Absence of Andreev bound states in β-$PdBi_2$ probed by point-contact Andreev reflection spectroscopy

Liqiang Che,[1] Tian Le,[1] C. Q. Xu,[2] X. Z. Xing,[3] Zhixiang Shi,[3] Xiaofeng Xu,[2] and Xin Lu[1,4,*]

[1]*Center for Correlated Matter and Department of Physics, Zhejiang University, Hangzhou 310058, China*

[2]*Department of Physics and Hangzhou Key Laboratory of Quantum Mattters, Hangzhou Normal University, Hangzhou 310036, China*

[3]*Department of Physics, Southeast University, Nanjing 211189, China*

[4]*Collaborative Innovation Center of Advanced Microstructures, Nanjing 210093, China*

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We report point-contact spectroscopic studies on high quality single crystalline β-$PdBi_2$ with a superconducting $T_c = 5.2$ K. Our measurements show a typical double-peak structure in the voltage-biased junction conductance at low temperatures, probably excluding the existence of topological Andreev bound states. The conductance curves can be well fitted with the standard Blonder-Tinkham-Klapwijk model for s-wave superconductors, yielding a superconducting gap $\Delta_0 \simeq 0.92$ meV with $2\Delta_0/k_BT_c \sim 4.1$. Our results strongly suggest that β-$PdBi_2$ is a conventional intermediate-coupling s-wave superconductor.

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The topological aspects of electronic states have become a research frontier in the field of condensed matter physics and have attracted intensive attention in recent years, where exotic states emerge, such as topological insulators, Weyl semimetals, and topological superconductors [1–4]. Among them, a topological superconductor hosts a fully gapped bulk state and gapless surface bound state. The long-sought-after Majorana fermions, their own antiparticles [5], are proposed to exist at the edge of a topological superconductor, which are not only of scientific interest for fundamental physics, but also a potential candidate for applications in spintronics and quantum computation [6]. Majorana fermions are claimed to have been observed in several hybrid artificial structures, such as an InAs nanowire in proximity with an Al superconductor in a magnetic field [7] or ferromagnetic Fe chains on a superconducting Pb film [8]. In such devices, Majorana fermions are manifested as a zero-bias conductance peak (ZBCP) in the tunneling spectra [9], while scanning tunneling spectroscopy (STS) on iron chains has explicitly identified localized Majorana fermions at both ends of the chain [8].

Tuning topological states through pressure or doping is proposed to be another effective way to induce topological superconductivity [10]. Recent mechanical point-contact spectroscopy (PCS) measurements on crystals of the three-dimensional (3D) Dirac semimetal Cd_3As_2 suggest that exotic superconductivity emerges in the local point-contact area, probably due to inhomogeneous stress exerted by the sharp tip [11,12]. Bulk superconductivity was also discovered in doped topological insulators such as $Cu_xBi_2Se_3$ [13] and $Sn_{1-x}In_xTe$ [14], even though $Cu_xBi_2Se_3$ shows a relatively small superconducting volume fraction. A pronounced ZBCP was observed in earlier soft PCS studies on both $Cu_xBi_2Se_3$ [15] and $Sn_{1-x}In_xTe$ [16], which is claimed to support the existence of Majorana fermions. However, recent STS and PCS measurements on $Cu_xBi_2Se_3$ instead favor a fully gapped conventional s-wave superconducting state in $Cu_xBi_2Se_3$ [17,18]. The controversy may be partly caused by the intrinsic inhomogeneity associated with doping or strain and it is thus desirable to search for clean topological superconducting systems. Recent spin- and angle-resolved photoemission spectroscopy (ARPES) measurements on an earlier reported superconducting compound, β-$PdBi_2$ with $T_c \sim 5$ K, show that several nontrivial topological surface bands cross the Fermi energy E_F [19], indicating that β-$PdBi_2$ could be a promising candidate for a stoichiometric topological superconductor and may offer a rare opportunity to explore Majorana fermions.

Several superconducting phases have been found in Pd-Bi binary systems [20]: noncentrosymmetric α-PdBi ($T_c \sim 3.8$ K) [21], α-$PdBi_2$ ($T_c \sim 1.7$ K), centrosymmetric β-$PdBi_2$ ($T_c \sim 5$ K), and γ-$Pd_{2.5}Bi_{1.5}$ ($T_c \sim 3.7$ K). Among them, the β-$PdBi_2$ phase has a tetragonal structure in the $I4/mmm$ space group with lattice parameters $a = 3.36$ Å and $c = 12.98$ Å. Chemical doping and high pressure studies [22] show that superconducting T_c monotonically decreases in hole-doped $PdBi_{2-x}Pb_x$, electron-doped Na_xPdBi_2, or under physical pressure. Band structure calculations of β-$PdBi_2$ showed the presence of multiple Fermi surface (FS) sheets, with an estimated electron-phonon coupling constant $\lambda_{\text{el-ph}} \sim 3.66$, indicating an intermediate-coupling strength [23,24]. Temperature-dependent upper critical field and earlier specific heat data [25] support the multigap nature of superconductivity in β-$PdBi_2$, with $2\Delta_1/k_BT_c \sim 2.5$ and $2\Delta_2/k_BT_c \sim 6$. However, low-temperature STS measurements [26] on β-$PdBi_2$ single crystals argue for multiband superconductivity in β-$PdBi_2$, where each band has the same gap magnitude of $\Delta_0 = 0.76$ meV ($2\Delta_0/k_BT_c = 3.53$), while recent muon spin relaxation (μSR), calorimetric, and Hall-probe magnetometry measurements also support a fully open single gap in β-$PdBi_2$ [27,28]. Complimentary to STS, point-contact spectroscopy is a powerful tool to probe and clarify the superconducting gap structure [29–32]. Meanwhile, it is also straightforward to identify Majorana fermions via the presence of surface Andreev bound states (ABS).

In this article, we report point-contact spectroscopy measurements to determine the superconducting gap structure in

*Corresponding author: xinluphy@zju.edu.cn

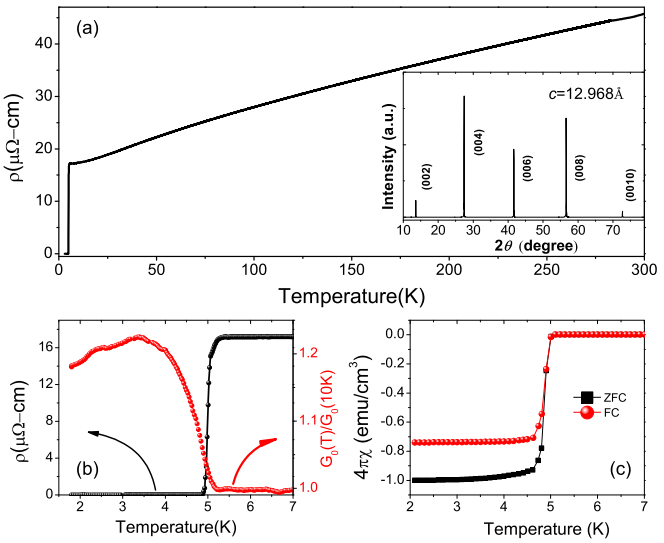

FIG. 1. (a) The electrical resistivity of a β-$PdBi_2$ single crystal, showing a superconducting transition temperature of 5.2 K, while the single crystal x-ray diffraction pattern at room temperature is shown in the inset. (b) The temperature dependence of zero-bias conductance of a point contact on a single crystal of β-$PdBi_2$, $G_0(T)$, showing a superconducting transition temperature consistent with resistivity measurements. (c) The magnetic susceptibility of a β-$PdBi_2$ single crystal. Squares and solid circles represent zero-field cooling (ZFC) and field cooling (FC), respectively, in a magnetic field of 10 Oe.

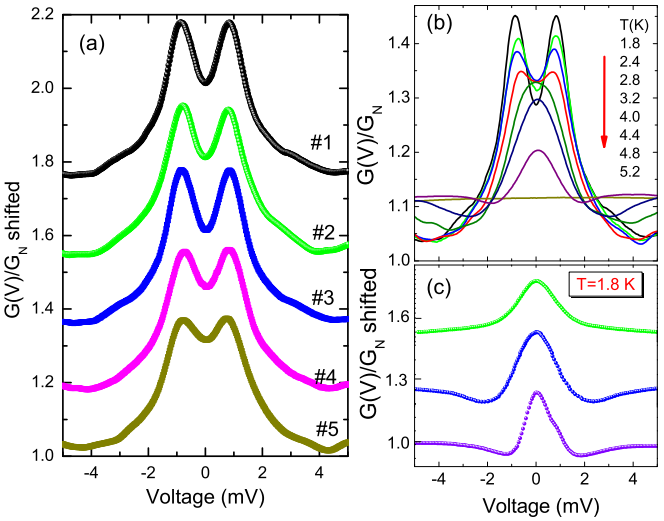

FIG. 2. (a) Point-contact spectra of β-$PdBi_2$ for different contacts at 1.8 K with the typical double-peak structure. The conductance curves are shifted for clarity. (b) The temperature evolution of $G(V)$ for one set of point-contact spectra; (c) zero-bias conductance peaks observed at 1.8 K, which are probably due to the contact heating effect.

high quality β-$PdBi_2$ single crystals. The conductance curves can be fitted with the standard Blonder-Tinkham-Klapwijk (BTK) model with a conventional s-wave BCS gap, suggesting the probable absence of Majorana fermions in β-$PdBi_2$.

β-$PdBi_2$ single crystals were grown via a melt-growth method, where stoichiometric mixtures of $Pd : Bi = 1 : 2$ were mixed thoroughly and then sealed in an evacuated quartz tube. The samples were heated to 700 °C, followed by cooling down to 450 °C at a rate of 3 °C/h. In order to avoid the formation of the α-$PdBi_2$ phase, the quartz tube was then rapidly quenched in iced water. Large β-$PdBi_2$ single crystals with a typical size of 5 mm were obtained, and they show a resistive superconducting transition at $T_c \sim 5.2$ K with a narrow transition width $\Delta T = 0.2$ K, as shown in Fig. 1(b). The magnetic susceptibility shown in Fig. 1(c) also shows a superconducting transition around 5 K and a full superconducting volume fraction, indicating high sample quality. The structure of the single crystalline samples was characterized by powder x-ray diffraction (XRD) at room temperature using a Rigaku diffractometer with Cu $K\alpha$ radiation and a graphite monochromator as shown in the inset of Fig. 1(a), where [001] crystallographic orientation of the tetragonal lattice can be confirmed with $c = 12.96$ Å and the presence of impurity phases can be excluded. The soft point-contact spectroscopy method was employed, where gentle contacts with β-$PdBi_2$ were prepared by attaching a 25-μm-diam platinum wire with a drop of silver paint at the end, on the freshly cleaved surface at ambient pressure and room temperature. In such a configuration, scattering across the interface is assumed to occur in thousands of parallel nanoscale channels between the individual silver particles and the crystal surface. The conductance curves as a function of bias voltage were measured with the conventional lock-in technique in a quasi-four-probe configuration. A Quantum Design physical property measurement system (PPMS) was used to cool the samples down to 1.8 K and apply a magnetic field. A representative curve of the point-contact zero-bias conductance as a function of temperature $G_0(T)$ is shown in Fig. 1(b), along with its resistivity near the superconducting transition, indicating the nondegradation of the surface layer, where the T_c is the same as the bulk.

Dozens of contacts have been measured on β-$PdBi_2$ crystals, and Fig. 2(a) shows some representative conductance curves at the lowest temperature $T = 1.8$ K for junctions perpendicular to the ab plane, which clearly exhibit two symmetric peaks around the bias voltage $\simeq \pm 0.82$ mV. Two symmetric side dips are noticeable at a larger voltage bias, which are probably caused by the current heating effect. The electronic mean free path ℓ at low temperatures is as small as $\ell = 18.0$ nm, estimated from the residual resistivity ρ_0 and specific heat coefficient γ of β-$PdBi_2$ ($\rho_0 \sim 17.0$ $\mu\Omega$ cm just above T_c and $\gamma \sim 13.0$ mJ/mol K^2), making most of the contacts not in the pure ballistic limit due to the limitation of the contact size. The junction heating effect cannot be avoided in all of our measured contacts [33,34]. We have analyzed the double-peak $G(V)$ curves with the standard BTK model to accurately determine the superconducting gap Δ [35], where optimal fitting can be achieved inside the voltage region $[-\Delta, \Delta]$ while a systematic deviation exists in the dip region. Such a deviation can generally cause a slight misestimation of the gap value [33], however, it can be neglected here since the dip voltages are quite distant from the superconducting gap, as in the case of YNi_2B_2C [36].

The temperature evolution of the point-contact spectra of β-$PdBi_2$ is shown in Fig. 2(b), where the double peaks shift to a smaller voltage and are smeared into one single zero-bias

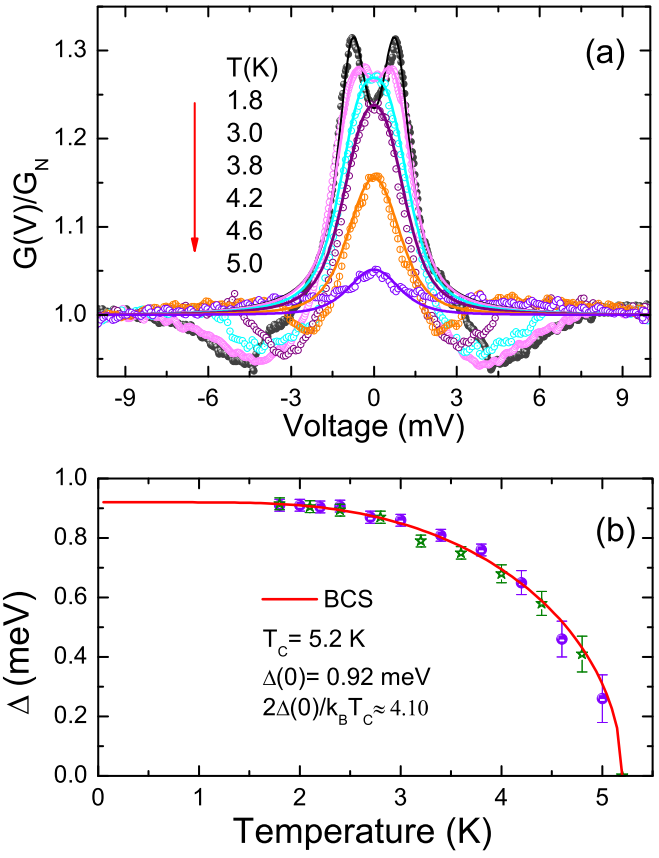

FIG. 3. (a) Temperature dependence of the normalized conductance curves for one set of Ag-paint/β-$PdBi_2$ point-contact spectra (dots) with BTK optimal fittings included for comparison (solid lines). (b) Two sets of BTK-fitted superconducting gaps Δ in β-$PdBi_2$ as a function of temperature, which follow the standard BCS curve (solid line), yielding $2\Delta_0/k_BT_c \sim 4.10$.

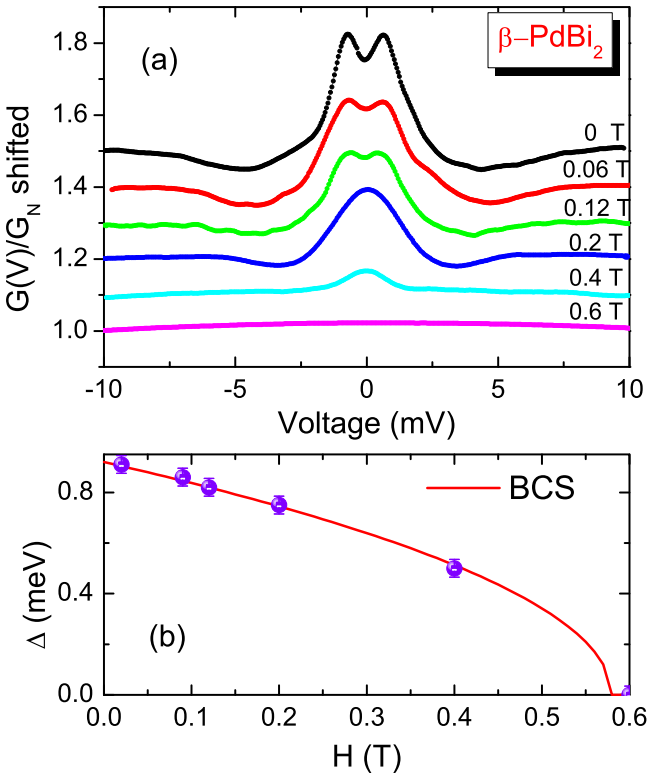

FIG. 4. (a) Point-contact spectra of β-$PdBi_2$ at 1.8 K in different magnetic fields, where the conductance curves are shifted for clarity and the superconductivity is completely suppressed in a field of 0.6 T. (b) BTK-fitted superconducting gap of β-$PdBi_2$ at 1.8 K under different magnetic fields in comparison with the theoretical predictions of a BCS superconductor in an applied field (solid line).

peak with increasing temperature, and finally disappear at T_c. Figure 3(a) shows one set of temperature-dependent conductance curves $G(V)$ for β-$PdBi_2$ and the BTK fitting curves are also included for comparison. Two sets of fitted gap values for two different point contacts on β-$PdBi_2$ as a function of temperature are plotted in Fig. 3(b), which are consistent. They follow the predicted behavior of a standard BCS superconductor, and the zero-temperature superconducting gap (Δ_0) is estimated to be 0.92 meV, yielding $2\Delta_0/k_BT_c \sim 4.10$, which is slightly larger than the BCS weak-coupling value 3.52. Our measured Δ_0 is corroborated by recent calorimetric and Hall-probe magnetometry measurements. However, the STS measurement on β-$PdBi_2$ revealed a single gap with $\Delta_0 = 0.76$ meV and $2\Delta_0/k_BT_c \sim 3.53$, where the smaller coupling strength is explained by the possible proximity effect from bulk to a metallic surface state [28]. The origin of this small discrepancy between different measurements is still an open issue.

We examined the effect of magnetic field on the point-contact spectra of β-$PdBi_2$ by applying a magnetic field up to 0.6 T perpendicular to the ab plane. The double-peak structure at 1.8 K is gradually smeared into a zero-bias peak in the conductance curve and the enhanced Andreev reflection completely vanishes at $B \simeq 0.6$ T, as shown in Fig. 4(a). This yields a superconducting coherence length $\xi = \sqrt{\frac{\Phi_0}{2\pi H_{c2}}} \sim 23.4$ nm, which is consistent with previous reports. Figure 4(b) shows the magnetic field dependence of the superconducting gap obtained from fitting the BTK model, and it follows the theoretical prediction for a one-gap type-II BCS superconductor in a magnetic field with the formula $\Delta = \Delta_0(1 - H/H_{c2})^{1/2}$ in the vortex state [37]. This result also suggests that β-$PdBi_2$ is a typical BCS superconductor.

As a signature of topological superconductors [38,39], the gapless surface ABS host the Bogoliubov quasiparticles as a realization of Majorana fermions in condensed matter systems, and the key experimental signature is the observation of a robust ZBCP in the tunneling conductance. However, a ZBCP is absent in most of our point-contact data on β-$PdBi_2$ and therefore the presence of topological Andreev bound states can be excluded on the surface of β-$PdBi_2$, even though topologically protected surface bands have been reported in ARPES. The fully gapped density of states in the reported low-temperature scanning tunneling spectra of β-$PdBi_2$ [26] also indicate the absence of Andreev bound states, while for intrinsic topological superconductors, the ZBCP should persistently occur for the junctions from the transparent to insulating limit. A ZBCP can sometimes occur in our point-contact measurements on β-$PdBi_2$, as shown in Fig. 2(c), which is likely extrinsic due to the heating effect for the contact

in the thermal limit. This is not likely to be a genuine signal of zero-energy Majorana fermions, since the double-peak structure in the conductance curves is predominantly observed. In a recent PCS study on microfabricated Au/$Cu_xBi_2Se_3$ junctions [18], the observed ZBCP was also claimed to be extrinsic. However, in the case of its noncentrosymmetric counterpart α-BiPd with a probable mixture of spin-singlet and spin-triplet pairing, gapless edge states with zero-energy Majorana modes are proposed to emerge, when the spin-triplet component dominates and sign changes exist in the superconducting gap [40]. Indeed, a pronounced ZBCP concomitant with the common superconducting double-peak feature was observed in the point-contact data, and it is interpreted as intrinsic ABS in α-BiPd [41]. We note that a ZBCP can also be observed due to a sign change of the superconducting gap function as in the cuprates or single-layer $2H$-TaS_2 and $2H$-$TaSe_2$ [42,43].

In conclusion, we have performed soft point-contact spectroscopy studies on high quality single crystalline β-$PdBi_2$ and the differential conductance curves are generally characterized by a double-peak structure, yielding a superconducting gap $\Delta_0 \simeq 0.92$ meV with $2\Delta_0/k_BT_c \sim 4.1$. The absence of an intrinsic ZBCP in the point-contact spectra of β-$PdBi_2$ and the good fit with the single-gap BTK model strongly suggest that β-$PdBi_2$ is a conventional intermediate-coupling BCS superconductor and that zero-energy Majorana fermions are probably absent.

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