Antiferromagnetism in the Kondo lattice compound $Ce_2Pd_3Si_5$

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The antiferromagnetic ordering state of the Kondo lattice compound $Ce_2Pd_3Si_5$ is ascertained by measuring the magnetic susceptibility χ, electrical resistivity ρ, thermoelectric power S, and specific heat C. The system undergoes an antiferromagnetic transition through two steps at $T_{N1}=8.0$ K and $T_{N2}=7.4$ K. The ordering occurred at T_{N1} might be incommensurate with the lattice, and followed by a change of magnetic structure from incommensurate to commensurate with the lattice at T_{N2}. The magnetic entropy reaches $0.8R\ln 2$ at 8.0 K. Thermoelectric power shows two positive peaks, one around 150 K and the other at 1.3 K, and a negative peak at 12 K. The crystal electric-field splitting levels are estimated to be $\Delta_1=90\pm10$ K and $\Delta_2=470\pm50$ K above the ground state, respectively.

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I. INTRODUCTION

The competition between Ruderman-Kittel-Kasuya-Yosida and Kondo interactions in CeT_2X_2 (T presents transition metals, and $X=$ Si, Ge) has been extensively studied because these systems show many interesting physical properties.[1] For example, $CeCu_2Si_2$ is a nonmagnetic heavy-fermion system showing superconductivity at low temperatures under ambient pressure. $CePd_2Si_2$, $CeCu_2Ge_2$, and many other systems order antiferromagnetically at low temperatures. $CeNi_2Si_2$ shows a valence fluctuation behavior. Recently, the variety of magnetic properties in the structurally related phase $Ce_2T_3X_5$ has attracted much attention. For example, antiferromagnetic transitions in $Ce_2T_3Ge_5$ ($T=$Rh, Ir and Ni) were reported.[2,3] $Ce_2Ni_3Si_5$ is known as a valence fluctuation compound.[4] In this family, $Ce_2Pd_3Si_5$ crystallizes in an orthorhombic $U_2Co_3Si_5$ type structure (space group $Ibam$), which adopts an orthorhombic superstructure of $ThCr_2Si_2$ type.[5] There are two short contradictory reports on its magnetic properties in the literature. Kitagawa *et al.*[6] observed an antiferromagnetic transition at 8.4 K. However, Godart *et al.*[7] did not find a magnetic transition down to 4.2 K. Furthermore, pressure-induced superconductivity was observed in the structurally related compound $CePd_2Si_2$.[8,9] For our interest in searching for a heavy fermion superconductor, it is worthwhile to investigate the magnetic properties on $Ce_2Pd_3Si_5$ in detail and to study the pressure effect on it. In this paper, we report the measurement results of electrical, magnetic, and thermal properties on $Ce_2Pd_3Si_5$ over a wide temperature range to investigate the magnetic nature of $4f$ electrons in this Kondo lattice compound.

II. EXPERIMENT

Polycrystalline samples of $Ce_2Pd_3Si_5$ and $La_2Pd_3Si_5$ were synthesized by arc melting the stoichiometric constitution elements in an argon atmosphere. The as-cast ingots were annealed for one week at 900 °C. Magnetic measurements were carried out by use of a commercial superconducting quantum interference device magnetometer (Quantum Design Co., Ltd.). The electrical resistivity ρ was measured using the conventional dc four-probe method. Thermoelectric power S was measured from 2 to 300 K with a slowly varying gradient technique by using the thermal couples of Chromel/Au+0.07 at. % Fe. The measurement of S from 2 to 0.2 K was carried out with a steady-state heat-flow technique by employing a $^3He-^4He$ dilute refrigerator. The specific heat C was measured with a quasiadiabatic method in temperature range from 0.4 to 100 K.

III. RESULTS AND DISCUSSION

It was confirmed by x-ray diffraction that both $Ce_2Pd_3Si_5$ and $La_2Pd_3Si_5$ are single-phase samples, crystallizing in an orthorhombic $U_2Co_3Si_5$-type structure. The experimental and calculated x-ray-diffraction patterns for $Ce_2Pd_3Si_5$ are shown in Fig. 1. The lattice parameters are $a=9.949$ Å, $b=11.816$ Å, and $c=5.970$ Å for $Ce_2Pd_3Si_5$, and $a=9.990$ Å, $b=11.901$ Å and $c=6.006$ Å for $La_2Pd_3Si_5$. They are in agreement with the earlier reported values.[6]

The temperature dependence of inverse magnetic susceptibility $1/\chi$ of $Ce_2Pd_3Si_5$ is shown in Fig. 2. Above 70 K, the magnetic susceptibility can be described fairly well by a Curie-Weiss law $\chi=N_A\mu_{\mathrm{eff}}^2/3k_B(T-\Theta_p)$, giving an effective

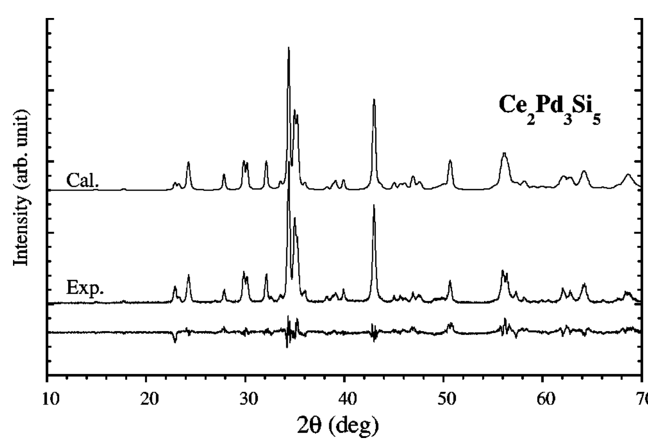

FIG. 1. The x-ray-diffraction patterns of $Ce_2Pd_3Si_5$. Top: calculated pattern. Middle: experimental pattern. Bottom: the difference between them.

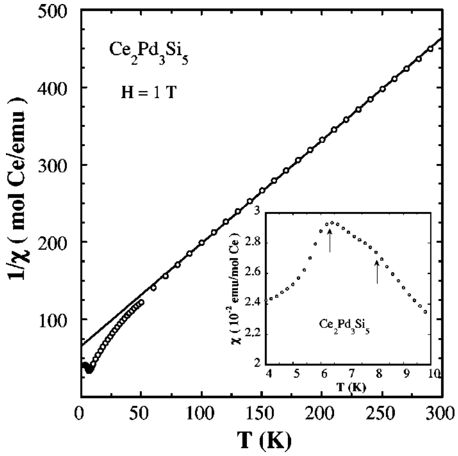

FIG. 2. Inverse magnetic susceptibility $1/\chi$ of $Ce_2Pd_3Si_5$. The solid line shows a Curie-Weiss law fitting result. The inset shows the magnetic susceptibility at low temperatures.

magnetic moment $\mu_{\mathrm{eff}}=2.44\mu_B$ and a paramagnetic Curie temperature $\Theta_p=-49$ K. The effective magnetic moment is close to the value of a free Ce^{3+} ion $(2.54\mu_B)$. The deviation from the Curie-Weiss law below 70 K could be due to the crystal electric-field (CEF) effect. The $\chi(T)$ data at low temperatures are shown in the inset of Fig. 2. A shoulder at 8 K and a peak at 6.5 K suggest that the antiferromagnetic transition occur in two steps. The former is close to the reported Néel temperature 8.4 K.[6] The latter, not observed in Ref. 6, was confirmed in our specific-heat measurement (to be discussed below).

The temperature dependence of electrical resistivity of $La_2Pd_3Si_5$ and $Ce_2Pd_3Si_5$ is shown in Fig. 3(a). ρ of $La_2Pd_3Si_5$ shows the behavior of a normal metal. On the other hand, ρ of $Ce_2Pd_3Si_5$ decreases with decreasing temperature, showing a minimum around 15 K. In the temperature range from 8 to 15 K, ρ increases due to the Kondo effect. The onset of the antiferromagnetic order gives rise to an abrupt drop of ρ below 8 K. The temperature dependence of the resistivity is very similar to that of Ref. 6.

The magnetic contribution to the resistivity ρ_{mag}, obtained by subtracting the lattice contribution, taken as that of $La_2Pd_3Si_5$, is plotted in Fig. 3(b) as a function of $\ln T$. There are two distinct $-\ln T$ dependent portions separated by a maximum around 70 K, which are often observed in antiferromagnetic Kondo systems with the presence of a CEF effect. A theoretical model was introduced by Cornut and Coqblin to explain this behavior.[10] According to this model, the ratio of the slopes of the $-\ln T$ dependent ranges at low and high temperatures should be 3/35 for a doublet ground state. As expected in the case for an orthorhombic structure, the ratio deduced from Fig. 3(b) is 3/33, being very close to 3/35. The temperature of the maximum of ρ_{mag} is related to the CEF splitting.[10]

The thermoelectric power of $La_2Pd_3Si_5$ and $Ce_2Pd_3Si_5$ is shown in Fig. 4 as a function of temperature. Like normal metals, S of $La_2Pd_3Si_5$ is small and approximately linear with temperature. The upturn at 20 K is likely due to the so-called phonon drag, which usually appears between

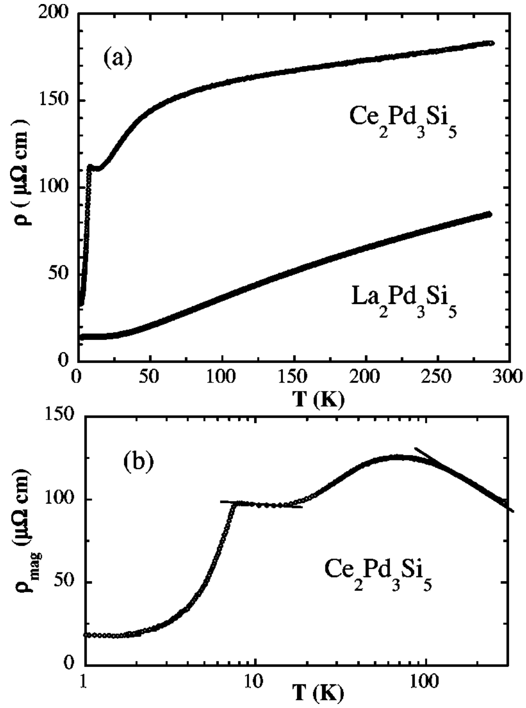

FIG. 3. (a) Electrical resistivity ρ of $Ce_2Pd_3Si_5$ and $La_2Pd_3Si_5$. (b) Temperature dependence of the magnetic contribution to the resistivity $\rho_{\mathrm{mag}}=\rho_{Ce_2Pd_3Si_5}-\rho_{La_2Pd_3Si_5}$.

$0.1\Theta_D$ and $0.3\Theta_D$ (Θ_D is the Debye temperature).[11] On the other hand, S of $Ce_2Pd_3Si_5$ shows a broad positive peak at 150 K and a deep negative peak centering at 12 K. Our result above 80 K is in agreement with an early reported one.[12] However, the negative peak was not observed due to the limited temperature range of their measurement. The positive peak is generally attributed to the interplay of the CEF effect and the Kondo effect,[13] corresponding to the maximum of ρ_{mag} mentioned above. The origin of the negative peak is explained as an indication of the existence of magnetic correlations.[14,15] Many experiments support this viewpoint.

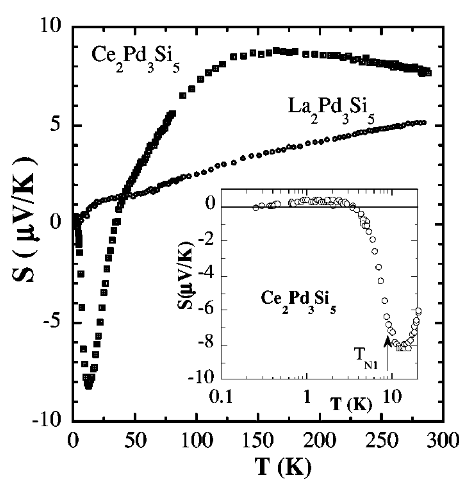

FIG. 4. Thermoelectric power S of $Ce_2Pd_3Si_5$ and $La_2Pd_3Si_5$. The inset shows S of $Ce_2Pd_3Si_5$ at low temperatures on a logarithmic scale.

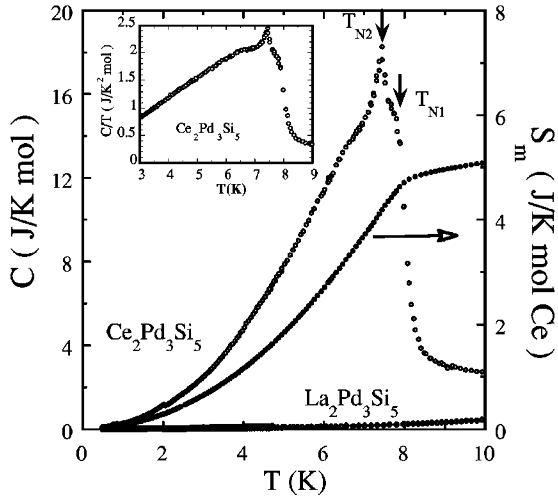

FIG. 5. Specific heat of $Ce_2Pd_3Si_5$ and $La_2Pd_3Si_5$. The magnetic entropy S_m is also shown (right axis). Inset: C/T vs T plot for $Ce_2Pd_3Si_5$ $(3\ \mathrm{K} \leqslant T \leqslant 9\ \mathrm{K})$.

For example, the negative peak could be weakened gradually and suppressed finally by pressure as in $CePd_2Si_2$ (Ref. 16) and $CeCu_2Si_2$,[17] or by chemical substitution as in $Ce(Pd_{1-x}Ni_x)_2Si_2$ (Ref. 18), and $CePd_{1-x}Ni_xAl$.[19]

The low-temperature thermoelectric power of $Ce_2Pd_3Si_5$ is shown in the inset of Fig. 4 on a logarithmic scale. It is noticeable that S changes sign again at 3.7 K, and shows another positive peak centering at 1.3 K. The positive peak of S below T_N is also observed in other antiferromagnetic Kondo systems; CePdSn (Ref. 20) and CePdGe.[21] It could be explained as experimental evidence of the existence of the Kondo effect in magnetically ordered states. The moderately enhanced electronic specific-heat coefficient $\gamma = 87$ mJ/mol Ce K^2 (see Fig. 6) supports this idea.

As discussed above, the antiferromagnetic nature of $4f$ electrons in $Ce_2Pd_3Si_5$ is confirmed from our measurements of χ, ρ, and S. However, the low-temperature data of χ suggest that the system undergo the antiferromagnetic transition in two steps. In order to gain insights into this issue further, specific-heat measurements were carried from 100 down to 0.4 K. The low-temperature result of C is shown in Fig. 5 with that of the nonmagnetic isostructural compound $La_2Pd_3Si_5$. The inset gives a C/T vs T plot for $3 \leqslant T \leqslant 9$ K.

The specific heat of $La_2Pd_3Si_5$ below 6 K can be described by $C = \gamma T + \beta T^3$, with $\gamma = 7.8$ mJ/mol K^2 and $\beta = 0.38$ mJ/mol K^4. The Debye temperature Θ_D was estimated to be 172 K.

As expected, the sharp peak at $T_{N2} = 7.4$ K and the shoulder at $T_{N1} = 8.0$ K correspond to the two anomalies in $\chi(T)$. We observed a shoulder at 8.0 K, which corresponds to the onset of an antiferromagnetic transition, because the two anomalies are very close to each other. The measurement below 15 K was carried out independently three times in order to confirm the fine structure. Double magnetic transitions were observed in other $R_2T_3X_5$ systems,[3,22,23] and very recently in $Tb_2Rh_3Si_5$.[24] The antiferromagnetic ordering that occurred at higher temperature could be incommensurate with the lattice, then the transition was followed by a change of magnetic structure from incommensurate to commensurate with the lattice at lower temperature. Neutron-scattering experiments on $Ce_2Pd_3Si_5$ are needed to understand the nature of the double transitions. The discrepancy in T_{N2} observed in $C(T)$ and $\chi(T)$ is due to the external magnetic field applied in the measurement for $\chi(T)$. The tendency of T_N's to decrease with the magnetic field was proven by measuring the low temperature $\chi(T)$ in several magnetic fields. The anomaly for T_{N2} could not observed in a field stronger than 3 T. T_{N1} decreased to about 7 K under a magnetic field of 7 T. An exact B-T phase diagram could not be drawn because of the broadness of the $\chi(T)$ peak. The measurement of the specific heat in a magnetic field could be useful for drawing a phase diagram.

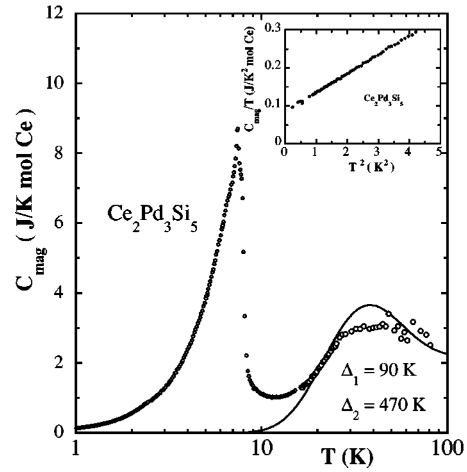

FIG. 6. Magnetic contribution to the specific heat C_mag of $Ce_2Pd_3Si_5$. The solid line shows the calculated Schottky contribution to the specific heat. Inset: C_mag/T vs T^2 plot.

The magnetic entropy S_m, calculated from the experimental data, is also given in Fig. 5. The entropy gain reaches $0.8 \ln 2$ at T_{N1}. The 20% loss of entropy could be due to the Kondo effect and/or to the short-range magnetic order.

The magnetic contribution to the specific heat was obtained by defining $C_\mathrm{mag}(T) = C(T)_{Ce_2Pd_3Si_5} - C(T)_{La_2Pd_3Si_5}$. Figure 6 shows the temperature dependence of C_mag below 100 K on a logarithmic scale. In addition to the peak due to the magnetic transition, a Schottky anomaly was observed. By fitting the data as the Schottky contribution to the CEF excitation, the two CEF splitting energies above the ground state were estimated: $\Delta_1 = 90 \pm 10$ K and $\Delta_2 = 470 \pm 50$ K, respectively. The solid line shows the calculated result. The inset of Fig. 6 shows the C_mag/T vs T^2 for $T < 2.5$ K. By extrapolating the data from 2.3 to 0.4 K, the $\gamma(0)$ value of $Ce_2Pd_3Si_5$ is estimated to be 87 mJ/mol Ce K^2, which is comparable to the reported value.[6] The enhanced γ value suggests the coexistence of the Kondo effect and magnetic ordering. This is consistent with the result of thermoelectric power at low temperatures.

As shown above, crystal electric fields influence the magnetic susceptibility, electrical resistivity, thermoelectric power, and specific heat. In order to see the consistence between the estimated CEF scheme from the measurement of $C(T)$ and other measurements, the susceptibility is calcu-

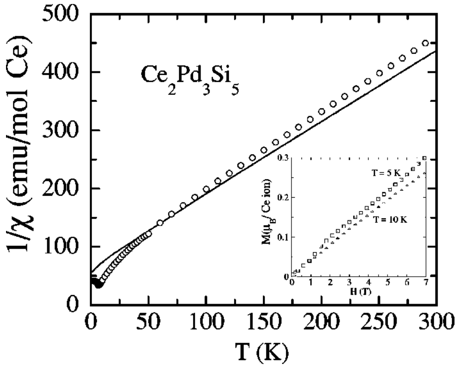

FIG. 7. Inverse magnetic susceptibility $1/\chi$ of $Ce_2Pd_3Si_5$. The solid line shows a calculated curve (see the text). The inset shows the magnetization vs field at 5 and 10 K.

lated by using a CEF model with exchange interaction between Ce ions,

$$\frac{1}{\chi}=\frac{1}{\chi_{\mathrm{CEF}}}+\lambda, \tag{3.1}$$

where χ_{CEF} is the susceptibility without exchange interaction, λ is the molecular field parameter, and χ is the susceptibility with exchange interaction. By using the set of parameters[25] $B_2^0=-880$ K, $B_2^2=100$ K, $B_4^0=286$ K, $B_4^2=40$ K, $B_4^4=490$ K, and $\lambda=55$ mol/emu, which reproduces the splitting energies $\Delta_1=90$ K and $\Delta_2=470$ K, we obtain the curve shown in Fig. 7 and a reduced magnetic moment of the ground state $\mu_z=0.2\mu_B$. Although the calculated curve is not quantitatively in agreement with the experiment, a deviation from Curie-Weiss law below 50 K is clearly seen. In the inset of Fig. 7, the field dependence of the magnetization is shown. The reduced magnetic moment due to the CEF effect and the Kondo effect is $0.3\mu_B$ at 7 T. It is less larger than the calculated one. An anomaly around 1.5 T on the curve for 5 K suggests a change in the magnetic structure. There are mainly two possible reasons for the disagreement between the experiments and the calculation. First, the calculation is for an ideal polycrystalline sample with isotropic molecular field parameters. In the case of low symmetry, usually there is a strong anisotropic effect.[26] Second, the fitting of the susceptibility and specific heat gives only approximate values of the splitting energies. For a quantitative analysis, one needs inelastic neutron-scattering data, and the magnetic measurements for single-crystal sample.

If we take the temperature of the maximum of ρ_{mag} at 70 K as T_K^h, the Kondo temperature for the ground state T_K^l is estimated to be 8 K by using the relation $T_K^h=(\Delta_1\Delta_2\ T_K^l)^{1/3}$ (Ref. 27). The Kondo temperature is likely close to its Néel temperature. Then $Ce_2Pd_3Si_5$ could be another good candidate to investigate pressure effects on the systems located around the quantum critical point, such as $CePd_2Si_2$.[8,9] According to the theoretical model of Bhattacharjee and Coqblin,[13] a broad peak of S due to the interplay of CEF and Kondo effects should occur at a temperature corresponding to $\Delta/6$–$\Delta/3$ (Δ is the overall CEF splitting). Clearly, this works for the present system. The influence of the CEF effect on physical properties is likely consistent in our measurements.

Another interesting feature of our results is a hump in $C(T)$ around 6.3 K, which is more visible in the C/T vs T plot in the inset of Fig. 5. Although a hump of specific heat below T_N is often observed in Gd-based compounds,[22,23] it is unusual in Ce-based compounds. Blanco *et al.*[28] showed that C_{mag} of an amplitude-modulated moment Gd-based system below T_N shows a hump with a decrease in the peak height at T_N. According to them, the magnitudes of the jump in C_{mag} at T_N for a Ce-based compound should be 13.11 and 19.66 J/mol K for the amplitude-modulated moment system and for the equal-moment system, respectively. The peak height of C_{mag} for $Ce_2Pd_3Si_5$ is 18.3 J/mol K, which is close to that of the equal-moment system. Therefore, although they explained the specific-heat results of some Gd compounds successfully, this mechanism is not likely applicable to the present system. Another theoretical model was proposed by Fishman and Liu[29] to explain the origin of the hump in C below T_N. According to this model, the hump could originate from quantum fluctuations. The hump takes place at a temperature $T^*=3T_N/(J+1)$ (where J is the total spin quantum number). In the case of $Ce_2Pd_3Si_5$ ($J=5/2$), $T^*=6/7T_{\mathrm{N}}=6$ K (the higher transition temperature is used). This is in good agreement with the temperature of the observed hump 6.3 K. This mechanism could also be applicable to $Gd_2Rh_3Si_5$.[24] It is noted that $Gd_2Rh_3Si_5$ ($J=7/2$), with $T_N=8.4$ K, shows a hump around $T^*=5$ K. More experimental results are needed to check this theoretical model.

In summary, the antiferromagnetically ordered ground state of $Ce_2Pd_3Si_5$ was ascertained by measuring the magnetic susceptibility, electrical resistivity, thermoelectric power, and specific heat over a wide temperature range. Two transitions, at 8.0 and 7.4 K, were observed. The former indicates the onset of antiferromagnetic order, and the latter could be due to the change of magnetic structure from incommensurate to commensurate with the lattice. The influence of crystal electric fields on physical properties was observed in all of our magnetic, thermal, and transport measurements. Neutron-scattering experiments are desired to determine the magnetic structure and to check the CEF splitting scheme.

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