Antiferromagnetic Kondo lattice compound CePt$_3$P

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A new ternary platinum phosphide CePt$_3$P was synthesized and characterized by means of magnetic, thermodynamic and transport measurements. The compound crystallizes in an antiperovskite tetragonal structure similar to that in the canonical family of platinum-based superconductors APT$_3$P (A = Sr, Ca, La) and closely related to the noncentrosymmetric heavy fermion superconductor CePt$_3$Si. In contrast to all the superconducting counterparts, however, no superconductivity is observed in CePt$_3$P down to 0.5 K. Instead, CePt$_3$P displays a coexistence of antiferromagnetic ordering, Kondo effect and crystalline electric field effect. A field-induced spin–flop transition is observed below the magnetic ordering temperature $T_N$ of 3.0 K while the Kondo temperature is of similar magnitude as $T_N$. The obtained Sommerfeld coefficient of electronic specific heat is $\gamma_e = 86 \text{ mJ/mol} \cdot \text{K}^2$ indicating that CePt$_3$P is a moderately correlated antiferromagnetic Kondo lattice compound.

The interplay among spin, charge and orbital degrees of freedom in transition metal compounds has triggered enormous research interests in condensed matter physics and material science. For a large family of layered 3$d$ electron superconductors (SCs) such as the copper oxides$^1$ and iron pnictides$^2$, the spin fluctuations caused by strong 3$d$ electron correlations play a vital role in the unconventional superconductivity. Besides these 3$d$ transition metal systems, several platinum-based SCs exhibit remarkably rich physical properties and therefore have also attracted considerable attention, partly owing to the moderately strong spin-orbit coupling of the platinum 5$d$ electrons. The most prominent example is the heavy fermion noncentrosymmetric (NCS) SC CePt$_3$Si, in which exotic superconductivity is observed below $T_c = 0.75 \text{ K}$: an admixture of spin-singlet and spin-triplet pairing symmetry, nodal gap structure and huge upper critical field ($B_{c2} \approx 4 \text{ T}$)$^4$. The delicate interplay between the cerium 4$f$ and the platinum 5$d$ electrons places this material on the border of the magnetic quantum critical point (QCP) but still in the antiferromagnetic (AFM) ground state, rendering the role of inversion symmetry unclear$^5$. Among a series of filled skutterudite $MT_{5/3}X_{12}$ ( $M$ = rare-earth or alkaline-earth metals, $T$ = transition metals and $X$ = P, As, Sb and Ge) with the cubic space group $Im\bar{3}$ (No. 204), PrPt$_4$Ge$_{12}$ was reported to exhibit time-reversal symmetry breaking from zero-field $\mu$SR measurements$^6$. As a result of the unexpectedly high transition temperature $T_c = 7.9 \text{ K}$ and the moderately enhanced Sommerfeld coefficient $\gamma = 76 \text{ mJ/mol} \cdot \text{K}^2$, PrPt$_4$Ge$_{12}$ has been extensively studied and multiband superconductivity has been proposed based on the analysis of the photoemission spectroscopy$^7$ as well as the magnetic penetration depth$^8$. Moreover, SrPtAs is recently reported to crystallize in a hexagonal structure (P6$_3$/mmc, No. 194) with weakly coupled PtAs layers forming a honeycomb lattice$^9$. The peculiar locally NCS structure within PtAs layers together with a strong spin-orbit coupling demonstrates SrPtAs as an attractive material to explore superconductivity with a spontaneous static magnetic field $B_s$$^{10}$.

It is interesting that among the platinum-based superconductors, the newly reported family of APT$_3$P (A = Ca, Sr and La) shares the structural similarity with that of iron pnictides$^1$. These compounds crystallize in a tetragonal structure with space group $P4/nmm$ (No. 129) with stacking in the order of 3$\times$ Pt$_3$P-A along the c-axis. The distorted antiperovskite Pt$_3$P octahedral unit alternates within the $ab$ plane, forming an antipolar pattern. The $z \rightarrow -z$ inversion operation is thus preserved. Due to the structural distortion, the platinum atoms take two different sites as Pt(I) and Pt(II) so that the Pt(II) and P atoms form a Pt$_3$P layer resembling the FeAs layer in the iron-based superconductors. Of course, the structure of APT$_3$P is also somewhat similar to that of CePt$_3$Si, but the latter is actually isotypic to the NCS compound CePt$_3$B with the space group $P4mm$ (No. 99)$^7$. The corresponding Pt$_3$Si unit has the polar structure under this space group leading to the absence of inversion symmetry.

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different from the antipolar structure in \( \text{APt}_3\text{P} \). Noticeably, the \( \text{APt}_3\text{P} \) family shows a significant variation of \( T_c \), i.e., \( T_c = 8.4 \) K, 6.6 K and 1.5 K for \( A = \text{Sr}, \text{Ca} \) and \( \text{La} \), respectively. It was reported theoretically that spin-orbit coupling (SOC) effect is significant in \( \text{LaPt}_3\text{P} \) but negligible in \( \text{CaPt}_3\text{P} \) and \( \text{SrPt}_3\text{P} \)\(^{12-14} \). The origin of significantly enhanced \( T_c \) in \( \text{SrPt}_3\text{P} \) is still debatable. It was suggested to be due to a possible dynamic charge-density-wave (CDW)\(^{12} \). However, a theoretical work by Zocco et al. indicated SOC could strongly renormalize the electron-phonon coupling of \( \text{SrPt}_3\text{P} \) and thus enhance the electronic density of states near the Fermi level\(^{15} \). Moreover, several theoretical works claimed that the CDW instability could not be reproduced in \( \text{SrPt}_3\text{P} \)\(^{13,14} \). The centrosymmetric (CS) compounds \( \text{APt}_3\text{P} \) reported so far do not involve the 4f electrons. The interplay between strong 4f electron correlation and superconductivity of 5d electrons in the \( \text{APt}_3\text{P} \) family remains an open issue.

In this paper, we report our successful synthesis of such a candidate compound \( \text{CePt}_3\text{P} \) in the platinum-based phosphides \( \text{APt}_3\text{P} \) family. We performed systematic measurements of the physical properties including the magnetic susceptibility, magnetization, specific heat and electrical resistivity. However, no evidence of superconductivity is observed down to 0.5 K in \( \text{CePt}_3\text{P} \), in contrast to other \( \text{APt}_3\text{P} \) compounds. Instead, the compound displays the rich physics involving the coexistence of magnetic ordering, Kondo coherence as well as crystalline electric field (CEF) effect. We shall discuss these properties and highlight the delicate 4f-5d interplay in this system.

### Results and Discussion

Figure 1 shows the Rietveld refinement of the XRD pattern of polycrystalline \( \text{CePt}_3\text{P} \) samples. Almost all peaks can be well indexed with the tetragonal structure with the space group \( \text{P4/nmm} \) (No. 129), except for a tiny peak of an impurity phase around 31.4° which might be \( \text{PtP}_2 \). The result of the Rietveld refinement\(^{16} \) shows a good convergence: \( R_w = 13.4\% \), \( S = 3.3 \). The refined lattice parameters of \( \text{CePt}_3\text{P} \) are \( a = 5.7123(7) \) Å and \( c = 5.4679(6) \) Å as listed in Table 1. The room temperature XRD patterns of \( \text{LaPt}_3\text{P} \) are also refined with \( R_w = 14.9\% \), \( S = 2.7 \)

### Table 1. Comparisons of physical parameters among the \( \text{APt}_3\text{P} \) family with \( A = \text{Sr}, \text{Ca}, \text{La} \) and \( \text{Ce} \). Atomic positions: \( A (0, 0, 0) \), Pt(I) (1/4, 1/4, 1/2), Pt(II) (0, 1/2, \( z_{\text{Pt(II)}} \)), P (0, 1/2, \( z_p \)). Note that data of Sr and Ca are taken from ref. 11.

| \( A \) | \( \text{SrPt}_3\text{P} \) | \( \text{CaPt}_3\text{P} \) | \( \text{LaPt}_3\text{P} \) | \( \text{CePt}_3\text{P} \) |
|---|---|---|---|---|
| \( a \) (Å) | 5.8694 | 5.6673 | 5.7597 | 5.7123 |
| \( c \) (Å) | 5.2822 | 5.4665 | 5.4736 | 5.4679 |
| \( T_c / T_N \) (K) | 8.4 | 6.6 | 1.5 | 3.0 (\( T_N^1 \)) |
| \( z_{\text{Pt(II)}} \) | 0.1409 | — | 0.1459 | 0.1582 |
| \( z_p \) | 0.7226 | — | 0.7691 | 0.8310 |
| \( \rho_0 \) (\( \mu \Omega \cdot \text{cm} \)) | 140 | — | 32 | 688 |
| \( \gamma_0 \) (mJ/mol⋅K\(^2\)) | 12.7 | 17.4 | 1.5 | 86 |

Figure 1. Rietveld refinement of the polycrystalline \( \text{CePt}_3\text{P} \) XRD pattern. Arrow marks an impurity phase which might be \( \text{PtP}_2 \). Inset shows a typical energy-dispersive x-ray spectrum with electron beams focused on the selected area of the as-grown sample.
Specific heat, contraction, both of that above 200 K, considering the negative Weiss temperature, the first anomaly marks the AFM ordering below 10 K. The refined lattice parameters of LaPt3P are determined from the peaks of derivative susceptibility, and the hump in the temperature-dependent molar magnetic susceptibility (inset to Fig. 3(a)) and the hump in the absolute value of $\chi$ ($\theta$ = 28.3 K may be attributed to the hybridization of the 4f electronic states with the conduction band. The derived effective moment $\mu_{eff} = 2.52 \mu_B$ is almost equal to that of a free Ce$^{3+}$ ion, indicating the trivalent Ce ion and well localized moment of Ce-4f$^1$ electrons at high temperature. $\chi_0$, is in the magnitude order of 10$^{-5}$. For $T < 100$ K, a change of the slope of $1/\chi(T)$ can be clearly observed and the fitting parameters are $\mu_{eff} = 2.11 \mu_B$ and $\theta = -15.3$ K. Here the change of the slope and the decreased value of $\mu_{eff}$ can be ascribed to the CEF effect. With decreasing temperature, $\chi(T)$ increases and shows a round peak around 3.0 K. Upon further cooling, another anomaly is observed near our base temperature. Two magnetic transition temperatures are determined from the peaks of derivative susceptibility $T_{d\chi/dT}$ as $T_{N1} = 3.0$ K and $T_{N2} = 1.9$ K (seen from Fig. 2(b)). Considering the negative Weiss temperature, the first anomaly marks the AFM ordering below $T_{N1}$ which is compatible with the magnetization measurement (discussed below). The second anomaly is attributed to a spin-reorientation. A similar phenomenon was observed in CeNiAsO. Further experimental studies, especially neutron diffraction measurement on single crystals of CePt$_3$P, are necessary to clarify the magnetic structure at low temperature.

The isothermal magnetization $M(B)$ of CePt$_3$P, measured in the $B$-sweep mode containing both field-up and down loops, is displayed in Fig. 3(a). In the AFM ordering state, $M(B)$ displays a linear field dependence when $B = 3.0$ T, but undergoes a weak step-like increase around 3.0 T. This anomaly, which is ascribed to a field-induced metamagnetic transition (MMT), can be independently determined to be $B_m = 3.0$ T by the peak in $MdB/dB$ curve (inset to Fig. 3(a)) and the hump in $\rho(B)$ curve (Fig. 3(b)) measured at $T = 2$ K. The expected hysteresis around $B_m$ is not observed and such absence of hysteresis around MMT was also reported in the single-crystalline samples.

**Figure 2.** (a) Temperature dependence of magnetic susceptibility, $\chi$, and inverse magnetic susceptibility, $1/\chi$, of CePt$_3$P measured under magnetic field $B = 0.1$ T on the left and right axis, respectively. Two dashed lines show the Curie-Weiss fit for $T > 200$ K and $T < 100$ K, respectively. Inset: enlarged plot of $\chi$ at $T < 5$ K. (b) The AFM transition temperature $T_{N1}$ and $T_{N2}$ determined from the derivative susceptibility $T_{d\chi/dT}$, specific heat $C(T)/T$ and derivative resistivity $d\rho/dT$ (The complete data of specific heat and resistivity will be shown in the following figures).
therefore, it can be fitted to a power law monotonously with increasing magnetic field at probably due to the CEF effect. Figure 3(b) shows the isothermal resistivity versus the applied field. Schottky anomaly, which is visible as a broad peak centered around 90 K in $B = 5$ T is much lower than the theoretical value of $2.14 \mu_B$ for the saturated moment of free Ce$^{3+}$ ions which is probably due to the CEF effect. Figure 3(b) shows the isothermal resistivity versus the applied field. $\rho$ decreases monotonously with increasing magnetic field at $T = 6$ K > $T_N$. Whereas at $T = 2$ K < $T_N$, a hump around $B_m = 3.0$ T is added to the decreasing trend. This feature is compatible with the MMT observed in the magnetization measurement.

The specific heats of CePt$_3$P and LaPt$_3$P divided by $T$, $C(T)/T$, are plotted in the main panel of Fig. 4(a) in a semi-logarithm scale. At room temperature, $C(T)/T$ saturates to about 135 and 140 J/mol·K for La and Ce compound, respectively, which are, within an acceptable error range, compatible with the classical Dulong-Petit law $3NR$ with $N = 5$ and $R = 8.31$ J/mol·K, where $R$ is the universal gas constant. The specific heat $C(T)$ of LaPt$_3$P is typical for nonmagnetic metals since no typical anomaly can be observed at high temperature. At low temperature, the specific heat of LaPt$_3$P is dominated by the electronic and phonon contributions for $T < \Theta_D/10$, therefore, it can be fitted to a power law $C/T = \gamma_{La} + \beta_{La}T^2$ over 10–20 K (data not shown). Here $\Theta_D$ is the Debye temperature, and $\gamma_{La}$ and $\beta_{La}$ denote the coefficients of the electronic and phonon contributions, respectively. It should be noted that there is a small jump around 1 K in the specific heat of LaPt$_3$P which should correspond to a superconducting transition though it is too small to observe in Fig. 4.

In the paramagnetic region above the magnetic transition, the specific heat of CePt$_3$P can be expressed as

$$C = \gamma_{Ce}T + \beta_{Ce}T^3 + C_{Sch},$$

where the coefficients $\gamma_{Ce}$ and $\beta_{Ce}$ are of electronic and phonon contributions of CePt$_3$P, respectively, while $C_{Sch}$ describes the Schottky anomaly term. A linear $T^2$-dependence is clearly seen in $C/T$ vs $T^2$ plot for temperature below 20 K (see inset to Fig. 4(a)). The derived Sommerfeld coefficient is $\gamma_{Ce} = (86 \pm 1) \text{mJ/mol·K}^2$. The value is moderately enhanced by a factor of 57 compared with that of LaPt$_3$P where $\gamma_{La} = (1.5 \pm 0.1) \text{mJ/mol·K}^2$, manifesting the correlation effect contributed from the Ce-4$f$ electrons. Therefore, CePt$_3$P is a Kondo lattice compound due to the strong $4f$ electron correlation and moderate effective $4f-5d$ hybridization. Note that $\gamma_{La}$ for LaPt$_3$P derived here is slightly smaller but still in the same magnitude order with that obtained in ref. 11. The reported phonon coefficients are in reasonable agreement with each other: $\beta_{Ce} = 0.98(1) \text{mJ/mol·K}^4$ for CePt$_3$P and $\beta_{La} = 0.94(1) \text{mJ/mol·K}^4$ for LaPt$_3$P, indicating similar phonon contributions. The Debye temperature $\Theta_D$ estimated by using $\Theta_D = (12\pi^4 NR / 5\beta)^{1/3}$ is $(215 \pm 1) \text{K}$ for CePt$_3$P and $(218 \pm 1) \text{K}$ for LaPt$_3$P, implying that the above analysis is quite self-consistent.

The Ce-4$f$ contribution to the specific heat of CePt$_3$P is then deduced by subtracting the measured specific heat of the nonmagnetic isosstructural reference sample LaPt$_3$P from the total specific heat of CePt$_3$P, i.e., $C_{Ce} = C_{Ce} - C_{La}$. The result is shown in the main panel of Fig. 4(b), plotted as $C_{Ce}/T$ vs $T$ in a logarithmic scale. The Schottky anomaly, which is visible as a broad peak centered around 90 K in $C_{Ce}/T$ curve, should be caused by the excitations between different CEF levels. The Schottky anomaly with three Kramers doublets (one doublet ground state and two excited doublets) for Ce$^{3+}$ ion with $j = 5/2$ experiencing a tetragonal crystal-field potential can be expressed by refs 21,22.
Here \( g_i = 2 \) is the degeneracy of the \( i\)th doublet state and \( \Delta_i \) is the energy difference between the ground state and the \( i\)-th excited state (see the schematic sketch drawn in the inset of Fig. 4(b)). Eq. 2 is applied to \( C_4f/T \) of \( \text{CePt}_3\text{P} \) over a temperature range of 50–130 K. The derived CEF energy differences are \( \Delta_1 = (20.9 \pm 0.1) \text{ meV} \) \((-240 \pm 1) \text{ K}) and \( \Delta_2 = (60.9 \pm 0.3) \text{ meV} \) \((-700 \pm 3) \text{ K}). This result may explain the slope change in \( 1/\chi(T) \) curve as well as the broad hump in both \( \rho_{\text{mag}} \) and \( S \). Furthermore, the large value of \( \Delta_1 \) is consistent with the reduced effective Ce moment below 100 K. The magnetic entropy gain \( S_m \) is calculated by integrating \( C_4f/T \) over \( T \) and plotted on the right axis in Fig. 4(b). One can see that \( S_m \) reaches about 0.51 R \( \ln 2 \) at \( T_N1 \) and \( R \ln 2 \) is recovered at \( \sim 50 \text{ K} \), indicating that the ground state with the AFM ordering of Ce\(^{2+} \) moments is Kramers two-fold degenerate. The plateau over the temperature range of \( T = 10–30 \text{ K} \) indicates that the first excited CEF level is far above \( T_N1 \). \( S_m \) reaches \( R \ln 4 \) at \( \sim 150 \text{ K} \) and increases substantially above the Schottky anomaly. For a Kondo lattice, the Kondo temperature can be estimated by the magnetic entropy at \( T_N \) via ref. 23

\[
C_{\text{Sch}} \approx \frac{R}{g_z + g_1 \exp(-\Delta_1/T) + g_2 \exp(-\Delta_2/T)} \times (g_z g_1 (\Delta_1/T)^2 \exp(-\Delta_1/T) + g_z g_2 (\Delta_2/T)^2 \exp(-\Delta_2/T) + g_z g_2 [(\Delta_2 - \Delta_1)/T] \exp(-\Delta_1/T + \Delta_2/T)).
\]

Figure 4. (a) Specific heat divided by temperature, \( C/T \), versus \( \log T \). The solid symbols are for \( \text{CePt}_3\text{P} \), while the open symbols represent the non-magnetic compound \( \text{LaPt}_3\text{P} \). The solid line is a fit to Eq. 5 for \( T \leq 1.9 \text{ K} \). (b) The Ce-4f contribution, \( C_4f/T \), and the magnetic entropy, \( S_m \), on the left and right, respectively, measured at zero magnetic field plotted in a logarithmic temperature scale for \( T = 0.4–200 \text{ K} \). The solid line shows the Schottky anomaly contribution \( C_{\text{Sch}} \). Inset to (a) shows \( C/T \) versus \( T \) together with the fitting parameters for \( \text{CePt}_3\text{P} \) (see the text): the Sommerfeld coefficient \( \gamma_{\text{Ce}} \), \( \beta_{\text{Ce}} \) and the Debye temperature \( \Theta_D \). The dashed line is a linear fit in the temperature range \( T = 10–20 \text{ K} \). Inset to (b) displays the schematic sketch of CEF energy levels for Ce\(^{2+} \) ion in \( \text{CePt}_3\text{P} \).
Based on the mean-field theory of Besnus et al. and Bredl et al., the specific heat jump $\delta C = C_{T\to N}$ is related to the Kondo temperature $T_K$ by the following formula:

$$\delta C(\zeta) = \frac{6D}{\psi''(\frac{1}{2} + \zeta)} \left[ \psi'(\frac{1}{2} + \zeta) + \zeta \psi''(\frac{1}{2} + \zeta) \right]^2.$$

(4)

Here $\zeta = (T_0/T) \pi$, $\psi$ denotes the digamma function and $\psi'$, $\psi''$, and $\psi'''$ are the first three derivatives of $\psi$. Then the Kondo temperature can be also estimated by applying Eq. 4, obtaining a ratio of $T_0/T = 0.88$, or $T_K \approx (2.7 \pm 0.1)$ K. Therefore, based on both magnetic entropy and specific heat jump, it is reasonable to estimate $T_K \approx 2$–6 K in this compound.

In the magnetically ordered state, the AFM spin-wave spectrum follows a dispersion relation of $\varepsilon_k = \Delta + Dk^2$. Here $\varepsilon_k$ is the excitation energy, $\Delta$ is the gap in the spin-wave spectrum, and $D$ is the spin-wave stiffness. The phonon contribution, $\beta_{\text{CeT}}$, can be subtracted from the total specific heat $C$ as $\Delta C = C - \beta_{\text{CeT}}$. At low temperature, $\Delta C$ is described by the following expression:

$$\Delta C(T) = \gamma_0 T + A_C T^2 \left[ \frac{T}{\Delta} \left( 1 + \frac{39}{20} \frac{T}{\Delta} \right) + \frac{51}{32} \left( \frac{T}{\Delta} \right)^2 \right] \exp(-\Delta/T),$$

(5)

where the coefficient $A_{\text{C}}$ is proportional to $D^{-3}$. Fitting the specific heat below $T_N$ (solid line in Fig. 4(a)) gives the fitting parameters $\gamma_0 = 247$ mJ/mol·K$^2$, $\Delta = 2.6$ K, and $A_{\text{C}} = 67.5$ mJ/mol·K$^4$. The considerably enhanced zero-temperature Sommerfeld coefficient $\gamma_0$ is about 3 times of $\gamma_{\text{Ce}}$ obtained in the paramagnetic state, indicating the formation of moderate-heavy quasiparticles in the antiferromagnetically ordered state. It is worthwhile noting that the obtained spin-wave gap $\Delta$ is of the order of magnitude often found in cerium intermetallics with AFM ground states.

The temperature variation of the electrical resistivity of CePt$_3$P, $\rho(T)$, is plotted in Fig. 5(a). The resistivity at room temperature is $\rho_{\text{room}} = 1140 \mu\Omega$·cm, a value rather typical for the Ce-based Kondo compounds with narrow $f$-band. The resistivity decreases with decreasing temperature and exhibits two features. A broad hump around 110 K reflects the 4$f$-electron contribution via Kondo scattering from different CEF levels. At low temperature, a pronounced peak in $\rho(T)$ around 3 K is directly visible, indicating the AFM ordering phase below $T_N = 3.0$ K. Above $T_N$, $\rho$ increases in a minus logarithmic temperature manner over $T = 5$–20 K, reflecting the Kondo-type
scattering. Further evaluation of d^2ρ/dT^2 requires information of the phonon contribution which could be taken from the homologous and isostructural analog, LaPt3P. The ρ(T) of LaPt3P, which is also presented in Fig. 5(a), can be well described by a Bloch-Grüneisen-Mott (BGM) relation:

$$\rho(T) = \rho_0 + 4R\Theta_B \left(\frac{T}{\Theta_B}\right)^5 \int_0^{\Theta_B/T} \frac{x^2 dx}{(e^x - 1)(1 - e^{-x})} = KT^3,$$

where ρ0 is the residual resistivity due to lattice defects, the second term denotes electron-phonon scattering, and the third one accounts for the contribution due to Mott’s s-d interband electron scattering. A least square fitting of the BGM formula to the experimental data over the temperature range 2–300 K leads to the following parameters: ρ0 = 32 μΩ·cm, ΘB = 160 K, R = 1.25 μΩ·cm/K, and K = 4.1 × 10^{-8} μΩ·cm/K^3. Note that the residual resistivity ρ0 is smaller than that in ref. 11. The parameter ΘB is usually considered as an approximation of the Debye temperature ΘD in spite of some contribution due to electron-electron correlations in ΘD. ΘB yielded from the specific heat data is 218 K which is in accordance with ΘB from the resistivity data. LaPt3P exhibits simple metallic behavior as we expected, without the characteristic features due to the interplay of Kondo and CEF effects in CePt3P mentioned above.

In order to analyze the magnetic contribution to the electrical resistivity of CePt3P, it is reasonable to assume that the phonon contribution in this compound can be properly approximated by that in LaPt3P, ρ_ph = ρ(La) − ρ0(La), so we have

$$\rho_{mag}(Ce) + \rho_0(Ce) = \rho(Ce) - \rho_{ph}.$$ (7)

The temperature dependence of ρmag and ρ0 derived in this way is presented in Fig. 5(b) in a semilogarithmic scale. As a distinct feature in a Kondo lattice system, a pronounced broad hump centered at T = 110 K becomes obvious in ρmag curve, which could be ascribed to the Kondo scattering from different CEF levels. According to Cornut and Coqblin21, this maximum provides an estimate of the CEF splitting energy scale ~200 K of Ce-4f electrons. The ratio Δ/Θc is about 3:27, reasonably close to the theoretical prediction.

The temperature dependence of dρ/dT from the homologous and isostructural analog, LaPt3P, the logarithmic slopes c_kLT and c_kHT in the low-temperature and high-temperature regions, respectively, are proportional to the squared effective degeneracy λ of the thermally populated levels: c_k = λ - 1. For cerium compounds with Ce4+ ion placed in a noncubic crystalline environment the ground multiplet splits into three doublets, thus the expected ratio is c_kLT / c_kHT = 3:35. In the case of CePt3P, with the coefficients c_kLT = −0.063 and c_kHT = −0.57 yielded from linear fitting of ρmag vs logT (see the dashed lines in Fig. 5(b)), the ratio is about 3:27, reasonably close to the theoretical prediction.

From the inset of Fig. 5(a), ρ drops rapidly below about 3.0 K owing to the reduction of spin-flip scattering upon entering the AFM ordered state. This magnetic transition temperature is determined from a slope change of dρ/dT in Fig. 2(b). Upon further cooling, a second slope change in ρ is observed around 1.9 K, corresponding to the pronounced kink in dρ/dT. Therefore, two magnetic transitions in CePt3P are apparent from the analysis of magnetic susceptibility χ(T), specific heat C(T) and electrical resistivity ρ(T), as shown in Fig. 2(b): the first transition Tjun corresponds to the AFM ordering temperature, while the second one Tjnu is presumably associated with the spin reorientation. The values of Tjun and Tjnu derived from different measurements agree well with each other. It is noted that while LaPt3P shows superconductivity around Tc = 1.0 K (from specific heat), no superconductivity is observed in CePt3P down to 0.5 K.

Considering the relativistic dispersion relation for the AFM magnon spectrum, the electrical resistivity ρ(T) for T < Δ can be well described by the following equations26,27:

$$\rho(T) = \rho_0 + AT^2 + B_0 \Delta^2 \left[ 1 + \frac{2}{3} \left( \frac{T}{\Delta} \right) + \frac{2}{15} \left( \frac{T}{\Delta} \right)^2 \right] \exp(-\Delta/T),$$ (8)

where ρ0 is the temperature-independent residual resistivity, the constant B0 is related to the spin-wave stiffness D by the proportionality D = 3/2 and Δ is the same gap in the spin-wave spectrum as in Eq. (5). AT^2 stems from the electron-electron scattering following the Fermi liquid theory, while the third term describes the electron-magnon scattering. This formula is applied to the electrical resistivity of CePt3P (dotted line in the inset of Fig. 5(a)) and a very good fit is obtained with the fitting parameters: ρ0 = 688 μΩ·cm, Δ = 4.0 K, A = 9.0 μΩ·cm/K^2 and B0 = 25 μΩ·cm/K^2. Considering the relatively short fitting range of temperature, the derived Δ value for the measured polycrystalline sample is still reasonably compared with that obtained from the specific heat data.

Based on the above analyses, CePt3P displays the coexistence of three important characteristics: AFM ordering of the cerium local moments due to the Ruderman-Kittel-Kasuya-Yosida exchange interaction, the Kondo effect due to the strong 4f electron correlation and moderate effective 4f-5d hybridization, and the CEF interactions. The AFM ordering at Tjun = 3.0 K is clearly identified by the pronounced anomalies in the temperature-dependent magnetic, thermodynamic and electrical measurements. In addition, another anomaly at Tjnu = 1.9 K is also visible from the physical properties, and is probably due to a change in the magnetic configuration within the AFM ordered phase. The behavior of ρ(T) and C(T) in the ordered region is well describable in terms of AFM spin-wave spectrum. The field-dependent behavior of the magnetization and electrical resistivity also indicates a MMT from the magnetic ordering to a spin-polarized state around B0 = 3.0 T. The magnetic structure of CePt3P is still unclear and the neutron diffraction or Mössbauer spectroscopy experiments are helpful to clarify the details of the magnetic structure.
The Kondo effect displays itself by the large value of Weiss temperature $\theta$ (compared with the ordering temperature), the reduced magnetic entropy and the specific heat jump at $T_N$, as well as the enhanced Sommerfeld coefficient $\gamma$. From the analysis of the specific heat data, the Kondo temperature $T_K$ is estimated to be in the range of 2–6 K. Its value can be also estimated from the magnetic susceptibility as $T_K \approx [\theta/4\pi]^{-1}$. In reasonable agreement with other estimates. Also, the Kondo effect is well manifested in the electrical resistivity for Kondo systems with strong CEF interactions which follows the negative logarithmic-temperature dependence as $\rho(T) = \rho_0 + c_k \ln T$, with Kondo coefficient $c_k \approx 0$. The inverse susceptibility $(1/\chi(T))$ curve shows a slope change between $T = 100–200$ K which is also attributed to the CEF effect. This temperature region is in accordance with the energy scale $\Delta_0 = 240$ K of the multiple Ce$^{3+}$ ion estimated from the Schottky contributions of the specific heat $\Delta_0$.

Finally, it is very interesting to compare this CS compound CePt$_3$P with the extensively studied NCS heavy fermion SC CePt$_3$Si ($T_N = 0.75$ K). The crystal structure of CePt$_3$P consists of alternative stacking of layers of Ce atoms and layers of distorted antiperovskite Pt$_6$P octahedral units along the c-axis. The Pt$_6$P octahedra is asymmetrically distorted perpendicular to the ab-plane but alternatively distributed in the ab-plane, resulting in a symmetric antipolar analogue of CePt$_3$Si. CePt$_3$Si shows antisymmetric spin-orbit coupling of the platinum 5$d$ electrons due to the absence of $z \rightarrow -z$ symmetry as well as mixing spin-singlet and spin-triplet pairing states. The parity mixing alone can hardly account for the heavy fermion phenomena unless the strong electron-electron correlation effects which are ensured by the presence of Ce$^{3+}$ ions are taken into consideration. Correspondingly, the suppression of superconductivity in CePt$_3$P may be attributed to the enhanced AFM ordering. CePt$_3$P is, therefore, probably placed further away from the magnetic QCP compared with CePt$_3$Si ($T_N = 2.2$ K). With an external control parameter $\delta$, such as doping or positive pressure, the system may be shifted towards $T_N = 0$, namely the QCP. It is thus of great interest to investigate whether superconductivity exists in CePt$_3$P at even lower temperature than 0.5 K; if superconductivity does exist, it will provide strong evidence for the proximity to a magnetic QCP in CePt$_3$P. Comparing with CePt$_3$P, the occurrence of superconductivity at $T_c = 0.75$ K in CePt$_3$Si implies that the NCS crystal structure may favor unconventional superconductivity within the AFM ground state.

Conclusion

In summary, we report the successful synthesis of a new compound CePt$_3$P. From the collected experimental data of magnetization, specific heat and transport measurements, this compound is characterized as an antiferromagnetic Kondo lattice with crystal electric field effect. Two successive magnetic transitions of Ce 4$f$ moments are observed: the magnetic ordering at $T_N = 3.0$ K and the spin reorientation at $T_{\theta2} = 1.9$ K. Considering the moderately enhanced Sommerfeld coefficient of $\gamma = 86$ mJ/mol $\cdot$ K$^2$ in the paramagnetic region and large value of $\gamma = 247$ mJ/mol $\cdot$ K$^2$ in the the AFM region, the Kondo effect and the AFM order should coexist in the ground state. Thus a relatively large Fermi surface formed by the heavy quasiparticles is expected in CePt$_3$P with a Kondo temperature $T_K \sim 2–6$ K. The $ab$ initio crystal-field and electronic band structure calculations are necessary to further complement the present results. Further experiments such as chemical doping are presently underway in order to tune the ground state from the AFM ordering to strongly-correlated paramagnetic region.

Experimental Methods

The polycrystalline sample of CePt$_3$P was synthesized by solid state reaction. Ce piece (99.8%), Pt powder (99.9%) and P lump (99.999%) of high purity from Alfa Aesar were used as starting materials. First, CeP was pre-synthesized by reacting Ce and P at 1173 K for 72 h. Secondly, powders of CeP and Pt were weighed according to the stoichiometric ratio, thoroughly ground and pressed into pellets. The pellets were then packed in Al$_2$O$_3$ crucibles and sealed in an evacuated quartz tube which were slowly heated to 1273 K and kept at that temperature for 7 days. Finally, the samples were thoroughly ground, cold pressed and annealed in vacuum to improve the sample homogeneity. For comparison, the polycrystalline sample LaPt$_3$P$_2$ was also synthesized in the similar process. All the preparation procedures except heating were carried out in an argon protected glove box with the water and oxygen content below 0.1 ppm. The obtained CePt$_3$P sample is less compact than LaPt$_3$P and both of them are quite stable in the air.

Powder x-ray diffraction (XRD) measurements at room temperature were carried out on a PANalytical x-ray diffractometer (Model EMPYREAN) with a monochromatic Cu $K_{\alpha1}$ radiation and a graphite monochromator. Lattice parameters were derived by Rietveld refinement using the program RIETAN 2000. The energy dispersive x-ray spectroscopy (EDS) analysis was performed on a EDS spectrometer attached to a field emission scanning electron microscope (FEI Model SIRION). The electron beam was focused on a crystalline grain and the chemical compositions were averaged on at least 4 EDS spectra from different grains. The electrical resistivity $\rho(T)$ was measured by the standard four-probe method in a Quantum Design physical property measurement system (PPMS-9). The dc magnetization was measured in a Quantum Design magnetic property measurement system (MPMS-5) with the temperature range of $T = 2–400$ K. The specific heat measurements were performed in the PPMS-9 down to about 0.5 K.

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Author Contributions

J.C., Z.W., S.Y.Z. and C.M.F. performed the experiment(s), J.C. and Z.W. analyzed the results. J.C. and Z.A.X. designed the research and wrote the manuscript. All authors reviewed the manuscript.

Additional Information

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