Magnetotransport evidence for the nontrivial topological states in the fully spin-polarized Kondo semimetal CeBi

Shuchun Huan\textsuperscript{a,1}, Xianbiao Shi\textsuperscript{b,c}, Lixuesong Han\textsuperscript{a}, Hao Su\textsuperscript{a}, Xia Wang\textsuperscript{a,d}, Zhiqiang Zou\textsuperscript{a,d}, Na Yu\textsuperscript{a,d}, Weiwei Zhao\textsuperscript{b,c}, Leiming Chen\textsuperscript{e,f}, Yanfeng Guo\textsuperscript{a,⁎}

\textsuperscript{a} School of Physical Science and Technology, ShanghaiTech University, Shanghai 201210, China
\textsuperscript{b} State Key Laboratory of Advanced Welding and Joining, Harbin Institute of Technology, Shenzhen 518055, China
\textsuperscript{c} Flexible Printed Electronic Technology Center, Harbin Institute of Technology, Shenzhen 518055, China
\textsuperscript{d} School of Materials Science and Engineering, Henan Key Laboratory of Aeronautic Materials and Application Technology, Zhengzhou University of Aeronautics, Zhengzhou, Henan 450046, China
\textsuperscript{e} School of Physical Science and Engineering, Henan Key Laboratory of Aeronautic Materials and Application Technology, Zhengzhou University of Aeronautics, Zhengzhou, Henan 450046, China
\textsuperscript{f} Analytical Instrumentation Center, School of Physical Science and Technology, ShanghaiTech University, Shanghai 201210, China

Article info
Received 5 November 2020
Received in revised form 12 April 2021
Accepted 14 April 2021
Available online 21 April 2021
Keywords:
CeBi
Magnetotransport
Nontrivial band structure

Abstract
Combination of nontrivial topology of band structure and magnetism in a single material would provide an excellent platform for studying their interplay as well as for discovering exotic physical properties.

1. Introduction
The Kondo-lattice system provides extraordinary opportunities in investigating the interplay between localized $f$ moments and itinerant electrons, which is capable of giving rise to an array of intriguing physical properties, such as heavy fermion behavior [1], unconventional superconductivity [2,3], complicated magnetic ordering [4–7], mixed-valence states [8] and Kondo insulating/semimetal phases [9], etc. The localized $f$ moments are generally coupled with the itinerant electrons via the antiferromagnetic (AFM) Kondo exchange which is competing with the Ruderman-Kittel-Kasuya-Yoshida (RKKY) interaction that favors the ordering of the $f$ moments [10–12]. Such a competition can increase the resistance at low temperature until the Kondo coherence temperature at which the itinerant electrons become entangled with the $f$ moments and cause a Landau Fermi liquid with largely enhanced effective electron mass [9,13]. Moreover, the strong electronic correlation, large spin-orbit coupling (SOC) and intricate crystal field splitting in a Kondo system are nearly degenerate in energy scale and are believed to tightly correlate with the electronic structure and hence the physical properties. Owing to the rich exotic quantum phenomena, this family of materials have been subjected to immense research interest.

In recent several years, the Kondo-lattice system has been tied with the nontrivial band structure topology. The binary cerium monopnictides CeX (X = P, As, Sb, and Bi) are such clear-cut examples [14–18]. They exhibit complicated magnetic behaviors closely related to the low-energy electronic structure against external conditions including temperature, pressure, and magnetic field, etc., known as the Devil’s staircase [19–22]. In the several Ce-based intermetallic compounds with low carrier density, nontrivial topological states with strong electronic correlation feature were already

https://doi.org/10.1016/j.jallcom.2021.159993
0925-8388/© 2021 Elsevier B.V. All rights reserved.
theoretically predicted, which however remain unverified experimentally. From the present studies, it seems that the electronic structures of CeBi are primarily topologically trivial except that of the heaviest CeBi [15,16]. CeBi crystallizes in the simple rock-salt structure with the space group Fm-3m. It is characterized by a very complicated magnetic phase diagram hosting several magnetic states [21,22]. In its electronic structure, the Bi p orbital contributes two hole pockets at the Γ point in the bulk fcc Brillouin zone (BZ) and the Ce 5d orbital denotes one electron pocket at the X point. The topological insulator (TI) state could emerge with the p-5d band inversion induced by the p-f mixing, i.e. the strong hybridization between the Bi p state and the crystal-field-split level of the Ce 4f state [23,24]. The nontrivial topological states in CeBi was detected by using the angle-resolved photoemission spectroscopy (ARPES) [15,17], showing Dirac-cone-like band dispersions on the (001) surface in the paramagnetic state associated with bulk p-f band inversion. Upon cooling down, undergoing two AFM transitions at around 25 K and 14 K, respectively, CeBi exhibits a double-Dirac cone band structure around the first AFM transition and then a single Dirac cone band structure around the second AFM transition, thus exposing an intimate relation between the electronic structure and magnetism. With the application of magnetic field, the AFM phases could transform into an induced ferromagnetic state with variation of magnetization in several steps [21,25]. However, the characteristic nontrivial topological surface states (TSSs) have not been detected yet for CeBi, because the TSSs expected at the Γ point of the surface BZ are buried under the projected Bi 6p trivial band and those at the M point are gapped by the mutual hybridization between the band inversions at two nonequivalent X points [15,17]. Moreover, the band structure of the ferromagnetic (FM) state remains unexplored. To achieve more insights into the nontrivial topological states, alternatively, magnetotransport measurements are useful through probing the Fermi surface (FS). In fact, the magnetotransport measurement was already employed as an effective route to determine the nontrivial topological band structure of CeSb, which unveiled that the external magnetic field can induce nontrivial topological states that are likely due to the spin splitting in the fully spin-polarized FM state according to the band structure calculations [26]. For CeBi, the magnetotransport measurements revealed strong correlation between the magnetism and magnetoresistance [27,28], while the relation between magnetotransport and the nontrivial topological states, especially in the spin-polarized state, has not been studied. We were thus motivated to perform magnetotransport measurements on CeBi.

2. Experiment details

The CeBi single crystals were grown by using indium as the flux. The raw materials were mixed in a molar ratio with Ce: Bi: In = 1: 1: 18 and placed into an alumina crucible. The assembly was sealed into a quartz tube under vacuum and was then heated up to 1150 °C in a furnace with holding at the temperature for 15 h. After the reaction, the furnace was cooled down to 750 °C at a temperature decreasing rate of 3 °C/h. At 750 °C, the assembly was taken out of the furnace and immediately put into a high speed centrifuge to remove the excessive indium flux. The CeBi crystals were then left in the crucible with the size of 1.2 × 1.0 × 0.3 mm³ as shown in Fig. 1(a).

Before physical properties characterizations, the phase and quality of CeBi were carefully examined. The crystals were characterized at 298 K on a Bruker D8 Venture single crystal X-ray diffractometer with Mo Kα (λ = 0.71073 Å). The electrical transport properties were measured in a commercial DynaCool Physical Properties Measurement System (PPMS) by attaching the Au wires onto the sample in a standard four-wire configuration as illustrated in Fig. 2(a). The magnetic properties were characterized on a commercial Magnetic Property Measurement System (MPMS-3). The magnetic susceptibility χ was measured in the zero-field-cooling (ZFC) and field-cooling (FC) modes with the magnetic field B = 0.1 T. First principles calculations were performed based on the density functional theory (DFT) encoded in the Vienna ab initio Simulation Package (VASP) [29,30]. For the spin-polarized and paramagnetic band calculations, the cutoff energy for the plane-wave basis set was set as 500 eV, the BZ sampling was done with a Γ-centered Monkhorst-Pack k-point mesh of size 14 × 14 × 14, and the total energy difference criterion was defined as 10⁻⁸ eV for self-consistent convergence. In order to simulate the paramagnetic CeBi, we treated the 4f electrons on Ce as core electrons. The modified Becke-Johnson (mBJ) [31,32] potential at the meta-GGA level was adopted to obtain the accurate band inversion strength and the band order. For the calculations in FM CeBi, the GGA+U method was adopted, and the exchange parameter U = 5.5 eV and J = 0.68 eV were applied to the Ce 4f states. The maximally localized Wannier functions [33,34] for Ce-d and Bi-p orbitals were constructed to determine the hopping parameter values for tight-binding model. The WannierTools package

![Fig. 1.](image1.png)

- (a) Optical image of CeBi single crystal. (b) NaCl-type crystal structure of CeBi with the space group Fm-3m. (c)-(e) Diffraction patterns in the reciprocal space along (h k 0), (h 0 l) and (0 k l) directions.

![Fig. 2.](image2.png)

- (a) Temperature dependence of the longitudinal resistivity ρxx at different magnetic fields. Figure insert is an illustration for the magnetotransport measurement setup. The dashed line with arrow shows the change of ρxx with increasing the magnetic field. (b) Temperature dependence of the magnetic susceptibility at B = 0.1 T. (c) Magnetic field dependent of longitudinal resistivity ρxx(B) at various temperatures up to 26 K. (d) Magnetic field dependent of isothermal magnetizations at various temperatures up to 26 K. The dashed line indicates the critical magnetic field for magnetization saturations at 2 K.
which works in the tight-binding framework, was used to compute the surface spectrum including the surface density of states and the Fermi arcs based on the iterative Green’s function method [36].

3. Results and discussion

The collected room temperature diffraction patterns could be satisfyingly indexed on the basis of a cubic structure in the space group Fm-3m (No. 225), with the lattice parameters a = b = c = 6.52 Å and α = β = γ = 90°, which are consistent with those in previous literatures [21,22]. Seen in Fig. 1(c)-(e), the perfect reciprocal space reflections in the single crystal X-ray diffraction patterns without any other miscellaneous points indicate that the crystals have a high quality.

As shown in Fig. 2(a), the longitudinal resistivity ρxx (B = 0) of CeBi at high temperature displays a typical semimetal behavior and a sharp cusp when the temperature was decreased down to Tc = 25.5 K, signifying the influence from the magnetic order at this temperature. The increase of magnetic field can gradually suppress the cusp in ρxx to high temperatures, which manifests the typical feature of the AFM order. After Tc, ρxx decreases sharply. With the application of magnetic field, ρxx shows an upturn at low temperature, which is commonly observed in topological semimetals such as CeSb [37], LaBi [38,39] and LaSb [40], etc. The temperature dependence of magnetic susceptibility χ(T) measured at B = 0.1 T clearly exhibits two anomalies upon cooling down to Tc = 26 K and TN/2 = 13 K, shown in Fig. 2(b). The previous powder neutron diffraction measurements unveiled that the two anomalies correspond to the paramagnetic to AFM transition at Tc and the type-I to type-IA AFM structure transition at TN/2 [21], respectively. The identified two magnetic transition temperatures are in good accordance with those in previous reports [41,42].

The temperature dependence of ρxx(B) presented in Fig. 2(c) displays the similar behavior as reported in earlier work [26,27], which decreases monotonically with increasing B above TN/2, while below TN/2 it starts to increase with the further increase of B, thus giving an extremely large magnetoresistance (XMR) of ~ 10% at 2 K and 9 T. Moreover, it is also visible that ρxx(B) (B > 0) and ρxx(B = 0) shows a crossing point at TN/2, exposing a transition from negative MR above TN/2, which is known to be accessed from the Landau level (LL) index fan presented. At a first glance, the kinks at B = 4.7 T signifying the magnetic phase transition from AFM to FM states are clearly visible in ρxx(B). When B is above 5T, ρxx(B) shows remarkable quantum oscillations, seen also in Fig. 2(a) after subtracting the polynomial background. It should be noted that when the temperature is above TN/2, quantum oscillations are invisible, implying that the double Dirac-cone structure is possibly far away from the Fermi level E0, which could not be detected by magnetotransport measurements. After carefully subtracted the polynomial background of the MR, denoted by Δρxx, striking SDH oscillations are displayed. The SDH oscillations at different temperatures from 2 to 6 K against the reciprocal magnetic field 1/B are plotted in Fig. 3(a), which could be well described by the Lifshitz-Kosevich (L-K) formula [44,45]:

\[ \Delta \rho_{xx} \propto R_i R_0 \cos \left( \frac{2\pi \beta F a B}{B} + \phi \right) \]

where \( R_i \) and \( R_0 \) are the Pauli and Fermi resistance, respectively, \( F = (h/2m^*q)A \) is the frequency of oscillation, \( \beta \) is the phase shift, \( \alpha_0 = E_B/m^*r_0 \) is the cyclotron frequency with \( m^* \) denoting the effective cyclotron mass, and \( T_0 \) is the Dingle temperature defined by \( T_0 = h/2\pi\hbar q^2 T_0 \) with \( T_0 \) being the quantum scattering lifetime. The fast Fourier transform (FFT) spectrum of the SDH oscillations at 2 K, depicted in Fig. 3(b), disclose three frequencies at \( F_a = 230 T, F_{2a} = 460 T \) and \( F_b = 554 T \). The corresponding external cross-sectional areas of the FS are \( A = 2.19 \) and 5.28 nm\(^2\), respectively, calculated by using the Onsager relation \( F = (h/2m^*q)A \). Since the \( F_b \) is too weak to be analyzed, we only performed analysis of \( F_a \). According to a comparison with the theoretical calculation results which will be presented later, the fundamental frequency \( F_a \) likely arises from the electron pocket centered at the X point of the BZ as shown in Fig. 6(b). The effective cyclotron mass \( m^* \) at the Fermi energy could be obtained by fitting the temperature dependence of the FFT amplitude using the temperature damping factor of the L-K equation expressed as \( R_i \), as is shown by the Fig. 3(d), giving \( m^* = 0.363 m_e \) where \( m_e \) denotes the free electron mass.

In a Dirac or Weyl system, the pseudo-spin rotation under a magnetic field generally can produce a nontrivial Berry phase \( \phi_B \) which could be accessed from the Landau level (LL) index fan

![Fig. 3](https://example.com/fig3.png)

(a) SDH oscillatory component as a function of 1/B after subtracting the polynomial background of ρxx(B), (b) FFT spectra of Δρxx(F), (c) Landau level index N plotted against 1/B at 2 K. Inset enlarges the intercepts of the fitting. (d) Temperature dependence of relative FFT amplitudes of the SDH oscillations of a band. The solid lines denote the fitting by using the L-K formula.
Table 1
Parameters derived from SdH oscillation for CeBi.

<table>
<thead>
<tr>
<th>$F$ (T)</th>
<th>$A$ (nm$^{-2}$)</th>
<th>$K_{\theta}$ (nm$^{-1}$)</th>
<th>$\nu_{F}$ (m/s)</th>
<th>$m'/m_{e}$</th>
<th>$T_{D}$ (K)</th>
<th>$\tau_{0}$ (s)</th>
<th>$\mu$ (cm$^{2}$/Vs)</th>
<th>Berry phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>230</td>
<td>2.19</td>
<td>0.835</td>
<td>2.667 $\times$ 10$^{4}$</td>
<td>0.363</td>
<td>7.97</td>
<td>1.53 $\times$ 10$^{-13}$</td>
<td>717.9</td>
<td>0.96m</td>
</tr>
</tbody>
</table>

Fig. 4. (a) Angle dependence of SdH oscillations at $T=2$ K. Figure inset shows the angular relationship between the magnetic field and current. (b) SdH oscillatory component as a function of $1/B$ after subtracting the polynomial background of $\rho_{xx}(B)$. (c) FFT spectra of $\Delta\rho_{xx}(B)$ for difference angles at 2 K. The dashed line indicates the angle dependence of main FFT peak.

Fig. 5. Electronic band structure of CeBi calculated by using the mBJ potential (a) without and (c) with SOC. The red and blue dots denote the contribution of Ce-$d$ and Bi-$p$ bands. Insets show the enlarged region around the X point. (b) The Fermi surface of CeBi, which is composed of an electron pocket centered at the X points and two hole pockets nested around the center of the BZ. (d) Calculated surface states of CeBi on the (001) surface.
Fig. 6. (a) Calculated band structure of CeBi in the spin-polarized FM state by GGA+U with $U=5.5$ eV and $J=0.68$ eV for the Ce-4f orbitals. A pair of Weyl nodes near the Fermi level along the $F-X$ direction, named as $w_1$ and $w_2$, are presented by the enlarged view in the red box. (b) The Fermi surface sheets of CeBi correspond to each band crossing of the Fermi level in (a). (c) The calculated angle-dependent dispersions of the FFT frequencies corresponding to the Fermi pockets shown in (b), where the black square line represents experimental data for $F_w$ and agrees well with Band 6 with the direction of magnetic field being rotated from [001] to [100].

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

The authors acknowledge the support by the National Natural Science Foundation of China (Grant No. 11874264), the strategic Priority Research Program of Chinese Academy of Sciences (Grant No. XDA18000000), the Shenzhen Peacock Team Plan (Grant No. KQTD20170809110344233), and the Bureau of Industry and Information Technology of Shenzhen through the Graphene Manufacturing Innovation Center (Grant No. 201901161514). L.M.C. is supported by the Key Scientific Research Projects of Higher Institutions in Henan Province (19A140018). Y.F.C. thanks the starting grant of ShanghaiTech University and the Program for Professor of Special Appointment (Shanghai Eastern Scholar). The authors thank the support from Analytical Instrumentation Center (#SPST-AIC10112914), SPST, ShanghaiTech University.

4. Conclusion

In summary, our magnetotransport measurement and first principles calculations reveal that the magnetic exchange has significant influence on the electronic band structure of the Kondo semimetal CeBi. The revealed nontrivial topological states from the magnetotransport measurements and first principles calculations of the fully spin-polarized magnetic structure correspond to the magnetically driven Weyl states. The results indicate that the topological states of CeBi could be manipulated by the application of external magnetic field, thus providing an excellent platform for the study of the interactions among the magnetism, nontrivial topological states, and the Kondo physics.

CRediT authorship contribution statement

Yanfeng Guo proposed the original idea; Shuchun Huan did the crystal growth with the help from Luxuesong Han. Shuchun Huan measured the magnetizations and magnetotransport properties with the help from Hao Su, Xia Wei, Xia Wang, Zhiqiang Zou. Shuchun Huan characterized the crystals and analyzed the crystal structure with the help from Na Yu. Xianbiao Shi did the first principles calculations under the direction of Weiwei Zhao. Yanfeng Guo and Shuchun Huan wrote the paper.

References


H. Heer, A. Ferrer, W. Halg, O. Vogt, Neutron spectroscopy in the cerium


