SUPERCONDUCTIVITY

Observation of half-quantum flux in the unconventional superconductor β-Bi_2Pd

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Magnetic flux quantization is one of the defining properties of a superconductor. We report the observation of half-integer magnetic flux quantization in mesoscopic rings of superconducting β-Bi_2Pd thin films. The half-quantum fluxoid manifests itself as a π phase shift in the quantum oscillation of the superconducting critical temperature. This result verifies unconventional superconductivity of β-Bi_2Pd and is consistent with a spin-triplet pairing symmetry. Our findings may have implications for flux quantum bits in the context of quantum computing.

The condensation of Cooper pairs gives rise to superconductivity (*1*). A key signature of the electron pairing is the quantization of the magnetic flux through a multiply connected superconducting body, in discrete units of $\Phi_0 = hc/2e$, where h is the Planck constant, c is the speed of light, and e is the elementary charge. Indeed, the observations of the fluxoid quantization served as the first experimental verifications of the Bardeen–Cooper–Schrieffer theory of conventional superconductors (SCs) (*2–4*). Shortly after the initial magnetometry measurements, Little and Parks further demonstrated oscillations of the superconducting transition temperature T_c as a function of the applied magnetic flux resulting from the corresponding periodicity of the free energy of the superconducting state (*5*). The minimum of the free energy, or the maximum of the T_c, is achieved when the applied magnetic flux takes the form $\Phi = n\Phi_0$, where n is an integer number. In the following decades, the Little-Parks effect, as a stringent test for the electron pairing, has been observed in numerous superconducting materials (*6–9*). However, in spin-triplet SCs, half-quantum magnetic fluxes (HQFs) of $(n + 1/2)\Phi_0$ have been predicted by Geshkenbein, Larkin, and Barone (GLB) to be energetically more favorable than integer ones (*10*). The idea was later extended to the spin-singlet high-T_c SCs (*11*) and realized in $YBa_2Cu_3O_{7-\delta}$ tricrystals with delicately designed crystalline boundaries (*12*, *13*), which, in conjuncture with the corner junction experiments (*14*, *15*), pinpointed the d-wave pairing symmetry. More recently, experimental indications of a different half-quantum vortex effect have been reported in the spin-triplet SC candidate Sr_2RuO_4 (*16*, *17*). This phenomenon manifests itself as a splitting of the integer-quantization steps under an additional in-plane magnetic field (*18*); it is not to be confused with the HQF effect proposed by GLB. The spin-triplet nature of Sr_2RuO_4 remains to be unequivocally concluded (*19–22*).

The past decade has witnessed a surging interest in topological superconductors (TSCs), which may host Majorana fermions (*19*, *20*, *23*). TSCs are considered to have a profound connection to the spin-triplet pairing (*24–26*). The search goes on in other superconducting materials, including doped topological insulators, noncentrosymmetric SCs (*19*, *20*), and iron-based SCs (*27*).

Of particular interest is the material β-Bi_2Pd with a centrosymmetric tetragonal crystal structure (*28*), which is reported to host spin-polarized topological surface states that coexist with superconductivity (*29*, *30*). One scanning tunneling spectroscopy study in particular reports observation of Majorana-bound states at the center of the vortices in epitaxial thin films (*31*). Controversy persists, however, because other tunneling spectroscopy and calorimetric studies in bulk specimens suggest the conventional s-wave pairing mechanism (*32–34*). To explore the nature of superconductivity in this material, we performed Little-Parks experiments on mesoscopic superconducting rings fabricated on textured β-Bi_2Pd thin films. We found that the flux quantization becomes $(n + 1/2)\Phi_0$. In other words, the oscillation of T_c as a function of the applied magnetic flux is shifted by a phase of π. This is the experimental signature of the HQF predicted by GLB (*10*). Our findings imply that the superconductivity of β-Bi_2Pd originates from an unconventional pairing symmetry consistent with spin-triplet pairing.

The fluxoid Φ′ of a superconducting loop was introduced by F. London as $\Phi' = \Phi + (4\pi/c)\oint\lambda^2\vec{j}_s\cdot d\vec{s}$ where Φ is the applied magnetic flux, λ is the London penetration depth, and $\vec{j}_s$ is the supercurrent density (*35*). Φ′ must take quantized values, with integral increments of a flux quantum Φ_0 (*2*, *4*, *35*). The applied magnetic flux Φ can take arbitrary values, which requires $\vec{j}_s$ to compensate it to maintain the quantized Φ′. This leads to periodic oscillations of the free energy, and in turn T_c, in response to the applied magnetic field (*5*). Usually, a circulating $\vec{j}_s$ is not required when the external field satisfies $\Phi = n\Phi_0$; for these values of the applied flux, the free energy of the superconducting state is the lowest and, as a result, the T_c is the highest. The maximum of the free energy and the minimum of T_c occur when $n - \Phi/\Phi_0 = \pm\frac{1}{2}$, as depicted in Fig. 1A. For unconventional SCs, the superconducting order parameter becomes anisotropic, retaining the symmetry of the underlying crystal lattices. In polycrystalline samples, it is possible, as suggested by GLB, for the phase factor of the complex order parameter to experience an additional phase shift of π along a path across the boundary of two crystal grains, resulting in a sign change in the corresponding free-energy term (*10*). An odd number of the π phase shifts accumulated around a superconducting loop will reverse minima and maxima of the total free energy. It is thus the maxima of T_c, instead of the minima, that occur when $n - \Phi/\Phi_0 = \pm\frac{1}{2}$, as shown in Fig. 1B; the fluxoid quantization becomes $\Phi' = (n + 1/2)\Phi_0$. In the absence of an external magnetic field, such a superconducting loop will hold an HQF as its ground state. GLB concluded that this is most likely to occur in polycrystalline p-wave SCs (*10*).

To examine the fluxoid quantization in β-Bi_2Pd, we fabricated submicrometer-sized ring devices using 50-nm-thick, (001)-textured β-Bi_2Pd thin films deposited on oxidized silicon substrates by magnetron sputtering (*36*). The size of the ring is important because the oscillation occurs in units of $\Phi_0 \approx 20$ Gauss-$(\mu m)^2$. For a ring of 1 μm by 1 μm, oscillations occur in field increments of ~20 Oe. Measuring much larger rings is far more demanding on the field resolution and makes it more difficult to determine the zero–external-field state in the presence of the remnant field of the magnet. For smaller rings, the size becomes comparable to the coherence length. A representative device geometry can be found in Fig. 1C, with a mean size of 0.8 μm by 0.8 μm. Control samples with the same device geometries were patterned using 28-nm-thick thin films of Nb, which is a conventional s-wave SC. The temperature dependence of the device resistance is shown in Fig. 1D. A broadening of the transition width (~1.5 K) compared with that of the as-grown films (<0.2 K) is typical for submicrometer-sized devices (*7–9*, *17*, *37*). The Little-Parks effect can be observed when the sample is placed at a fixed temperature within the superconducting transition regime, where the variation of the T_c manifests as oscillations of the

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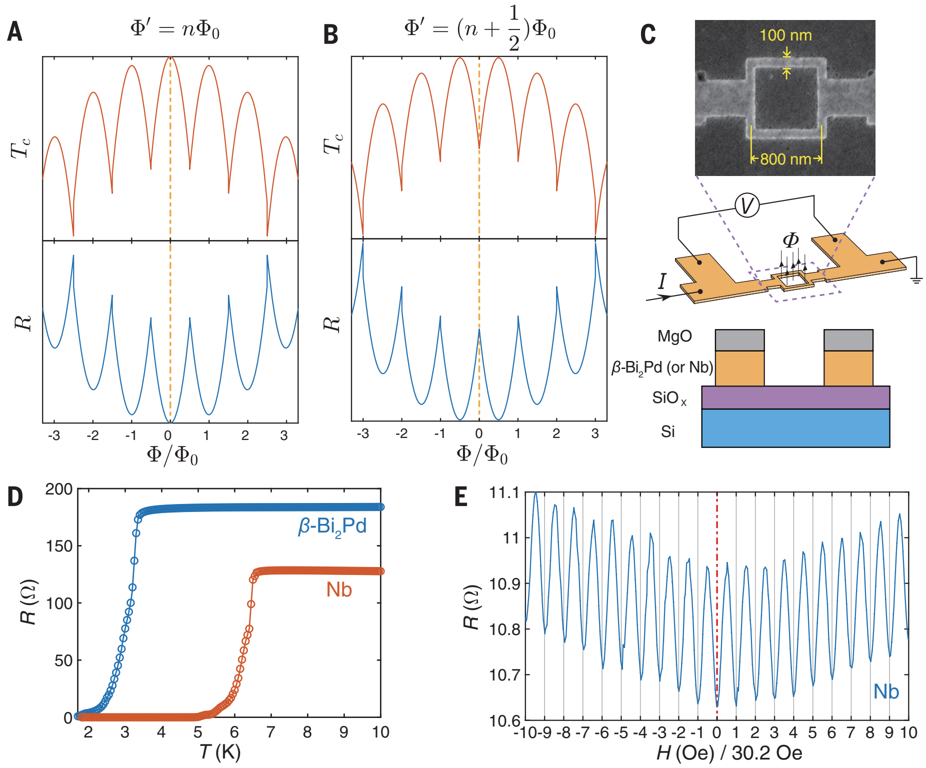

Fig. 1. Little-Parks effect and the experimental setup. (**A**) Schematic drawing of the Little-Parks effect of conventional s-wave SCs. The critical temperature (upper panel) and the resistance (lower panel) oscillate as a function of the applied magnetic flux in the period of one magnetic flux quantum $\Phi_0 = hc/2e$. The fluxoid takes integer-quantized values of $\Phi' = n\Phi_0$. (**B**) Schematic drawing of the effect of the half-quantum fluxoid manifested as a π phase shift in the Little-Parks oscillation. The fluxoid takes fractionally quantized values of $\Phi' = (n + 1/2)\Phi_0$. (**C**) Top: scanning electron microscope image of a representative superconducting ring device. Middle: schematic drawing of the experimental setup. Bottom: schematic drawing of the cross section of the ring structure. The dimensions are not drawn to scale. (**D**) Temperature dependence of the resistance of the β-Bi_2Pd and Nb ring devices. The film thicknesses of β-Bi_2Pd and Nb are 50 and 28 nm, respectively. (**E**) Little-Parks effect of the Nb ring device showing the ordinary case depicted in (A). The resistance oscillates as a function of the perpendicular magnetic field. The sample was held at a constant temperature of 5.7 K in the vicinity of the normal-superconducting phase transition.

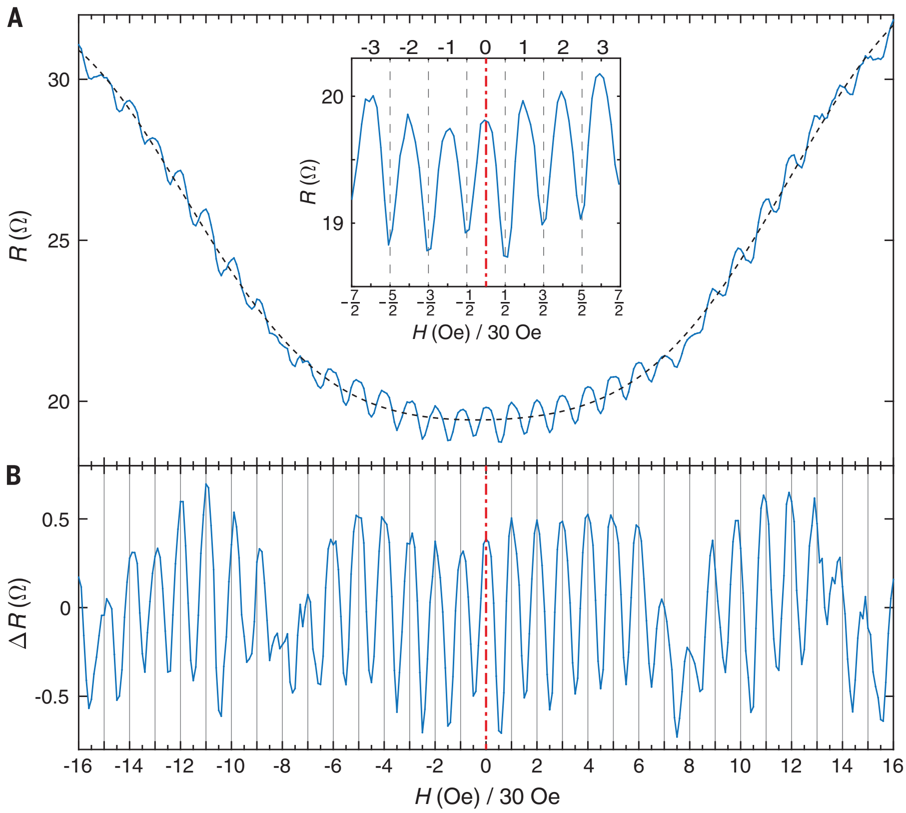

Fig. 2. Little-Parks effect of the β-Bi_2Pd ring device. (**A**) Oscillations of the β-Bi_2Pd ring device resistance as a function of the perpendicularly applied magnetic field. The sample was held at a constant temperature of 2.5 K. The *x*-axis is displayed in the units of the oscillation period 30 Oe, in agreement with the expected magnetic flux quantum for the device geometry (800 nm by 800 nm in area). The black dashed line denotes the aperiodic background. The inset is a magnified view of the low field region of (A). The vertical black dashed lines denote the applied magnetic flux of $\Phi = (n + 1/2)\Phi_0$, which corresponds to the oscillation minima. The red dot-dashed line denotes the zero external field. (**B**) Little-Parks oscillation in which the background has been subtracted from the raw data as presented in (A). The gray vertical lines denote the applied magnetic flux of $\Phi = n\Phi_0$, which corresponds to the oscillation maxima.

resistance (*5*). Figure 1E presents a typical result of the Little-Parks experiment obtained from the Nb ring device. The observed oscillation period is 30.2 Oe, in good agreement with 32.3 Oe as expected for Φ_0 of the 800 nm by 800 nm ring area. The resistance minima, which correspond to the T_c maxima, occur when $\Phi = n\Phi_0$, as routinely observed for s-wave SCs (*6*) and high-T_c cuprate d-wave SCs (*7*, *37*), both singlet SCs. Up to ~70 oscillations have been observed on a roughly parabolic-shaped background. The background is commonly observed in Little-Parks experiments, believed to originate from the misalignment of the magnetic field and the finite line width of the ring

(6, 38, 39). As a precaution against trapping vortices, the measurements were always performed after zero-field cooling from 10 K.

The Little-Parks oscillations of the β-Bi_2Pd ring device are shown in Fig. 2A. The same oscillation period of ~30 Oe is observed. A smooth background can be subtracted from the raw data (36), and the resulting Δ*R* versus *H* oscillations are presented in Fig. 2B. The magnitude of the resistance oscillations translates to ~0.015 K variations of T_c, consistent with theoretical expectations for the Little-Parks effect (40). In stark contrast to the case of Nb, however, $\Phi = n\Phi_0$ now corresponds to the resistance maxima (or the T_c minima); the resistance minima and the T_c maxima are observed when the applied magnetic flux is $(n + 1/2)\Phi_0$. The $\frac{1}{2}\Phi_0$ shift of the free-energy minima indicates that the fluxoid quantization of $(n + 1/2)\Phi_0$ is energetically preferred. When the external magnetic field is zero, the superconducting ring circulates a finite $\vec{j}_s$ to sustain one HQF, which accounts for the lowest T_c and the highest free energy. The system has a lower energy when the external field supplies $\pm\frac{1}{2}\Phi_0$ and $\vec{j}_s$ can become zero. The shape of the magnetoresistance oscillation trace is symmetric with respect to the zero magnetic field, which shows that the effect is not caused by defect-trapped vortices. We also verify that the result is robust against the different field-sweeping directions and current densities (36). The HQF is repeatedly observed in numerous β-Bi_2Pd rings with various geometrical device shape factors (36).

In Fig. 3, we demonstrate the temperature dependence of the Little-Parks effect in β-Bi_2Pd. The π phase shift persists from the emergence of the Little-Parks effect at 2 K, through the highest temperature of 2.6 K, before the oscillation disappears presumably owing to the loss of coherence over the length scale of the ring device. This persistence suggests the predominance of the characteristic pairing symmetry that gives rise to the HQF (41).

Below, we discuss the implications of our experimental observations. The GLB HQF is an experimental signature for unconventional pairing mechanisms, not restricted to the p-wave pairing; indeed, HQF was first observed in d-wave SC tricrystals (12). The orientations of the crystal boundaries had to be carefully designed or HQF would not exist (12, 13). HQF has not been observed in polycrystalline specimens of high-T_c SCs, although the Little-Parks experiment has been conducted on microstructured mesh of polycrystalline $YBa_2Cu_3O_7$ thin films (7). By contrast, in our experiment, HQFs were observed in most of the β-Bi_2Pd ring devices (36). Considering the previous literature reporting the link between β-Bi_2Pd and the spin-triplet pairing (29–31), a contributing factor to the robustness of the HQF state might be the characteristic anisotropy of the p-wave pairing. The order parameter reverses sign when rotating 180°, whereas for the d-wave, the sign reversal occurs upon rotating 90°. This protects the HQF from moderate disorders on the crystal grain boundaries compared with that gauged for d-wave SCs (12, 13). Nevertheless, the observation of HQF is unequivocal evidence for unconventional superconductivity and is consistent with p-wave pairing in β-Bi_2Pd.

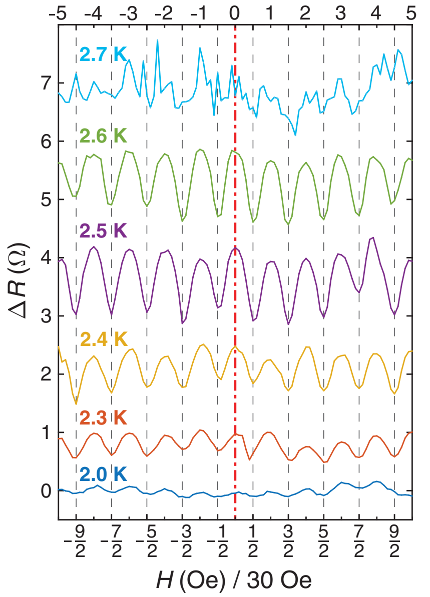

Fig. 3. Temperature evolution of the Little-Parks effect of the β-Bi_2Pd ring device. Oscillations of the resistance as a function of applied magnetic field with the background subtracted for six different values of temperature are shown. The vertical black dashed lines denote the applied magnetic flux of $\Phi = (n + 1/2)\Phi_0$. Results are for the same device presented in Fig. 2 (800 nm by 800 nm in area).

The convenient realization of HQFs in polycrystalline β-Bi_2Pd may find immediate applications in superconducting quantum bits (qubits). In flux qubits, two quantum states with opposite directions of circulating supercurrent serve as the basis states (42). Implementation of flux qubits has been demonstrated using conventional s-wave SCs (43). The operation of such qubits requires an external magnetic field to supply precisely $\Phi = 1/2\Phi_0$, to create the superposition of the two quantum basis states. This requirement is specific to a particular qubit on the basis of its dimensions, hindering device integration. By contrast, a superconducting ring of β-Bi_2Pd hosts HQF as its ground state; in the absence of any external field, it is spontaneously a superposition of two quantum basis states with left-handed and right-handed circulating supercurrent. Such a field-free qubit may enable practical application of flux qubits for quantum computing.

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ACKNOWLEDGMENTS

We thank Yi Li and C. C. Tsuei for valuable discussions. E-beam lithography was conducted at the University of Delaware Nanofabrication Facility (UDNF) and the NanoFab laboratory of NIST (CNST). We thank K. Lister and R. Kasica for assistance with the nanofabrication processes. **Funding:** This work was supported by the U.S. Department of Energy (DOE), Basic Energy Science award no. DESC0009390. X.X. was supported in part by SHINES, an EFRC funded by U.S. DOE Basic Energy Science award no. SC0012670. **Author contributions:** Y.L. and C.L.C. conceived the project. X.X. synthesized and characterized the thin film samples. Y.L. fabricated the devices. Y.L. and X.X. conducted the electrical transport measurements. M.-H.L and M.-W.C conducted the cross-section TEM measurements. Y.L., X.X., and C.L.C jointly discussed the results and wrote the manuscript with contributions from all authors. **Competing interests:** The authors declare no competing interests. Y.L., X.X., and C.L.C. are authors of a patent application filed through Johns Hopkins University that relates to this work (application no. 62/847,028 filed 13 May 2019). **Data and materials availability:** Data reported in this paper are archived online at Harvard Dataverse (*44*).

SUPPLEMENTARY MATERIALS

science.sciencemag.org/content/366/6462/238/suppl/DC1
Materials and Methods
Supplementary Text
Figs. S1 to S9
References (*45*–*47*)

3 July 2018; resubmitted 26 December 2018
Accepted 17 September 2019
10.1126/science.aau6539

Science

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Science **366** (6462), 238-241.
DOI: 10.1126/science.aau6539

Unconventional oscillations

At sufficiently low temperatures, superconductors expel an applied magnetic field. However, if the topology of the superconductor is nontrivial—for example, if there is a hole in the sample—there can be a nonzero magnetic flux inside the hole. This flux can only take certain discrete values, and the superconducting critical temperature has maxima at the corresponding values of the magnetic field. Li *et al.* studied these so-called Little-Parks oscillations in superconducting rings made out of polycrystalline thin films of β-Bi_2Pd. They found that the phase of the oscillations was shifted by π compared with oscillations observed in most superconductors, as predicted for certain unconventional pairing symmetries.

Science, this issue p. 238

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