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Antiferromagnetic Kondo-lattice in the layered compound $\text{CePd}_{1-x}\text{Bi}_2$ and comparison to the superconductor $\text{LaPd}_{1-x}\text{Bi}_2$

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Layered compound $\text{CePd}_{1-x}\text{Bi}_2$ with the tetragonal ZrCuSi_2 -type structure was obtained from excess Bi flux. Magnetic susceptibility data of $\text{CePd}_{1-x}\text{Bi}_2$ show an antiferromagnetic ordering below 6 K and are anisotropic along the c axis and the ab plane. The anisotropy is attributed to crystal-electric-field (CEF) effects and a CEF model which is able to describe the susceptibility data is given. An enhanced Sommerfeld coefficient γ of $0.191 \text{ J}\cdot\text{molCe}^{-1}\cdot\text{K}^{-2}$ obtained from specific heat measurement suggests a moderate Kondo effect in $\text{CePd}_{1-x}\text{Bi}_2$. Other than the antiferromagnetic peak at 6 K the resistivity curve shows a shoulder-like behavior around 75 K which could be attributed to the interplay between Kondo and CEF effects. Magnetoresistance and Hall effect measurements suggest the interplay reconstructs the Fermi surface topology of $\text{CePd}_{1-x}\text{Bi}_2$ around 75 K. Electronic structure calculations reveal the Pd vacancies are important to the magnetic structure and enhance the CEF effects which quench the orbital moment of Ce at low temperatures.

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A. Introduction

Ce-based intermetallics exhibit a wide range of novel behaviors such as magnetic ordering, Kondo effect, heavy fermion behavior and superconductivity. These phenomena arise from the competition between Ruderman-Kittel-Kasuya-Yosida (RKKY) and Kondo interactions and can be described using the Kondo-lattice model (so-called Doniach phase diagram).¹ When the ground state is dominated by the Kondo interaction, the system is non-magnetic due to the Kondo effect, for instance in CeCu_6 .² When the ground state is dominated by the RKKY interaction, the system orders magnetically. When the strengths of these two interactions are comparable, the ground state is Kondo-type but still magnetic. CeAl_2 and CeB_6 are typical examples of Kondo-type antiferromagnets.^{3,4}

Recently, we reported that $\text{LaPd}_{1-x}\text{Bi}_2$ is a superconductor below 2.1 K while the isostructural compound $\text{CePd}_{1-x}\text{Bi}_2$ has an antiferromagnetic (AFM) transition at 6 K.⁵ In this article, we present detailed magnetic and transport properties, and theoretical calculations for $\text{CePd}_{1-x}\text{Bi}_2$, which shows the anisotropy of antiferromagnetism and the presence of Kondo and crystal-electric-field (CEF) effects in this material. The interplay between Kondo and CEF effects governs the transport behavior of $\text{CePd}_{1-x}\text{Bi}_2$ between its Neel temperature (T_N) and 75 K at which the Fermi surface is obviously reconstructed by the interplay. These results indicate that $\text{CePd}_{1-x}\text{Bi}_2$ is a new Kondo-lattice antiferromagnet.

B. Experimental Details

Single-crystalline $\text{CePd}_{1-x}\text{Bi}_2$ was grown using bismuth flux.⁶ The starting materials Ce, Pd and Bi with the mole ratio 1:1:12 and the total mass 3 g were weighed, mixed and placed in an alumina crucible. All handling was performed in a glove box with a protective argon atmosphere (both H_2O and O_2 are limited below 0.1 ppm). Then the alumina crucible was jacketed by an evacuated silica tube. The tube was heated to 900 °C in a box furnace and kept at 900 °C for 10 h. A slow-cooling process at the rate 5 °C/h was carried out from 900 °C to 500 °C, and at 500 °C the excess Bi flux was removed by centrifugation.⁷ The obtained crystals were shiny silver-color plates with a typical dimension of $5 \times 5 \times 0.5 \text{ mm}$ and stable in the air.

Single crystal X-ray diffraction (SCXRD) was carried out on a STOE diffractometer. Data reduction was performed with the software X-Area,⁸ and the structure was solved by direct methods using the SHELXTL software.⁹ The resulting structure parameters are listed in Table I.

The magnetic susceptibility data for $\text{CePd}_{1-x}\text{Bi}_2$ were collected with a superconducting quantum interference device (SQUID) in a Quantum Design Magnetic Property Measurement System (MPMS-3).

Thermodynamics and transport measurements including specific heat, resistivity, magnetoresistance and Hall effect were done on the Quantum Design Physical Property Measurement System (PPMS). We employed the thermal relaxation technique¹⁰ to perform the specific heat measurements. Resistivity, magnetoresistance and Hall effect measurements were simultaneously carried out using a six-probe geometry.¹¹

TABLE I: Crystal and structure refinement data at room temperature for $\text{CePd}_{1-x}\text{Bi}_2$.

Empirical formula	$\text{CePd}_{0.78(2)}\text{Bi}_2$
Formula weight	641.07
Crystal system	Tetragonal
Space group	$P4/nmm$
Unit cell dimensions	$a = 4.6136(19) \text{ \AA}, \alpha = 90^\circ$ $b = 4.6136(19) \text{ \AA}, \beta = 90^\circ$ $c = 9.650(6) \text{ \AA}, \gamma = 90^\circ$
Volume	$205.39(17) \text{ \AA}^3$
Z	2
Density (calculated)	10.366 g/cm^3
Absorption coefficient	99.419 mm^{-1}
$F(000)$	520
Reflections collected	609
Independent reflections	134 [$R_{\text{int}} = 0.1016$]
Completeness to $\theta = 24.92^\circ$	97.8%
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	134/0/12
Goodness-of-fit	1.031
Final R indices [$>2\sigma(1)$]	$R_{\text{obs}} = 0.0388, wR_{\text{obs}} = 0.0579$
R indices [all data]	$R_{\text{all}} = 0.0538, wR_{\text{all}} = 0.0602$
Largest diff. peak and hole	2.410 and $-2.922 \text{ e} \cdot \text{\AA}^{-3}$
Atomic coordinates:	
Ce	$2c [\frac{1}{4}, \frac{1}{4}, 0.2687(3)]$ Occupancy = 1, $U_{\text{eq}} = 0.0013(1)$
Pd	$2b [\frac{3}{4}, \frac{1}{4}, \frac{1}{2}]$ Occupancy = 0.78(2), $U_{\text{eq}} = 0.0014(2)$
Bi	$2a [\frac{3}{4}, \frac{1}{4}, 0]$ Occupancy = 1, $U_{\text{eq}} = 0.0015(1)$
Bi	$2c [\frac{1}{4}, \frac{1}{4}, 0.6593(2)]$ Occupancy = 1, $U_{\text{eq}} = 0.0018(1)$

C. Experimental Data and Discussion

2. Magnetic Properties

1. Crystal Structure

Figure 1(a) shows a typical plate-like crystal of $\text{CePd}_{1-x}\text{Bi}_2$. The compound adopts the tetragonal ZrCuSi_2 -type structure and features partial occupancy of Pd atoms as determined by single crystal X-ray diffraction, Figure 1(b). The composition was refined as $\text{CePd}_{0.78(2)}\text{Bi}_2$ after the diffraction data are corrected for absorption using an analytical expression. In the structure, the Pd_{1-x}Bi layer adopts the same anti-PbO-type structure as the FeAs layer in the iron-based superconductors,^{12,13} while the additional Bi atoms form an extended Bi square net. Reciprocal space reconstruction of single-crystal X-ray diffraction data from a $\text{CePd}_{0.78(2)}\text{Bi}_2$ crystal is shown in Figure 1(c). The $(hk0)$ reflections are very sharp, indicating excellent crystalline quality. Extra reflections corresponding to superstructures were not observed in reciprocal space, suggesting the Pd vacancy defects are randomly disordered in the structure.

The molar magnetic susceptibilities $\chi(T)$ collected with the field applied along the c axis and the ab plane respectively and their inverses $1/\chi$ are shown in the main frame of Figure 2 and its inset. Large anisotropy is observed in $\text{CePd}_{0.78(2)}\text{Bi}_2$: On one hand, the magnitude of magnetic susceptibility in two directions is different, especially at low temperatures. On the other hand, when the field is parallel to the c axis a sharp peak is observed at 6 K indicating an AFM ordering of the Ce moments, but when the field is parallel to the ab plane no peak is found. The similar behavior was observed in $\text{CeNi}_{0.8}\text{Bi}_2$,¹⁴ suggesting that the magnetic structure of $\text{CePd}_{0.78(2)}\text{Bi}_2$ is similar to that of $\text{CeNi}_{0.8}\text{Bi}_2$.¹⁵ The anisotropy of magnetic susceptibility persists up to the highest temperature measured (300 K). This anisotropy doubtless reflects a high-lying crystal field doublet ($\Delta/k_B > 300 \text{ K}$) which might arise from strong anisotropy in the $4f$ -conduction hybridization.

We tentatively fit the susceptibility data in two direc-

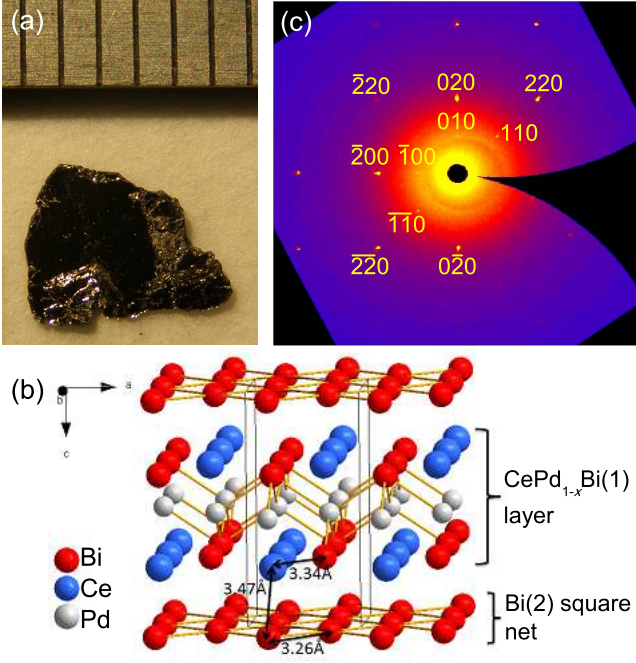


FIG. 1: (Color online) (a) Photograph of a typical $\text{CePd}_{0.78(2)}\text{Bi}_2$ crystal. (b) Layered crystal structure of $\text{CePd}_{0.78(2)}\text{Bi}_2$. (c) Reciprocal space reconstruction of single-crystal X-ray diffraction data from a $\text{CePd}_{0.78(2)}\text{Bi}_2$ crystal.

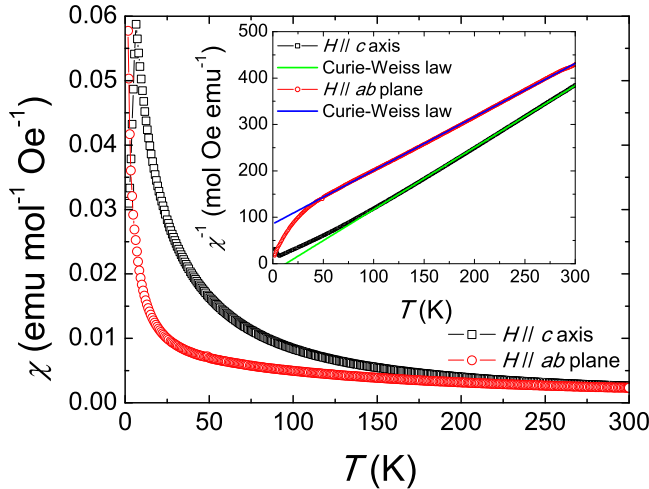


FIG. 2: (Color online) Temperature dependence of magnetic susceptibilities $\chi(T)$ (main frame) and their inverses $1/\chi$ (inset) for $\text{CePd}_{0.78(2)}\text{Bi}_2$ with the field applied along the c axis and the ab plane respectively.

tions with the Curie-Weiss law

$$\chi = \frac{C}{T - \Theta_P}. \quad (1)$$

From the fitting procedure, we get the paramagnetic Curie temperatures $\Theta_P = 12.8$ K (when $H \parallel c$) and -74.7 K (when $H \parallel ab$), the effective magnetic moments $\mu_{\text{eff}} = 2.45 \mu_B/\text{Ce}$ (when $H \parallel c$) and $2.63 \mu_B/\text{Ce}$ (when $H \parallel ab$).

The observed values of μ_{eff} are very close to that one would expect for a free Ce^{3+} ion ($2.54 \mu_B/\text{Ce}$), indicating that the magnetic moment comes from the trivalent Ce ion state. The deviation from the Curie-Weiss behavior below 100 K (when $H \parallel c$) and 50 K (when $H \parallel ab$) respectively can be attributed to the CEF effect on the ground state.

For a tetragonal point symmetry, $4mm$ (C_{4v}), at the Ce site, the CEF Hamiltonian can be written as

$$H_{\text{CEF}} = B_2^0 O_2^0 + B_4^0 O_4^0 + B_4^4 O_4^4, \quad (2)$$

where B_n^m are the CEF parameters which can be determined from the experimental data, and O_n^m are Stevens operator equivalents obtained using the angular momentum operators.^{17–19}

For Ce^{3+} , the Hund's rule multiplet is $J = \frac{5}{2}$, and we have diagonalized the Hamiltonian described by Equation (2) using a basis of the six $|m_J\rangle$ states ($|\frac{5}{2}\rangle$, $|\frac{3}{2}\rangle$, $|\frac{1}{2}\rangle$, $|\frac{1}{2}\rangle$, $|\frac{3}{2}\rangle$, $|\frac{5}{2}\rangle$). The Hamiltonian splits the levels into three Kramer's doublets. The eigenvectors were then employed to determine the molar magnetic susceptibility with the field parallel (χ_c) and perpendicular (χ_{ab}) to the c axis. We assume that the measured magnetic susceptibility contains contributions from the crystal field states (χ_i^{cf}) and the molecular field (λ_i),^{16,20} such that:

$$\frac{1}{\chi_c} = \frac{1}{\chi_c^{\text{cf}}} - \lambda_c, \quad (3)$$

$$\frac{1}{\chi_{ab}} = \frac{1}{\chi_{ab}^{\text{cf}}} - \lambda_{ab}. \quad (4)$$

Formulas for χ_c and χ_{ab} can be found in [20, 21] and references therein, which we list here for convenience:

$$\chi_c = (g_J \mu_B)^2 \frac{N_A}{Z} \sum_n \exp\left(\frac{-E_n}{kT}\right) \left[\frac{|\langle n | J_z | n \rangle|^2}{kT} + 2 \sum_{m \neq n} \frac{|\langle n | J_z | m \rangle|^2}{E_m - E_n} \right], \quad (5)$$

$$\chi_{ab} = (g_J \mu_B)^2 \frac{N_A}{Z} \sum_n \exp\left(\frac{-E_n}{kT}\right) \left[\frac{|\langle n | J_x | \tilde{n} \rangle|^2}{kT} + 2 \sum_{m \neq n, \tilde{n}} \frac{|\langle n | J_x | m \rangle|^2}{E_m - E_n} \right]. \quad (6)$$

$|n\rangle$ and $|m\rangle$ represent eigenstates of H_{CEF} , $|\tilde{n}\rangle$ is the Kramer's conjugate wavefunction of $|n\rangle$, g_J is the Lande g-factor, μ_B is the Bohr magneton, N_A is Avogadro's number, Z is the partition function for the eigenstates of H_{CEF} , and E_n represents the energy-level of $|n\rangle$, and J_z and J_x are the operators for the z and x components of the total angular momentum.

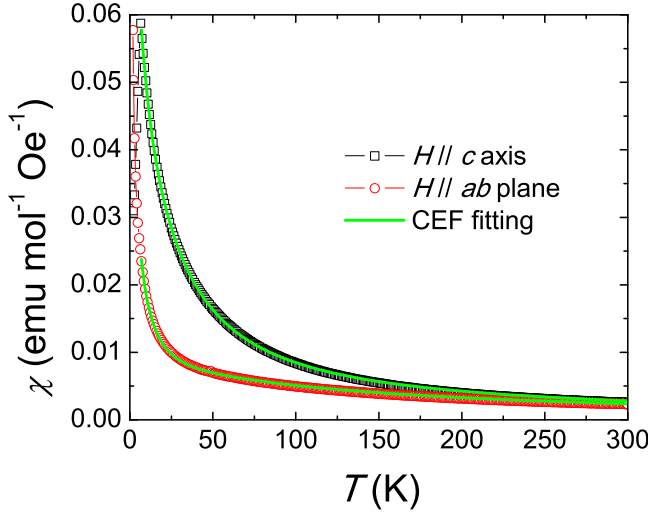


FIG. 3: (Color online) Fit to the magnetic susceptibility data based on the CEF model.

The value of B_2^0 can be determined using the high temperature expansion of the magnetic susceptibility¹⁷⁻¹⁹ which gives B_2^0 as

$$B_2^0 = \frac{10}{3} \frac{\Theta_{ab} - \Theta_c}{(2J - 1)(2J + 3)}, \quad (7)$$

here Θ_{ab} represents the paramagnetic Curie-Weiss temperature in the direction of ab plane and Θ_c in the direction of c axis. It should be noted the above Equation (7) is only valid for isotropic exchange interactions (i.e., isotropic molecular field parameters).

Taking the values of $\Theta_{ab} = -74.7$ K and $\Theta_c = 12.8$ K obtained in the fitting procedure of Curie-Weiss behavior into the above Equation (7), we get $B_2^0 = -9.11$ K (-0.785 meV). However, with $B_2^0 = -9.11$ K fixed and B_4^0 , B_4^4 varied, fits to the magnetic susceptibility data were not optimal. This indicates the magnetic exchanges anisotropic and hence the B_2^0 value estimated above is not valid.

Then we allowed B_2^0 , B_4^0 , and B_4^4 to vary and optimization of the crystal field parameters yielded an excellent fit to the susceptibilities along both directions, as shown in Figure 3, and the obtained crystal field parameters were $B_2^0 = -4.79$ K, $B_4^0 = -0.74$ K, and $B_4^4 = 4.96$ K, while the values of λ_{ab} and λ_c of -14.65 and -10.01 emu⁻¹ mol Oe, respectively. Note that the magnitudes of the obtained parameters were comparable to those reported from CeNi_{0.8}Bi₂.¹⁴ The wavefunctions and energies of the obtained states are listed in Table II.

3. Specific Heat

The AFM transition at 6 K is reconfirmed by the sharp peak observed in the specific heat of CePd_{0.78(2)}Bi₂ as a function of temperature, as shown in Figure 4(a)

TABLE II: Energy-level schemes, and the corresponding wave functions for CePd_{1-x}Bi₂.

Energy	$ \frac{5}{2}\rangle$	$ \frac{3}{2}\rangle$	$ \frac{1}{2}\rangle$	$ \frac{-1}{2}\rangle$	$ \frac{-3}{2}\rangle$	$ \frac{-5}{2}\rangle$
361 K	-0.406	0	0	0	-0.914	0
361 K	0	-0.914	0	0	0	-0.406
100 K	0	0	1	0	0	0
100 K	0	0	0	1	0	0
0 K	0.914	0	0	0	-0.406	0
0 K	0	-0.406	0	0	0	-0.914

and 4(b). By neglecting the contribution of fluctuating magnons above T_N , the specific heat can be separated into electronic and phonon parts: γT and βT^3 . The $C/T \sim T^2$ curve is well fitted in a linear relationship in Figure 4(a). In other words, the part of $T_N < T < \sqrt{180}$ of the experimental specific heat data can be well described with the formula

$$\frac{C}{T} = \gamma + \beta T^2. \quad (8)$$

From the fitting, we estimate γ and β to be 0.191 J·mol·Ce⁻¹K⁻² and 0.00218 J·mol·Ce⁻¹K⁻⁴, respectively.

The value of the Sommerfeld coefficient γ reflects a large effective mass of electrons and suggests a moderate heavy fermion behavior, or Kondo effect. Taking $\beta = 0.00218$ J·mol·Ce⁻¹K⁻⁴ in the formula

$$\Theta_D = \left(\frac{12\pi^4 N R}{5\beta} \right)^{\frac{1}{3}}, \quad (9)$$

we can obtain the Debye temperature $\Theta_D = 150$ K. Here N refers to the the number of atoms in the chemical formula and R is the gas constant.

In Figure 4(b), the specific heat data of a non-magnetic phonon reference compound LaPd_{0.80(2)}Bi₂ are also plotted. (The LaPd_{0.80(2)}Bi₂ crystal used for the specific heat measurement doesn't have bulk superconductivity above 2 K) Subtracting the specific heat of the reference compound LaPd_{0.80(2)}Bi₂ from that of CePd_{0.78(2)}Bi₂, as shown in Figure 4(b), we can get the magnetic contribution (green line) to the specific heat and calculate the magnetic entropy (blue line) using the integral

$$S_{\text{mag}} = \int \frac{C_{\text{mag}}}{T} dT. \quad (10)$$

The magnitude of the specific heat jump associated with the AFM transition is ≈ 7 J·mol·Ce⁻¹K⁻¹, which is higher than that of CeNi_{1-x}Bi₂,²² and is used to calculate the Kondo temperature, T_K , later on. At T_N , the magnetic entropy is 3.45 J·mol·Ce⁻¹K⁻¹, which reaches 60 percent of the theoretical $R \ln 2 = 5.76$ J·mol·Ce⁻¹K⁻¹,

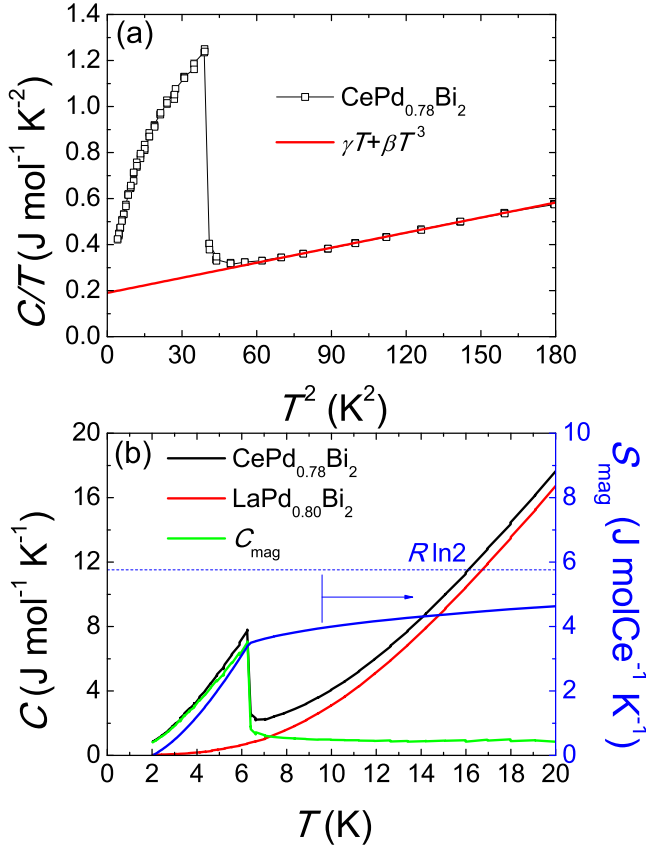


FIG. 4: (Color online) (a) Specific heat divided by temperature C/T for $\text{CePd}_{0.78(2)}\text{Bi}_2$ as a function of T^2 . Red line shows a linear fit to the data above T_N . The slope and intercept of the red line represents β and γ respectively. (b) Specific heat C versus temperature T for $\text{CePd}_{0.78(2)}\text{Bi}_2$ and its non-magnetic phonon reference compound $\text{LaPd}_{0.80(2)}\text{Bi}_2$. After the specific heat of $\text{LaPd}_{0.80(2)}\text{Bi}_2$ is subtracted from that of $\text{CePd}_{0.78(2)}\text{Bi}_2$, the magnetic contribution to the specific heat C_{mag} is obtained and leads to a magnetic entropy S_{mag} .

where $R \ln 2$ represents the entropy of the doublet ground state of Ce^{3+} ions. Kondo compounds with a magnetic ground state show less ordering of spins due to the suppressing effect of the Kondo interaction on the RKKY interaction. This degenerate magnetic ground state accounts for the reduced experimental magnetic entropy at T_N .^{23,24}

To estimate the Kondo temperature T_K of $\text{CePd}_{0.78(2)}\text{Bi}_2$, we used the method described by Bredl et al.,²⁵ where in the mean field approach the heat capacity jump ΔC_{mag} of a Kondo-lattice compound is related to its Kondo temperature. The expression of ΔC_{mag} is

$$\Delta C_{\text{mag}} = \frac{6N_A k_B}{\psi''' \left(\frac{1}{2} + x \right)} \left[\psi' \left(\frac{1}{2} + x \right) + x \psi'' \left(\frac{1}{2} + x \right) \right]^2, \quad (11)$$

where $x = (T_K/T_N)/2\pi$ and ψ' , ψ'' , and ψ''' are the first,

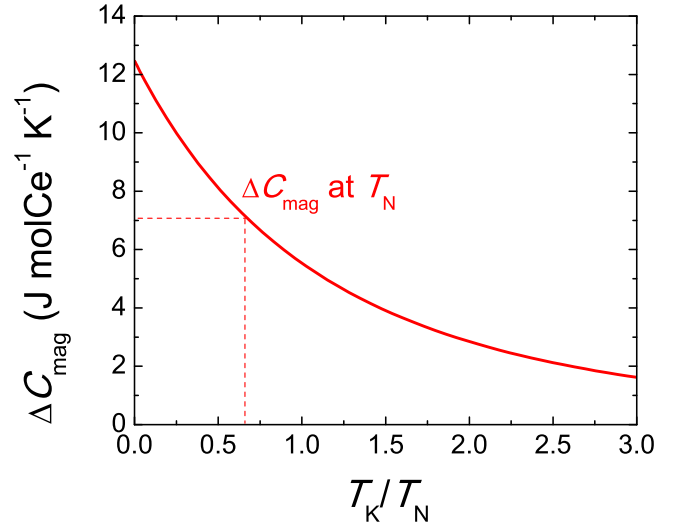


FIG. 5: (Color online) Estimation of the Kondo temperature from the heat capacity jump of magnetic transition.

second, and third derivative of the polygamma function and N_A and k_B are Avogadro's number and the Boltzmann constant respectively. A plot of ΔC_{mag} versus T_K/T_N is shown in Figure 5, from which we can conclude the Kondo temperature for $\text{CePd}_{0.78(2)}\text{Bi}_2$ is 4.0 K.

4. Resistivity

The temperature dependence of resistivity for $\text{CePd}_{0.78(2)}\text{Bi}_2$ is shown in Figure 6(a). Above 75 K, the zero-field resistivity shows a linear behavior and is weakly dependent on temperature. The weak dependence reflects a strong scattering effect in the conductive layers. The strong scattering effect could be attributed to the Pd vacancy defects in the Pd_{1-x}Bi layer. The large number of Pd vacancies can be thought of as non-magnetic impurities and play the role of scattering centers. Around 75 K the zero-field resistivity turns down gradually and then rises again at 20 K, forming a broad shoulder at 75 K and a resistivity minimum at 20 K. The minimum at 20 K is a typical Kondo-type response in resistivity. At 6 K, a sharp peak corresponding to the AFM transition is observed. The broad shoulder is possibly associated with the interplay between Kondo and CEF effects as found in some other Ce-based compounds such as CeNiX_2 ($X = \text{Si, Ge, Sn}$), $\text{Ce}_2\text{T}_3\text{Ge}_5$ ($T = \text{Ni, Rh, Ir}$) and CeNiBi_2 .^{26,28-30} At the field of 4.5 T and 9 T, the peak at T_N vanishes and shifts to lower temperatures gradually as the upturn of resistivity is also suppressed. This means the AFM ordering can be suppressed to lower temperatures and even quenched by high fields.

The resistivity of superconducting $\text{LaPd}_{0.85(2)}\text{Bi}_2$ is also plotted in Figure 6(a). The magnetic contribution to the resistivity ρ_{mag} can be obtained by subtracting the

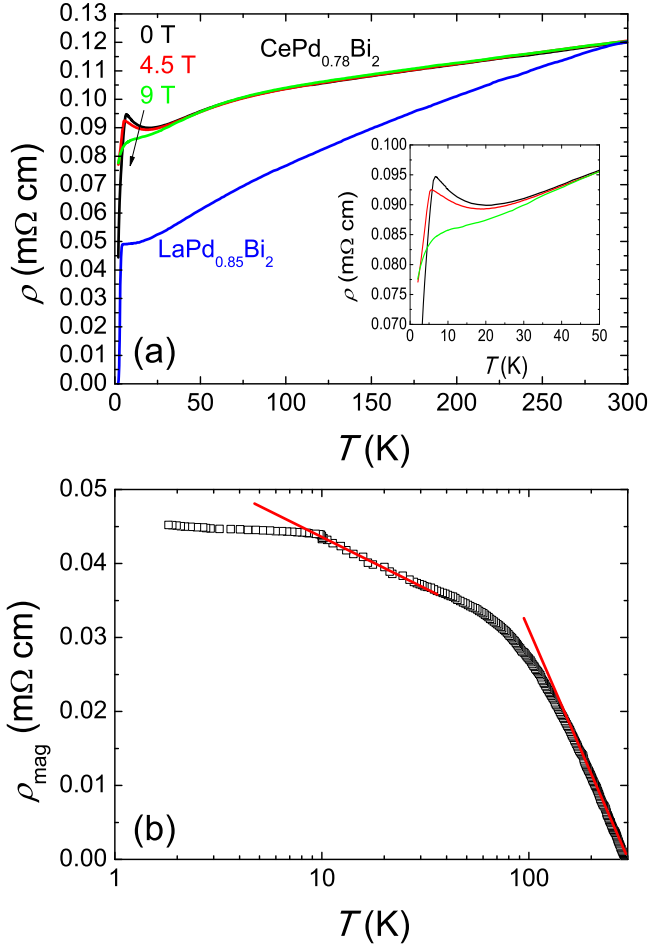


FIG. 6: (Color online) (a) In-plane resistivity of CePd_{0.78(2)}Bi₂ and superconducting LaPd_{0.85(2)}Bi₂. The fields were applied parallel to the c axis.

resistivity of LaPd_{0.85(2)}Bi₂ from that of CePd_{0.78(2)}Bi₂. In Figure 6(b), ρ_{mag} is plotted as a function of $\ln T$. ρ_{mag} is almost linear with $\ln T$ in two different temperature regions which are separated by a hump at about 75 K. According to the model of Cornut and Coqblin,²⁷ such a behavior can be expected for a Kondo-type interaction in the presence of crystal fields. The linear behaviors in two different temperature regions represent the Kondo scattering in the crystal-field ground state and in the whole multiplet of the $J = \frac{5}{2}$ state, respectively. The hump at 75 K can be considered as the energy of the overall crystal-field splitting.

5. Magnetoresistance

Magnetoresistance (MR) is a powerful tool to investigate the electronic scattering process. Here MR is expressed as

$$\Delta\rho = \frac{\rho(H) - \rho_0}{\rho_0}, \quad (12)$$

where $\rho(H)$ and ρ_0 represents the longitudinal resistivity at a magnetic field H and that at zero field, respectively. The field dependences of MR at temperatures near or above 75 K are shown in Figure 7(a) while those below 75 K in Figure 7(b). The curves in Figure 7(b) reveal a rather different feature compared to those in Figure 7(a). When $T \geq 75$ K, the MR is positive and exhibits a linear relationship with H . In sharp contrast, when $T < 75$ K, the MR becomes negative and exhibits a clear nonlinear dependence. The abnormal behavior at 5 K is attributed to the presence of AFM ordering. Collecting all the MR values at 9 T, we plot them as a function of temperature in Figure 7(c). One can see the MR is positive in sign and small in value at or above 75 K, and below 75 K the MR versus T curve diverges to the negative area and then increases rapidly in absolute value. The dramatic evolution of MR shows the scattering effect changes from conventional lattice scattering and impurity scattering (above 75 K) to a more complex scattering (below 75 K) which could be caused by the gradual emergence of the heavy Fermion behavior or CEF splitting or both.

The semiclassical transport theory predicts that Kohler's rule should be satisfied for a single-band metal with an isotropic Fermi surface.³¹ Sometimes this rule is also applicable for a multiband system when the number of charge carriers from each band is independent of temperature and the scattering rates of different bands have a similar temperature dependence.³² Kohler's rule can be written as

$$\frac{\Delta\rho}{\rho_0} = F\left(\frac{\mu_0 H}{\rho_0}\right). \quad (13)$$

This equation means that the $\Delta\rho/\rho_0$ versus $\mu_0 H/\rho_0$ curves for different temperatures, the so-called Kohler's plot, should be scaled to a universal curve if the rule is obeyed. The scaling based on the Kohler's plot for our sample is shown in Figure 7(d). It is obvious Kohler's rule is violated in our system indicating CePd_{0.78(2)}Bi₂ is a multiband system and the carrier contribution from each band varies with temperature.

6. Hall Effect

The Hall coefficient measured on CePd_{0.78(2)}Bi₂ is displayed in Figure 8. Above 75 K, the Hall coefficient R_H remains nearly temperature-independent and converges to $-1.65 \times 10^{-4} \text{ cm}^3/\text{C}$, which is consistent with the negligible positive MR and the linear behavior in resistivity above 75 K. A rough estimate from the single-band model leads to a carrier density of $3.8 \times 10^{22} / \text{cm}^3$ at these temperatures while the negative sign of Hall coefficient indicates above 75 K the transport of CePd_{0.78(2)}Bi₂ is dominated by electrons. Deviation from linearity and sign reversal is observed below 75 K in the Hall coefficient versus temperature (R_H vs T) function.

It is worth noting that the superconducting LaPd_{0.85(2)}Bi₂ has an almost constant Hall coeffi-

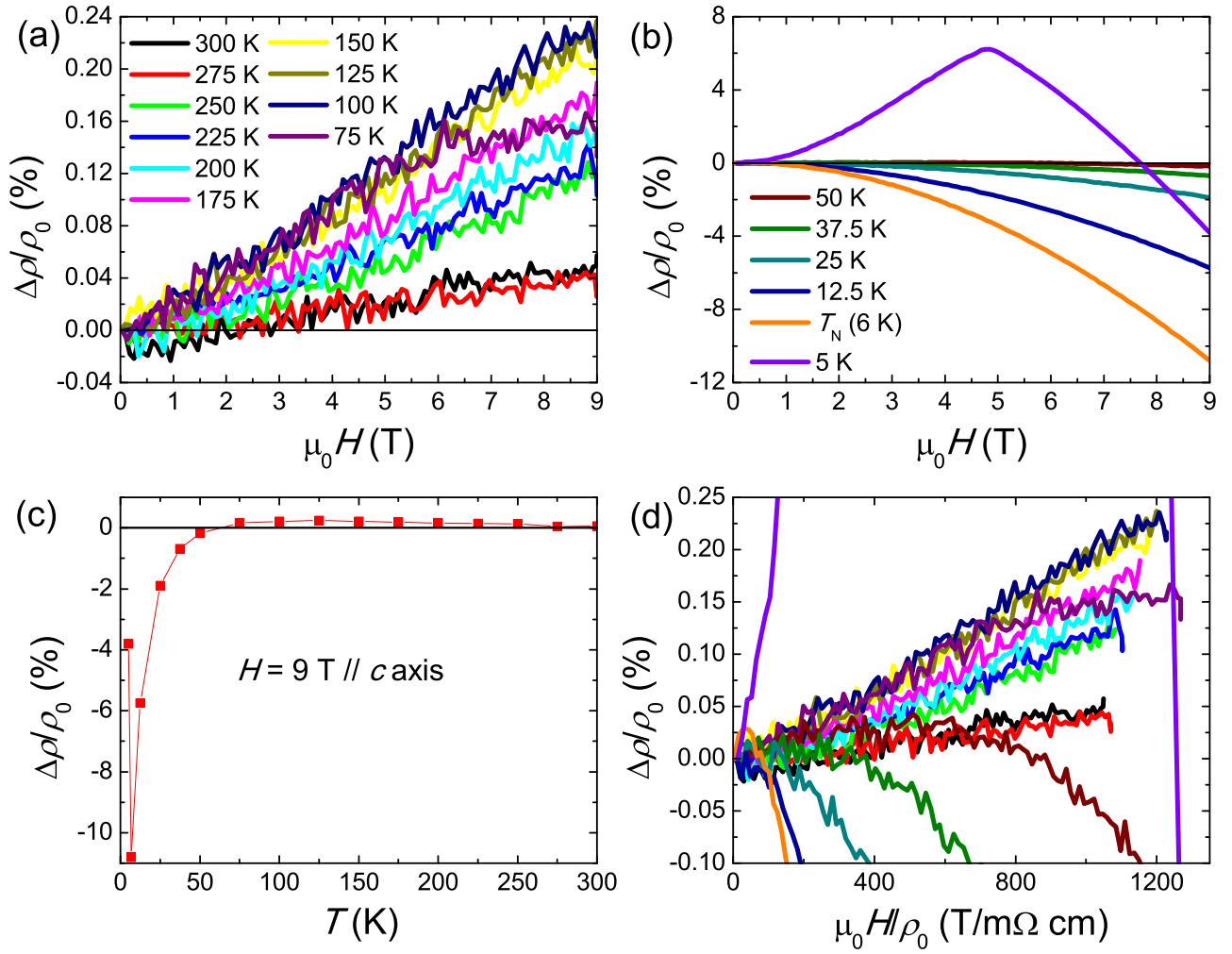


FIG. 7: (Color online) Field dependence of magnetoresistance (MR) for CePd_{0.78(2)}Bi₂ with (a) $T \geq 75$ K and (b) $T < 75$ K. (c) Temperature dependence of MR for CePd_{0.78(2)}Bi₂ at the field of 9 T. (d) The Kohler's plot of MR.

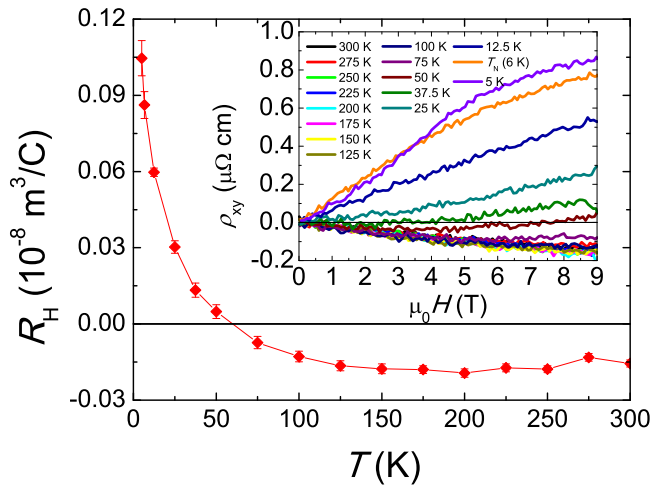


FIG. 8: (Color online) Main frame: Temperature dependence of Hall coefficient R_H for CePd_{0.78(2)}Bi₂ measured with the field perpendicular to the ab plane. Inset: Hall resistivity ρ_{xy} versus magnetic field $\mu_0 H$ at different temperatures.

cient of -1.7×10^{-4} cm³/C from 2 to 300 K, over the whole temperature region.⁵ In addition, LaPd_{0.85(2)}Bi₂ does not exhibit the shoulder-like behaviour but is nearly linear all the way in resistivity.⁵ The close Hall coefficient and the similar linear behavior of resistivity between CePd_{0.78(2)}Bi₂ above 75 K and LaPd_{0.85(2)}Bi₂ from 2 to 300 K suggest that from 75 and 300 K CePd_{0.78(2)}Bi₂ and LaPd_{0.85(2)}Bi₂ have a similar Fermi surface that does not vary in this temperature region. However, below 75 K, the interplay between Kondo and CEF effects in CePd_{0.78(2)}Bi₂ obviously reconstructs its Fermi surface topology. The partial gap of the Fermi surfaces removes the density of states on some Fermi pockets and may leave one of the hole pockets partially or fully ungapped.

7. Theoretical Calculations

To gain a fuller understanding on the physical properties, we also performed density-functional theory (DFT) calculations based on the local density approximation (LDA) with the full-potential, all-electron, linear-muffin-tin-orbital method.³³ We used the LDA+ U scheme³⁴ to approximate the localized nature of the Ce 4*f* electrons and took the $U = 7.5$ eV and $J = 0.68$ eV.³⁵ We included spin-orbit coupling interactions, which play an important role in this compound.

We performed calculations for several magnetic arrangements, including ferromagnetic (FM); A-AFM: with inter-plane AFM coupling and intra-plane FM coupling; C-AFM: with lines of Ce ions coupled ferromagnetically in a given direction [100] but with alternate lines having opposite spin orientation; and G-AFM: with Ce ions coupled antiferromagnetically with all of their nearest neighbors. To account for the possible magnetic anisotropy, we carried out calculations with magnetization aligning along the [100], [110], [111] and [001] directions, respectively. Our calculations reveal an A-AFM magnetic ground state configuration of CePdBi₂, however the numerical magnetic easy axis is [110], which is different than our experimental results. We present the density of state (DOS) of CePdBi₂ in Figure 9(a). As shown in this Figure, the Ce-4*f* state is quite narrow and located far from the Fermi energy. The Pd-4*d* states mainly disperse from -4.5 eV to Fermi level, while the Bi-6*p* bands are much wider. Regardless of magnetic configuration and magnetic easy-axis, the calculated spin moment is around $0.98 \mu_B$, indicating the Ce in CePdBi₂ is trivalent. On the other hand, the calculated orbital moment is around $-1.55 \mu_B$, which is considerably smaller than that of a free Ce³⁺ ion, clearly illustrating the importance of CEF effects in CePdBi₂.

The Pd-4*d* bands are almost fully occupied and have only a small contribution to the Fermi energy. We thus performed virtual crystal approximation calculations by adding holes into the unit cell as a uniform background to simulate the effect of Pd vacancies.³⁶ As shown in Figure 9(b), the major effect is downshift of the Fermi level. Our calculations found that the magnetic easy axis of CePd_{0.78}Bi₂ now becomes [001], which is consistent with our experimental measurements, and the magnetic configuration of CePd_{0.78}Bi₂ is still A-AFM. As shown in Figure 9(b), doping does not change the valence of Ce, and the numerical spin moment remains around $1 \mu_B$ ($0.97 \mu_B/\text{Ce}$). Doping however enhances the CEF effects, and consequently the orbital moment of CePd_{0.78}Bi₂ is quenched to $0.81 \mu_B$. As mentioned above, the energy of CEF is around 75 K, which is comparable with that of CeMSb₂ ($M = \text{Cu, Au and Ni}$).¹⁶ When the temperature is lower than the CEF energy, the orbital moment will be quenched as shown in the DFT calculations, and the magnetic behavior will deviate from the Curie-Weiss law. This agrees with our experimental magnetic susceptibility data and is also consistent with the observed

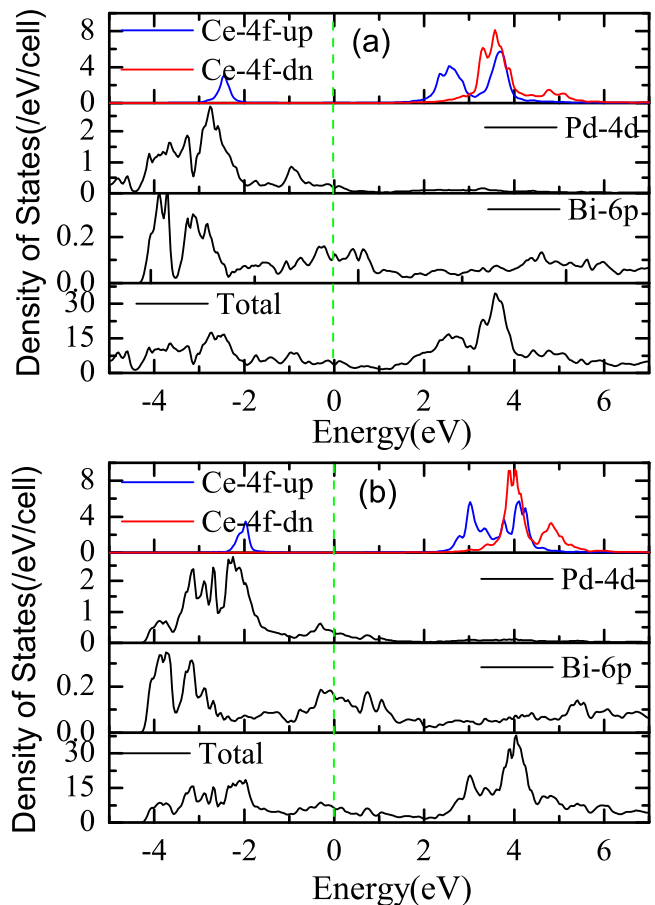


FIG. 9: (Color online) Electronic density of states (DOS) from LDA+ U +SO calculations. Fermi energy E_F is set to zero. (a) CePdBi₂: A-AFM with [110] easy axis; (b) CePd_{0.78}Bi₂: A-AFM with [001] easy axis.

Fermi surface reconstruction around 75 K.

D. Conclusions

The layered compound CePd_{1-x}Bi₂ shows antiferromagnetic Kondo-lattice behavior. In CePd_{1-x}Bi₂, the results of resistivity, magnetoresistance and Hall effect jointly reveal a conventional-metal behavior above 75 K and a strong interplay between Kondo and CEF effects below 75 K. The coexistence and competition of Kondo and RKKY interactions as well as CEF effects in CePd_{1-x}Bi₂ quench any potential superconductivity such as the one found in LaPd_{1-x}Bi₂.⁵ In other words, the Fermi surface topology of LaPd_{1-x}Bi₂ is very important to its superconductivity. The strength of f - d hybridization (or the degree of delocalization of the f electrons) in CePd_{1-x}Bi₂ is moderate. This moderate strength induces a Kondo interaction in CePd_{1-x}Bi₂ but is not enough to eliminate the RKKY interaction, so that the local moment ordering occupies the ground state. The Fermi surface reconstruction caused by Kondo and

CEF effects and the magnetic ordering induced by RKKY interaction make heavy fermion superconductivity like in CeCu_2Si_2 ³⁷ have no chance to emerge. However, the possibility of pressure-induced superconductivity exists around the quantum critical point where the AFM ordering vanishes simultaneously.

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