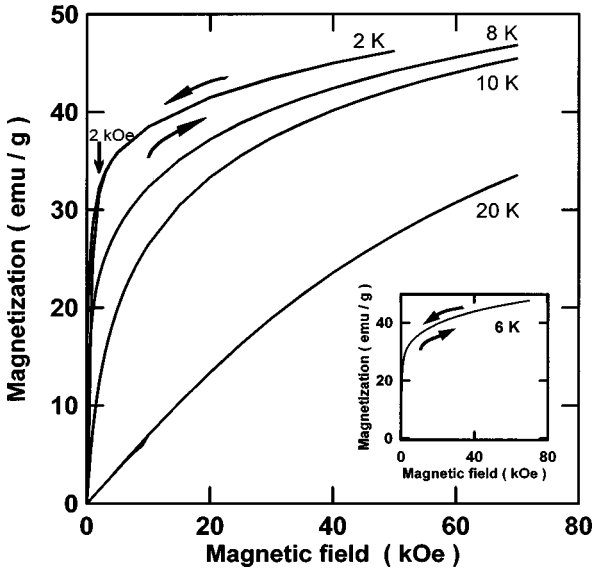

FIG. 3. The field dependence of the magnetization $M(H)$ of Pr_2CuSi_3, at 20, 10, 8, and 2 K. The inset is $M(H)$ at 6 K.

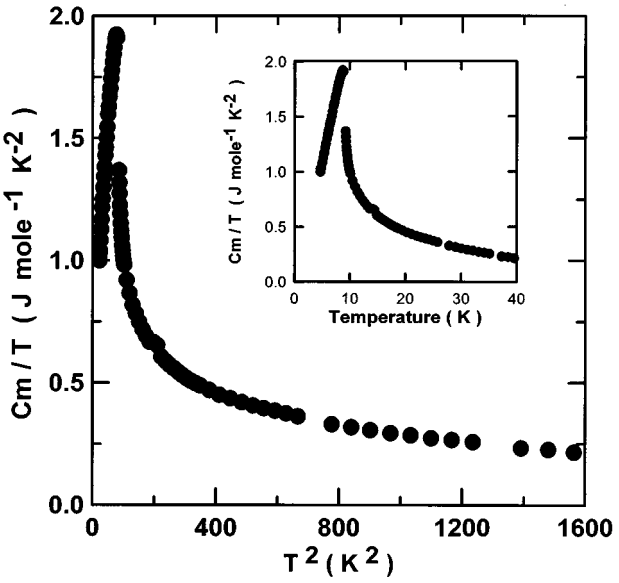

FIG. 5. The C_m/T versus T^2 of Pr_2CuSi_3 between 20 and 40 K. The inset is C_m/T versus T.

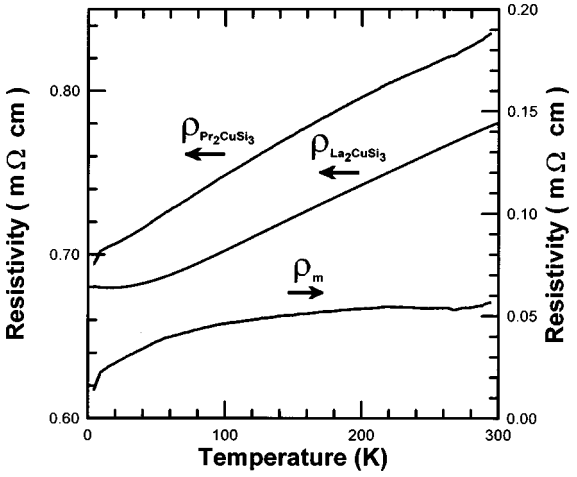

FIG. 6. The electrical resistivities of Pr_2CuSi_3 and La_2CuSi_3 versus temperature between 4.2 and 300 K. The magnetic resistivity $\rho_m(T)$ of Pr_2CuSi_3 is defined as $\rho_m(T)=\rho(Pr_2CuSi_3)-\rho(La_2CuSi_3)$.

$-C(La_2CuSi_3)$. The C_m/T versus T^2 is shown in Fig. 5. Between 20 and 40 K, $C_m(T)/T=\gamma+\beta T^2$ with $\beta=0.200\times 10^{-3}$ J mol^{-1} K^{-4} and $\gamma=0.505$ J mol^{-1} K^{-2}. It is seen that $\gamma\cong\gamma_1-\gamma_2$ and $\beta\cong\beta_1-\beta_2$. The temperatures of our specific-heat measurements are not low enough to determine the entropy accurately. The corresponding C_m/T versus T is shown in the inset of Fig. 7. A rough estimate of the magnetic entropy is 18.95 J K^{-1} mol^{-1} which is only about half of $2R$ ln 9.

The electrical resistivities of $\rho(T)$ of Pr_2CuSi_3 and La_2CuSi_3 between 4.2 and 300 K are shown in Fig. 6. The resistivity of Pr_2CuSi_3 decreases linearly with decreasing temperature down to 8 K. At 8 K the slope of $\rho(T)$ changes. The quick reduction of $\rho(T)$ which corresponds to the 8-K peak in specific-heat measurements also suggests a phase transition at 8 K.

III. DISCUSSION

The γ of Pr_2CuSi_3 is 0.505 J mol^{-1} K^{-2} which is much larger than those of normal metals. Praseodymium compounds usually do not form heavy-fermion materials. However, a strong Kondo Fermi-liquid state has been recently observed in $PrInAg_2$.[8]

The temperature dependence of resistivity of Pr_2CuSi_3 is similar to that of $PrInAg_2$. The resistivity may be considered a consequence of the following contribution:

$$\rho(T)=\rho_{\rm imp}+\rho_{\rm ph}(T)+\rho_m(T),$$

where $\rho_{\rm imp}$ is due to the scatter of impurities and lattice imperfections, $\rho_{\rm ph}(T)$ is the contribution due to the electron-phonon interaction, and any other scattering mechanism is contained in $\rho_m(T)$. Since, in the specific heats the lattice contributions of Pr_2CuSi_3 and La_2CuSi_3 are roughly identical, $\rho_{\rm ph}(T)$ of both compounds might be also the same. Therefore,

$$\rho_m(T)\cong\rho(Pr_2CuSi_3)-\rho(La_2CuSi_3).$$

Between 300 and 100 K, $\rho_m(T)$ slowly decreases with decreasing temperature. The fall of $\rho_m(T)$ at $\sim$50 K might indicate correlated electrons. Although the specific heat of Pr_2CuSi_3 exhibits heavy-fermion behavior, the resistivity is uncharacteristic. For example, there is no evidence of logarithmic increase of $\rho(T)$ with decreasing temperature and there is no indication of a coherence peak. However, we still cannot rule out this possibility.

As indicated in Fig. 4, there is no Schottky-type anomaly between 4.2 and 100 K. Although we could not exclude such a possibility at high temperature, the crystal field levels larger than 100 K will not contribute to the low-temperature heat capacity. Therefore, except for the heavy-fermion mechanism, the possible mechanisms that will enhance the γ value are (1) low-lying crystal levels or magnetic ordering at very low temperature, or (2) the nonmagnetic-atom-disorder-spin-glass (NMAD-spin-glass) behavior suggested by Gschneidner *et al.*[3]

The lattice parameters of Pr_2CuSi_3 are nearly the same as those of the corresponding hexagonal $PrSi_2$. According to the argument of Chevalier *et al.*,[6] in the AlB_2 type of Pr_2CuSi_3 , Pr is in the Al-site; Si and Cu occupy the B-site randomly. Pr^{3+} ions are located on the layers separated by sheets composed of Si and Cu atoms. The randomness of Si and Cu introduces a varying electron environment around the Pr ions. It is these random Pr-Pr exchange interactions that give rise to the spin-glass behavior, and this accounts for the large observed γ value.

Therefore, as indicated in Fig. 2, the drop in of $\chi(T)$ at low temperature can be interpreted as follows: When Pr_2CuSi_3 is cooled from 300 to 2 K in zero field, it will form a spin-glass ordering; therefore, below a characterized temperature T_f, $\chi(T)\sim 0$. The steep increase in susceptibility at 4.2 K is an anomaly due to the magnetometer.

Studying the spin glass by SQUID technique was discussed by Mydosh.[9] First, we cooled the Pr_2CuSi_3 sample in the zero field to 4.5 K and applied a 5-G magnetic field at 4.5 K. Then we heated the sample while measuring the susceptibility $\chi(T)$ to 20 K (ZFC). Second, we cooled the sample back down from 20 to 4.5 K in a 5-G field while recording $\chi(T)$ (FC). After a ZFC and a FC processes $\chi(T)$ was measured by cycling the temperature back and forth in a 5-G field. Figure 7 illustrates the temperature dependence of $\chi(T)$ for Pr_2CuSi_3 in a 5-G field in the different cooling process (FC versus ZFC). If T_g is defined by the onset of difference between FC and ZFC, $T_g\cong 9$ K. As indicated in Fig. 7, the FC susceptibility traces the same path in cooling and warming processes. When the magnetic field increases, the spin-glass state will depress. The T_g is $\sim$4 K in a 1000 G. In a spin-glass state, it takes many decades to turn the magnetic moments toward the field direction. Even after 4 h, the magnetic moment of Pr_2CuSi_3 is still not saturated.

The hysteresis of $M(H)$ at 2 K (Fig. 3) might be also due to the time dependence of $M(H)$ in a spin-glass state. If this

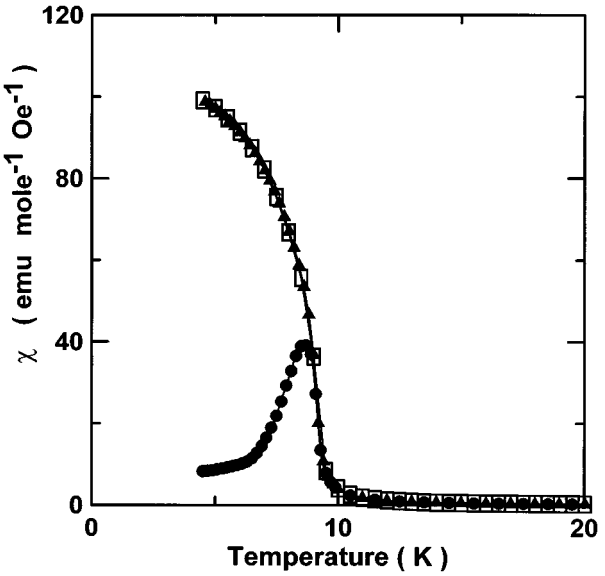

FIG. 7. The temperature dependence of $\chi(T)$ for Pr_2CuSi_3 at a 5-G field, the sample was cooled in the zero field and applied the field at 4.5 K. We heated the sample while measuring the magnetization M from 4.5 to 300 K (●), and then cooled the sample from 300 to 4.5 K (□), and finally heated the sample again from 4.5 to 300 K (▲) within the constant field.

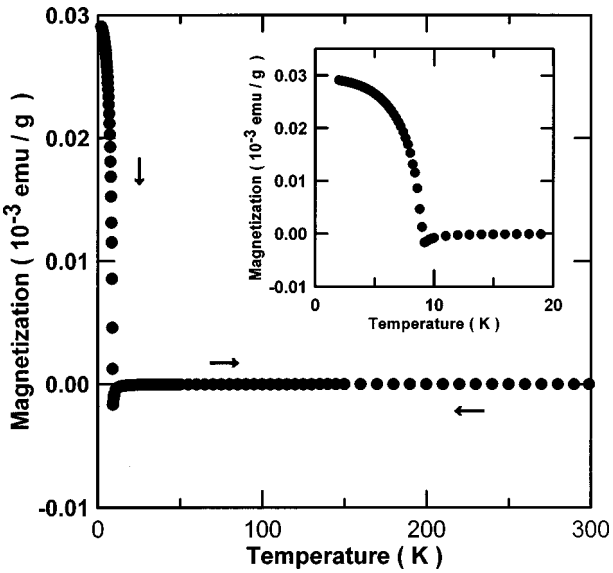

FIG. 8. The temperature dependence of magnetization $M(T)$ in a zero magnetic field. The inset is $M(T)$ between 2 and 20 K.

argument is correct, the spin-glass behavior of Pr_2CuSi_3 will be apparent even if the field is above 2 KOe.

Two uranium compounds U_2NiSi_3 and U_2CoSi_3 that have the hexagonal AlB_2 structure also display ferromagnetic and spin-glass-like behaviors. Kaczorowski and Noel[4] reported that U_2CoSi_3 first exhibited a ferromagnetism at $T_c=10$ K and then showed spin-glass-like properties below about $T_f=8$ K. The T_C and the T_f of U_2CoSi_3 are 25, 22 K, respectively. Although the structure of U_2CuSi_3 is the tetragonal α-$ThSi_2$, this compound will also have ferromagnetic and spin-glass properties with $T_C=30$ K and $T_f=26$ K. This kind of compound is called reentrant spin glass or ferroglass.[10,11] However, there is no persuasive theorem to explain why magnetic moments will lose the arrangement and transfer from a ferromagnetic ordering to a spin-glass-like state. In a low magnetic field (5 G), the T_C and the T_f of Pr_2CuSi_3 are 10, 8 K, respectively. However, without magnetic field, there is no spontaneous magnetic ordering in Pr_2CuSi_3. Therefore, in the zero magnetic field, Pr_2CuSi_3 is a simple spin glass instead of a reentrant spin glass. An alternative to a loss of ferromagnetism at the spin-glass transition is the freezing of ferromagnetic domains. The very low-field susceptibility measurement might clarify this argument.

In Pr_2CuSi_3, Pr^{3+} ions are located on layers separated by sheets of Si and Cu atoms. The possible mechanism of the spin glass in Pr_2CuSi_3 is that at 8 K, the magnetic moments of Pr^{3+} ions on a same layer form a ferromagnetic order, but there is no magnetic correlation between two different Pr^{3+} layers. Below 8 K, different Pr^{3+} layers correlate antiferromagnetically. After a magnetic field is applied, the competition between Pr-Pr interaction and Pr-field interaction accounts for the reentrant-spin-glass property in Pr_2CuSi_3.

Although there is no magnetic correlation between two different Pr^{3+} layers, the magnetic moments of all layers will be not canceled entirely. We may still observe a ferromagnetic phase. Below 8 K, different Pr^{3+} layers correlate antiferromagnetically. Therefore, if this argument is correct, we should observe a very small spontaneous ferromagnetic ordering and an antiferromagnetic ordering in a zero magnetic field. The mass of the sample for spontaneous ferromagnetic ordering is 0.084 57 g; therefore, there are $N=2.37\times10^{20}$ Pr^{3+} ions in the sample. The effective moment of each Pr^{3+} ion is $\mu_{\text{eff}}=3.54\mu_B$, such that $N\mu_{\text{eff}}=7.78$ emu and magnetization $M(0)=92.0$ emu/g. Figure 8 is the temperature dependence of magnetization $M(T)$ in a zero magnetic field. As shown in Fig. 8, there is a very small [$M(2\text{ K})=0.03$ emu/g] spontaneous ferromagnetic ordering at ~9 K. Below 7 K, the tendency of increase of $M(T)$ is significantly reduced, which is consistent with an antiferromagnetic ordering among Pr^{3+} layers. Further experiments, for example, neutron scattering, are needed to characterize the unusual properties of Pr_2CuSi_3.

IV. CONCLUSIONS

The structure of Pr_2CuSi_3 is consistent with the hexagonal AlB_2 type. Pr_2CuSi_3 is ferromagnetic with a Curie temperature of 10 K. At low temperature, Pr_2CuSi_3 exhibits clear spin-glass behaviors. In a magnetic field above 2 KOe, the spin-glass behavior still exists.

The $C(T)$ of Pr_2CuSi_3 can be fitted by $C(T)=\gamma_2 T+\beta_2 T^3$, with $\beta_2=1.84\times10^{-4}$ J mol^{-1} K^{-4} and $\gamma_2=0.509$ J mol^{-1} K^{-2}. The γ_2 of Pr_2CuSi_3 is much larger than those of normal metals. The magnetic entropy is about 19 J K^{-1}mol^{-1} which is only about half of $2R$ ln 9. The magnetic entropy much less than $2R$ ln 9 will further support the reality of spin-glass state. This compound might be classified as a nonmagnetic atom-disorder spin glass.

ACKNOWLEDGMENT

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