Magnetic, thermal, and transport properties on single crystals of antiferromagnetic Kondo-lattice Ce$_2$PdSi$_3$

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Magnetization, heat capacity, electrical resistivity, thermoelectric power, and Hall effect have been investigated on single-crystalline Ce$_2$PdSi$_3$. This compound is shown to order antiferromagnetically below Néel temperature ($T_N$) $\sim$ 3 K. The Sommerfeld coefficient far below $T_N$ is found to be about 110 mJ/K$^2$ mol Ce, which indicates the heavy-fermion character of this compound. The transport and magnetic properties exhibit large anisotropy with an interplay between crystalline-electric-field (CEF) and Kondo effects. The sign of thermoelectric power is opposite for different directions at high temperatures and the ordinary Hall coefficient is anisotropic with opposite sign for different geometries, indicating the anisotropic Fermi surface. The CEF analysis from the temperature dependence of magnetic susceptibility suggests that the ground state is $\{\pm \frac{1}{2}\}$. The first and the second excited CEF doublet levels are found to be located at about 30 and 130 K, respectively. The Kondo temperature is estimated to be the same order as $T_N$, indicating the presence of a delicate competition between the Kondo effect and magnetic order.

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I. INTRODUCTION

There has been considerable interest in understanding the interplay among the crystalline-electric-field (CEF) effect, the indirect exchange [Ruderman-Kittel-Kasuya-Yoshida (RKKY)] interaction among the 4$f$ magnetic moments and the Kondo effect in Ce compounds, since these are the decisive factors of the physical properties in these compounds. It is therefore worthwhile to carry out careful investigation in new Ce compounds. With this motivation, we report here the results of magnetic susceptibility ($\chi$), magnetization ($M$), heat-capacity ($C$), electrical-resistivity ($\rho$), thermoelectric-power ($S$), and Hall-coefficient ($R_H$) measurements on single-crystalline Ce$_2$PdSi$_3$, grown for the first time.

This compound has been reported to form in an AlB$_2$-derived hexagonal crystal structure and to exhibit Kondo effect. The intensity of investigation in the RE$_2$XSi$_3$ (RE = rare earth, X = transition metal) series, crystallizing in the above-mentioned structure, increased only in the recent years and these compounds have been reported to exhibit many unusual features in the magnetic, thermal, and transport properties (see, for instance, Refs. 1–10 and references therein). Gd$_2$PdSi$_3$ exhibits Kondo-lattice-like anomalies, e.g., a resistivity minimum above $T_N$, accompanied by a large negative magnetoresistance. These features, presumably due to a novel mechanism, are not common to Gd compounds. Ce$_2$CoSi$_3$ is a mixed-valent compound, a small La substitution for Ce induces a non-Fermi-liquid behavior in $\rho$. Eu$_2$PdSi$_3$ exhibits two distinct magnetic transitions, with the possibility of quasi-one-dimensional magnetism for the high-temperature transition and unusual magnetic characteristics. Particularly considering that the Gd-based compound in the Pd series has been found to show many interesting anisotropic features, it is tempting to carry out detailed studies on the single-crystalline Ce$_2$PdSi$_3$ as well. Previous magnetic, electrical-resistance, and heat-capacity measurements on this compound were performed only in the polycrystalline form and no clear magnetic ordering could be detected. Thus the present studies extended to much lower temperatures, particularly on single crystals, serve as a first thorough characterization of the bulk properties of this compound.

II. EXPERIMENTAL DETAILS

Single crystals of Ce$_2$PdSi$_3$ have been prepared by the Czochralski pulling method using a tetra-arc furnace in an argon atmosphere. The single-crystalline nature has been confirmed by back-reflection Laue technique. The magnetic measurements were carried out with a Quantum Design superconducting quantum interference device (SQUID) magnetometer. The heat capacity was measured by a quasiadiabatic heat-pulse method using a dilution refrigerator. The electrical-resistivity and Hall-effect measurements have been performed by a conventional dc four-probe method in the temperature interval of 0.5–300 K. The thermoelectric-power data have been taken by the differential method using a Au-Fe (0.07%)-chromel thermocouple.
III. RESULTS AND DISCUSSIONS

Figure 1(a) shows the temperature dependence of the inverse magnetic susceptibility $\chi^{-1}(T)$, measured in a magnetic field $H = 1$ kOe for both $H//[10\overline{1}0]$ and $H//[0001]$. There is a large difference in the absolute values of $\chi$ for two geometries, apparently due to CEF effect. The effective magnetic moment ($\mu_{eff}$) and the paramagnetic Curie temperature $\Theta_P$ are estimated from the high-temperature linear region to be about $2.60 \mu_B$/Ce and $3.6$ K for $H//[10\overline{1}0]$ and $2.65 \mu_B$/Ce and $-107$ K for $H//[0001]$, respectively. These values of $\mu_{eff}$ are very close to that expected for a free trivalent Ce ion ($2.54 \mu_B$). The large negative value of $\Theta_P$ for $H//[0001]$ and a small positive value for $H//[10\overline{1}0]$ are presumably due to CEF effect. The large anisotropy in $\Theta_P$ may also indicate the existence of anisotropy in the exchange interaction which depends on the CEF level scheme. The expanded view of the temperature dependence of $\chi$ is shown in the inset of Fig. 1(a). There is no difference between the field-cooled and the zero-field-cooled measurements of $\chi$ down to 1.9 K within the experimental accuracy, indicating the absence of any spin-glass-like behavior. This fact is in contrast to the formation of spin-glass state in the isostructural $U_2PdSi_3$. There is a peak in $\chi(T)$ at around 2.8 K for $H//[10\overline{1}0]$ and at 2.5 K for $H//[0001]$. These peaks can be ascribed to the antiferromagnetic ordering. The occurrence of the peak at slightly different temperatures for two directions might be due to the anisotropic field dependence of $T_N$ for two directions, since the heat-capacity measurement in absence of a magnetic field shows a peak at around 3 K as shown below. Recent neutron-diffraction data on polycrystals also suggests the occurrence of antiferromagnetic (AF) ordering below 2.5 K in a sinusoidally modulated AF structure.

We have tried to analyse the $\chi(T)$ data using a CEF model, considering hexagonal site symmetry of Ce in $Ce_2PdSi_3$. According to the Hutchings’ notation, the CEF Hamiltonian for $J = 5/2$ ion with the hexagonal point symmetry is given by

$$\mathcal{H} = B_n^n O_n^n + B_m^m O_m^m, \quad (1)$$

where $B_n^n$ and $O_m^m$ represent the CEF parameters and the Steven’s equivalent operators, respectively. The results of this CEF analysis using Eq. (1), employing the $\chi(T)$ data at the paramagnetic region, leads to $B_{20}^2 \simeq 10.1$ K, and $B_{40}^4 \simeq 0.11$ K. This set of parameters corresponds to a crystal-field level scheme with the three doublets $|\pm \frac{5}{2}\rangle$, $|\pm \frac{3}{2}\rangle$ and $|\pm \frac{1}{2}\rangle$ at around 0, 28 K ($\Delta_1$), and 130 K ($\Delta_2$), respectively. Accordingly, the calculated values of $\chi^{-1}$ are shown by the solid lines in Fig. 1(a), which indicates that the anisotropy in $\chi(T)$ is mainly induced by the CEF effect. However, there is a deviation of the calculated $\chi^{-1}$ from the experimental values, particularly at low temperatures. The following explanations can be offered to this deviation: According to Sytula et al., Pd and Si atoms are random in this crystal structure (space group $P6/mmm$). Therefore this randomness or disorder between Pd and Si sites may produce local modification of the CEF effects due to the distribution of the CEF parameters. Alternatively, if Pd and Si are well ordered (space group $P6_3/mmc$, see Ref. 10), there are two different crystallographic environments for Ce ions, in which case the CEF effect may be different for these two sites. All these factors are neglected in the present CEF calculations.

The isothermal magnetization at 2 K is shown in Fig. 1(b). $M$ varies distinctly in different ways with the applied magnetic field for $H//[10\overline{1}0]$ and $H//[0001]$. This anisotropy in $M$ is presumably due to the CEF effect. The magnetic moments at $H = 50$ kOe for two directions are $\sim 1.18$ and $\sim 0.25 \mu_B$/Ce for $H//[10\overline{1}0]$ and $H//[0001]$, respectively. The larger magnetic moment...
for $H//[10\overline{1}0]$ indicates the $a$-$b$ plane as the easy plane of magnetization, and the $|\pm\frac{\pi}{2}\rangle$ doublet as the ground state, in agreement with the CEF analysis from $\chi(T)$ described above. These two facts are also consistent with the proposed magnetic structure of Ce$_2$PdSi$_3$ based on neutron-diffraction experiment, i.e., the Ce magnetic moments lie in the $a$-$b$ plane.$^{10}$

Figure 2 shows the temperature dependence of heat capacity $C(T)$ for Ce$_2$PdSi$_3$. The magnetic (4f contribution) entropy is presented by the solid line. The inset shows the $C/T$ vs $T^2$ plot at temperatures well below $T_N$ where phonon contribution can be neglected.

$C = \gamma T + \beta T^3$ with $\beta \simeq 862$ mJ/K$^4$ mol Ce and the parameter $\beta$ mainly comes from the contribution of an antiferromagnetic-magnon part. For Y$_2$PdSi$_3$, the non-magnetic compound serving as a reference for phonon contribution, the $\gamma$ value is 4.5 mJ/K$^2$ mol Y. The moderately large value of $\gamma$ for Ce$_2$PdSi$_3$ suggests that even in the magnetically-ordered state Ce$_2$PdSi$_3$ may be classified as a heavy fermion. The solid line in Fig. 2 shows the magnetic entropy ($S_{4f}$) estimated from the 4f contribution to $C$. $C_m$ is obtained by employing the C values of Y$_2$PdSi$_3$ (Ref. 1) as a reference for the lattice contribution taking into account the difference of Debye temperatures of the two compounds by using the procedure suggested in Ref. 14. At $T_N$, $S_{4f} \simeq 2.3$ J/K mol Ce is $\sim 40\%$ of $R \ln 2$ expected for a complete removal of the two fold degeneracy of a CEF ground-state doublet. This reduced entropy value might be due to the substantial Kondo-derived reduction of the Ce moments and/or a presence of short-range correlations above $T_N$. Tentatively assuming a Kondo-derived reduction, the magnetic entropy $S_{4f}(\simeq 0.4 R \ln 2)$ at $T_N$ yields the Kondo temperature $T_K \simeq 8$ K, according to the Bethe-ansatz for a spin-$\frac{1}{2}$ Kondo model (see Refs. 16 and 17). The theoretical calculations of $C(T)$ using $T_K \simeq 8$ K, however, cannot reproduce the experimental curve above $T_N$. This deviation indicates the presence of short-range-AF correlations above $T_N$; the presence of these correlations is, in fact, detected in a recent neutron-scattering experiment$^{13}$ and a possible contribution from an excited CEF level (28 K) even at the measured temperature range.

The temperature dependence of resistivity $\rho(T)$ for Ce$_2$PdSi$_3$ with the current $J//[0001]$ and $J//[10\overline{1}0]$ as well as in polycrystalline Y$_2$PdSi$_3$ is shown in Fig. 3. $\rho$ for both current directions gradually decreases with decreasing temperature down to about 20 K showing a broad hump around 100 K; below 20 K, there is a weak upturn giving rise to a minimum at around 20 K, followed by a drop below 8 K. The $\rho(T)$ in Y$_2$PdSi$_3$ shows usual metallic behavior, however there is a drop in $\rho$ below 6 K, presumably attributable to the presence of traces of the superconducting phase YPdSi$_3$. As known for many other Ce alloys, the broad hump in Ce$_2$PdSi$_3$ can be ascribed to the combined effect of CEF and Kondo effect. The magnetic contribution to the resistivity $\rho_m = \rho(Ce_2PdSi_3) - \rho(Y_2PdSi_3)$, obtained by using $\rho(T)$ data for $J//[0001]$ in Ce$_2$PdSi$_3$, is shown in the inset: the ratio of the slopes of the $\rho_m$ vs $\ln T$ plot at high to low temperature turns out close to $35/3$ confirming that the ground state is a doublet (see Ref. 19). It clearly reveals the presence of a peak at around 50 K which might be related with $T_N$ enhanced by CEF effect as proposed by Hanzawa et al.$^{14}$ Correspondingly, there is also a broad hump in $S(T)$ (see Fig. 4). The minimum in $\rho(T)$ around 20 K is either due to the Kondo effect or a consequence of magnetic-precursor effect as noted for some Gd alloys$^{15}$ It may be noted that the drop in $\rho$ sets in at 8 K, much above the $T_N$, similar to CePt$_2$Ge$_2$.$^{14}$
FIG. 3. The electrical resistivity ($\rho$) of single-crystalline Ce$_2$PdSi$_3$ as a function of temperature (0.5–300 K) for $J//[10\overline{1}0]$ and $J//[0001]$ and polycrystalline Y$_2$PdSi$_3$. The inset shows the magnetic contribution to the resistivity as a function of ln $T$.

and such a feature in magnetically ordered Kondo lattices arises from a combination of indirect exchange interaction and the Kondo effect. There is a small difference in absolute values for two geometries, which might be due to the combined effect of anisotropy in the Fermi surface and preferably oriented microcracks. It may also be remarked that the residual resistivity is large even for the single crystal, which might be due to a presence of crystallographic (Pd-Si) disorder or a combined effect of disorder and a dominance of Kondo contribution even in the magnetically ordered state.

Figure 4 shows the temperature dependence of thermoelectric power ($S$) in Ce$_2$PdSi$_3$ as well as in Y$_2$PdSi$_3$ (polycrystal). In Ce$_2$PdSi$_3$, for the temperature gradient $\Delta T//[10\overline{1}0]$, $S$ is positive at room temperature, then it gradually increases with decreasing temperature and shows a broad hump around 100 K. There is a change of sign around 50 K with a minimum around 17 K. On the other hand, for $\Delta T//[0001]$, $S$ has a large negative value at room temperature and decreases with decreasing temperature showing a broad hump around 100 K. $S(T)$ for this direction also shows a minimum, however, at a temperature slightly higher than that for $\Delta T//[10\overline{1}0]$. Thus $S(T)$ in Ce$_2$PdSi$_3$ is highly anisotropic with the directions of the thermal gradient. The anisotropy in the Fermi surface might be one reason behind this anisotropy, since $S(T)$ in the isostructural Gd$_2$PdSi$_3$ is also anisotropic. For nonmagnetic Y$_2$PdSi$_3$, $S(T)$ has a large negative value at room temperature and decreases gradually with temperature. In Ce$_2$PdSi$_3$, the broad hump can be attributed to the interplay between CEF and Kondo effect. The origin of the minimum at $T_{min}$ ≃ 17 K is not clear yet, however, the possible explanation may be the Kondo scattering in the CEF ground state or the growth of AF correlations as in the case of CeAuAl$_3$. Tentatively assuming the Kondo-derived origin, $T_K$ ≃ 8 K would be obtained using the relation $T_K \approx \frac{1}{2} T_{min}$ that holds for CeAl$_2$ and CeCu$_2$ (see Ref. 15). However, the temperature dependence of $C$ above $T_N$ suggests that this estimation of $T_K$ is a rough one, indicating that both Kondo effect and AF correlations
may play a role for this minimum. For $\Delta T//[10\overline{1}0]$, $S(T)$ is similar to the behavior in the typical magnetically ordered heavy-Kondo compounds, e.g., CeCu$_2$ and CeAl$_2$, though the overall temperature dependence of $S$ in Ce$_2$PdSi$_3$ is rather weaker. If the crystallographic disorder is the dominant origin of the large residual resistivity, the Kondo contribution to $S(T)$ could be suppressed. Since, according to the Gorter-Nordheim rule, the thermoelectric power for more than one scattering mechanisms can be expressed as $S_{\text{alloy}} = [\rho_1 S_1 + \rho_2 S_2] / \rho$, where the subscripts 1 and 2 correspond to different scattering mechanisms. In the present case, 1 represents the Kondo scattering and 2 represents the other scatterings. Therefore a large $\rho_2$ can suppress the Kondo contribution $S_1$. The large negative thermoelectric power in Y$_2$PdSi$_3$ might arise from the 4$d$ band of Pd, as in the case of the 3$d$ band of Co in YCo$_2$.

The $S(T)$ curve for $\Delta T//[0001]$ at high temperatures is almost parallel to that of Y$_2$PdSi$_3$, therefore a significant effect of the Pd-4$d$ band on $S(T)$ even in Ce$_2$PdSi$_3$ cannot be ruled out. The temperature dependence of Hall coefficient ($R_H$) for $H = 15$ kOe, shown in Fig. 5(a), also reflects the anisotropic nature of this material. For both geometries (as labeled in the figure) $R_H$ is positive at room temperature and increases gradually with decreasing temperature. At low temperatures $R_H$ becomes highly anisotropic and shows a positive peak for both geometries, in the vicinity of $T_N$ (see the inset). The large anisotropy observed in $R_H$ is also reflected in the $\chi(T)$ data taken at $H = 15$ kOe (not shown), indicating that the anisotropy in $R_H$ is of magnetic origin. The positive value of $R_H$ at all temperatures and a positive peak at the vicinity of $T_N$ are similar to those in the antiferromagnetic Kondo-lattice compound CeAl$_2$. In contrast, $R_H$ ($\simeq 0.9 \times 10^{-10}$ m$^3$/C at 300 K) in Y$_2$PdSi$_3$ is almost temperature independent. Clearly, there is a dominant 4$f$ contribution in Ce$_2$PdSi$_3$. The Hall coefficient in magnetic materials like those in Ce compounds is generally a sum of two terms: an ordinary Hall coefficient ($R_0$) due to Lorentz force and an anomalous contribution arising from magnetic scattering (skew scattering) in the paramagnetic state $R_H = R_0 + A\rho\chi$, where $A$ is a constant. Using this relation, $R_0$ is estimated by plotting $R_H$ versus $\rho\chi$ [Fig. 5(b)]. From Fig. 5(b), it is obvious that the plot is linear for both $H//[10\overline{1}0]$ and $H//[0001]$ in the paramagnetic state with a value of $R_0 \simeq -3.2 \times 10^{-10}$ m$^3$/C and $1.0 \times 10^{-9}$ m$^3$/C, and $A \simeq 7.4 \times 10^{-16}$ mol/C and $4.8 \times 10^{-16}$ mol/C, respectively. This linear behavior indicates the presence of dominant skew scattering in Ce$_2$PdSi$_3$. In the vicinity of $T_N$, however, the data deviate from the high-temperature linear variation. $R_0$ of different sign with the anisotropic values for two geometries indicates the presence of anisotropy in the Fermi surface, in agreement with the $S(T)$ data.

IV. SUMMARY

Summarizing, we have investigated the magnetic behavior of recently synthesized Ce$_2$PdSi$_3$ in the single-crystalline form and the results show strong anisotropic behavior of the measured properties. The paramagnetic Curie temperature for $H//[10\overline{1}0]$ is positive, however, the value is negative for $H//[0001]$. The sign of the thermoelectric power is different for the two measured crystallographic orientations at high temperatures. Distinct features due to an interplay between CEF and Kondo effect have also been observed in the thermoelectric power and resistivity data. The ordinary Hall-coefficient is anisotropic with opposite sign for the two measured geometries. The results establish that this compound is an antiferromagnetic Kondo lattice with $T_N = 3$ K. The magnitude of $T_K$ is also estimated to be of same order as $T_N$ and this fact suggests a delicate competition between the
Kondo effect and indirect exchange interaction. Therefore it would be of interest to investigate this compound under high pressure.

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