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Unconventional periodicities of the Little-Parks effect observed in a topological superconductor

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Abstract

In superconductors, the condensation of Cooper pairs gives rise to fluxoid quantization in discrete units of $\Phi_0 = hc/2e$. The denominator of $2e$ is the signature of electron pairing, which is evidenced by a number of macroscopic quantum phenomena, such as the Little-Parks effect and the Josephson effect, where the critical temperature or the critical current oscillates with the periodicity of Φ_0. Here we report the observation of novel Little-Parks oscillation periodicities of $2\Phi_0$, $3\Phi_0$ and $4\Phi_0$, besides the conventional Φ_0, in mesoscopic rings of epitaxial β-Bi_2Pd, a topological superconductor. These unexpected new findings suggest new physics to account for the novel quantizations.

The most distinctive feature of superconductivity is the presence of the complex-valued many-particle wave function that sustains phase coherence over macroscopic distances. One of its experimental manifestations is the fluxoid quantization in a superconducting ring. The single-value nature of the wave function dictates a universal phase change of 2π for any closed path around the ring. As a result, the fluxoid Φ' can only take on quantized values in integer steps of $\Phi_0 = hc/e^*$, where h is the Planck constant, c is the speed of light, and e^* the effective charge. As a key evidence of electron pairing, e^* is found to be $2e$ of the Cooper pairs [1]. The quantization unit of Φ_0, or the 2π periodicity, has been confirmed by numerous experiments including magnetometry [2, 3], the Little-Parks effect [4] and the Josephson effect / quantum interference experiments [5, 6].

The Little-Parks effect concerns the quantum oscillation of the superconducting critical temperature, T_c, as a function of the applied magnetic flux threading through the enclosed area of a superconducting ring, reflecting the periodic oscillation of the free energy. The T_c oscillation is experimentally observed by measuring the magnetoresistance of the ring at temperatures just below T_c. The first experiment by Little and Parks in superconducting tin rings [4], which formally establishes integer fluxoid quantization [7], demonstrates two distinctive hallmarks: (i), the resistance oscillates only with a single period of Φ_0; and (ii), the minima of resistance occur when the applied flux is $\Phi = n\Phi_0$, where n is an integer. These key features reprise in all singlet superconductors (SCs) including s-wave SCs [8, 9] and d-wave SCs [10–12], in both single-crystalline and polycrystalline forms. For the unconventional superconductor Sr_2RuO_4, the integer quantization also holds up well [13] unless a large additional in-plane magnetic field is applied [14–16].

Unlike the commonly observed even-parity spin-singlet pairing, in a topological superconductor with spin-triplet pairing, the gap function has odd parity and experiences a sign change upon inversion. This crucial sign change can facilitate a π phase shift at crystalline grain boundaries as first predicted theoretically [17], giving rise to half-integer fluxoid quantization $\Phi' = (n + 1/2)\Phi_0$. The manifestation in the Little-Parks effect is that resistance minima appear at half-integer quanta instead, breaking Hallmark (ii). This half-quantum fluxoid (HQF) was recently reported in polycrystalline β-Bi_2Pd [18], an intrinsic topological superconductor [19–22]. The Little-Parks oscillation of the polycrystalline β-Bi_2Pd, despite the HQF, remains exactly 2π-periodic, leaving Hallmark (i) intact.

We report in this article the experimental observation of multiple non-2π periodicities in the

Little-Parks effect of epitaxial β-Bi_2Pd ring devices. Although no HQF is observed in epitaxial β-Bi_2Pd samples, an expected outcome due to the absence of crystalline grain boundaries, it is evident that the quantization oscillation is never purely Φ_0-periodic. The decisive yet unexpected departure from Hallmark (i), a fundamental feature of fluxoid quantization, indicates exciting new physics. The underlying mechanism invites future theoretical deliberations.

We prepare 70 nm-thick epitaxial β-$Bi_2Pd/SrTiO_3(001)$ and β-$Bi_2Pd/MgO(001)$ thin films by magnetron sputtering. The as-grown films exhibit T_c of about 3.5 K. The thin films are subsequently patterned into sub-micron mesoscopic ring devices by electron-beam lithography. The Little-Parks experiment setup is depicted in Fig. 1(b). The ring device, shown in scanning electron microscopic image, is 800 nm × 800 nm in size, marked by the scale bar. The length of the side is measured between the midpoints of the opposite sides of the square. We have prepared 7 different designs with various ring sizes and geometries, as shown in Figs. 1(b) and 1(c). This helps us to reliably determine the Φ_0-corresponding oscillation period in term of magnetic field. The Little-Parks effect is observed when the ring device is placed at a fixed temperature within the superconducting transition regime, where the variation of the T_c manifests as oscillations of the electrical resistance [4]. In Fig. 1(d) we compare a representative epitaxial ring of β-$Bi_2Pd/SrTiO_3$ (Device A, Type-IV design) to our previous results from a polycrystalline ring of β-Bi_2Pd/Si [18] with the same ring design, where the color shades indicate the temperature windows in which the Little-Parks effect was observed. Evidently the Little-Parks regimes are located at virtually identical transition stages. The T_c transition behaves similarly for all the ring designs we have examined. Fig. 1(e) compares the smallest design (Device B) and the largest design (Device C), where they only differ in the absolute values of resistance, dictated by the device line widths. In general, the Little-Parks effect is observed in the temperature window between 2 K and 3 K. Above 3.2 K, no oscillations can be observed in magetoresistance. A representative experimental result, the resistance of Device A as a function of the applied field, is presented in Fig. 1(f). Oscillatory features are observed on top of a roughly parabolic-shaped background. The aperiodic background is commonly observed in Little-Parks experiments, presumably originates from field misalignment and finite device line width [8, 23, 24], which can be approximated by a polynomial fitting (dashed line) and subsequently removed. The Little-Parks oscillation $\Delta R - H$ is revealed after subtracting the background from the raw data, as shown in Fig. 1(f).

The period of the Little-Parks oscillation is dictated by the area of the ring with respect to the value of $\Phi_0 \approx 20.7$ Gauss-μm^2. For the ring size of 800 nm-by-800 nm as demonstrated in

Fig. 1(b), the expected Φ_0-period for two-electron pairing is 32.3 Oe. Experimentally observed oscillation periods agree closely with the expected values. An example of a polycrystalline niobium ring manifesting a uniform oscillation period of 30.2 Oe is presented in Fig. 2(a). Indeed, both hallmarks of the ordinary Little-Parks effect as a result of the integer fluxoid quantization is on display in this classical example of an s-wave SC: a unified period of the oscillation by Φ_0 and a series of resistance minima at $n\Phi_0$. On the other hand, in polycrystalline β-Bi_2Pd rings, as we have reported earlier, the Little-Parks oscillation can exhibit HQF of $(n + \frac{1}{2})\Phi_0$ as a result of the anisotropic triplet pairing state [18]. One such example is demonstrated in Fig. 2(b), where the resistance minima appear at half-integer quanta, distinctively different from the case of integer-fluxoid quantization in Nb. Nevertheless, the Little-Parks effect with HQF is still strictly 2π-periodic. In the right panels of Figs. 2(a) and 2(b), the Little-Parks oscillation is converted to the frequency domain by Fourier transform analysis. In both cases, the spectral weight occurs only at the period of Φ_0, indicating the exclusive 2π periodicity.

The HQF originates from a π phase shift added to the superconducting wave function across certain crystalline grain boundaries [17]. In the absence of grain boundaries, such π phase shifts and hence HQF should not occur in epitaxial superconducting rings irrespective of the gap parity, and none has been observed in epitaxial rings of β-Bi_2Pd. As an example, the Little-Parks effect observed in Device A [Figs. 1(f) and 2(c)] shows no signs of HQF. Indeed, HQF is *completely* absent in the total of 30 epitaxial ring samples we have measured. Striking new features emerge, however, when one examines the periods of the Little-Parks oscillations in epitaxial samples. In Fig. 2(c), The same data of ΔR oscillation in Device A from Figs. 1(f) is plotted as a function of Φ/Φ_0, where the Φ_0-period is determined to correspond to 33.5 Oe of the applied field, consistent with the expected value of 32.3 Oe. The resistance minima of Device A are separated roughly by $2\Phi_0$ with 4π periodicity, instead of Φ_0 as in both Figs. 2(a) and 2(b). Deviations in the positions of the minima from the exact even-integer quanta are indicative of the mixture of longer periodicities. The Fourier transform analysis shows a dominating spectral peak at $2\Phi_0$, indicating the 4π periodicity. Smaller contributions can also be found at $3\Phi_0$ and $4\Phi_0$. In contrast, the spectral weight of the conventional 2π periodicity is negligible at Φ_0. The presence of the 2π-periodic fluxoid quantization can only be hinted by the kink-like feature in the ΔR-Φ curve near $\pm$ 3 Φ_0. In the Fourier spectrum, the spectral weight of the 2π-periodic component can be recovered after removing the spectral noise (Figs. S3 and S4, see the Supplemental Materials for further details [25]).

Evidently the dominating non-2π periodicities of the Little-Parks oscillations in Device A shatter Hallmark (i). It bears profound implications as the conventional wisdom expects the exclusively 2π-periodic fluxoid quantization universally for all superconducting loops, regardless of their single-crystalline / polycrystalline nature or any details of the particular device, such as size, shape, presence of defects, *etc*. We have surveyed a total of 30 epitaxial β-Bi_2Pd rings and, in stark contrast, not a single ring displays exclusively the 2π periodicity. Non-2π periodicities are always observed. Multiple periodicities may coexist, with noticeable variations in the amplitudes among samples. Fig. 3(a) shows the Little-Parks effect observed in Device B, a 450 nm-size ring (type-I) fabricated using an epitaxial β-Bi_2Pd/MgO thin film. Above 3 K, a superposition of 2π and 4π periodicities is observed. Below 3 K, a prominent $3\Phi_0$-periodic component emerges, indicating 6π periodicity. The presence of 2π, 4π and 6π periodicities can be confirmed by the Fourier transform analysis as shown in Fig. 3(b), unambiguously demonstrating the simultaneous presence of multiple periodicities. Figs. 3(c) and 3(d) showcase an example of 6π dominance, observed in Device C, a 900 nm-size ring (type-VI) of epitaxial β-Bi_2Pd/$SrTiO_3$. The prevailing 6π periodicity is unequivocally demonstrated in both the ΔR-Φ curves [Fig. 3(c)] and the Fourier transform spectra [Fig. 3(d)]. At 2.5 K, a weak high-pitch oscillation with the period of $\frac{1}{2}\Phi_0$ emerges. The spectral weight of this π periodicity, however, is not immediately recognizable from the Fourier transform spectra due to the small oscillation amplitude. Nevertheless, the π-periodic contribution to the Fourier spectra could be distinguished following the analysis presented in Section IV and Fig. S6 of the Supplemental Materials. Dominating 8π periodicity at all temperatures can be observed in Device D, a 600 nm-size ring (type-III) of epitaxial β-Bi_2Pd/$SrTiO_3$. Prominent peaks corresponding to the 8π periodicity are evident in the Fourier transform spectra shown in Fig. 3(f). A smaller 2π-periodic component can also be observed at the lower temperatures such as 2.4 K and 2.6 K.

A spike-like feature may emerge at the zero magnetic field in the ΔR-Φ curves. Such feature can be seen in Device D [2.9 K of Fig. 3(e)] and Device A [Fig. 2(c)]. It only appears at higher temperatures, above 2.7 K. Its sharp decay at finite magnetic field and the non-repeating nature suggests that the spike is unrelated to the Little-Parks effect and not indicative of any periodicities. Further discussions about its likely origin can be found in the Supplemental Materials (Section VI).

The observation of non-2π periodicities in epitaxial β-Bi_2Pd rings came as a surprise, to which there are no comprehensive explanation readily available. It is pertinent to first discuss what the

observed effect is *not*. The unconventional non-2π periodicities are not the result of a spurious determination of the Φ_0 period. We have examined 7 ring designs with various sizes and aspect ratios. The fluxoid quantization period in term of magnetic field can be calculated as $H_{2\pi} = \frac{\Phi_0}{\mu_0 A} = \frac{hc}{2e\mu_0 L^2}$, where $A = L^2$ is the effective area of the ring device, and L is the side length of a square ring measured between the middle points of the arms. In every ring device, we find the observed Φ_0 period in good agreement with the expected values calculated from the design geometry. The result can also be compared with the Φ_0 periods determined from our previous studies employing polycrystalline rings devices [18, 26], where only the conventional 2π periodicity is present. The comparison to expected period and among experiments is presented in Fig. 4(a). All experimental data show excellent agreement with the calculated Φ_0-period ($H_{2\pi}$). We also plot two other curves if we erroneously determined Φ_0-period, to be two times with $H_{2\Phi_0} = \frac{hc}{e\mu_0 L^2}$ (green curve) or half of the correctly determined Φ_0 with $H_{\frac{1}{2}\Phi_0} = \frac{hc}{4e\mu_0 L^2}$ (blue curve). It is evident that all the experimental data are located at the Φ_0 curve without exceptions. We have correctly identified the Φ_0-period. This also reaffirms that the non-2π periodicities are not results of any particular device geometries. At any rate, the non-2π periodicities differ from the conventional 2π periodicity by at least a factor of 2, too large to be discounted by flux focusing or uncertainties in calculating the effective loop area. Nor can these potential artifacts account for the coexistence of multiple periodicities, repeatedly observed in epitaxial β-Bi_2Pd ring devices.

We can also rule out the Aharonov-Bohm effect, which is on the scale of e^2/h in terms of conductance [28, 29]. The observed Little-Parks effect, converted to magnetoconductance oscillations, can be 2 to 3 orders of magnitude greater in amplitude (see Section VII of the Supplemental Materials). Multiple flux jumps have been reported in conventional s-wave SCs when $T \ll T_c$ [30, 31]. It is well understood that they do not occur in the resistive state in the vicinity of T_c where the Little-Parks effect is observed [31], and therefore can be ruled out as alternative interpretations for our results (see Section VIII of the Supplemental Materials).

The 30 epitaxial ring devices studied in this work allows us to summarize the statistical representativeness of the observed periodicities by counting their numbers of occurrences in the histogram presented in Fig. 4(b). Each device could offer multiple counts, matching the number of periodicities observed therein. While the conventional 2π periodicity is still observed in most devices, there is not a single epitaxial ring that displays exclusively the 2π periodicity. The occurrence of the 4π, 6π and 8π periodicities are only slightly less. On the other hand, the π periodicity is far less frequent than the other non-2π periodicities, only observed in about one tenth of the

devices. Apart from the 4 representative devices presented in Figs. 2 and 3, we include more examples for each non-2π periodicities in the Supplemental Materials (Figs. S7-S9). It is evident that devices exhibit different combinations of periodicities of π, 2π, 4π, 6π and 8π. For a particular epitaxial ring device, the predominate periodicity is 2π and 4π.

The superconducting Cooper pairs bear the effective charge of $2e$, which defines the value of Φ_0 and hence the 2π periodicity. Applying the same argument, the non-2π periodicities would imply quasiparticles with effective charges being a fraction of $2e$. The 4π, 6π and 8π periodicities would correspond to e^* being e, $\frac{2}{3}e$ and $\frac{1}{2}e$, respectively. In topological superconductors, it has been proposed that the fractional Josephson effect could give rise to 4π periodicity [32–35], which is actively explored by numerous experiments [36–38]. 8π periodicity has also been proposed in the presence of strong interactions [39–41]. The theoretical discussions of unusual periodicities are often conducted in the context of the Josephson current-phase relation. One may expect that the Little-Parks effect to demonstrate the same oscillation period as the Josephson effect. After all, the T_c oscillation and the I_c oscillation would eventually reflect the same oscillation of the free energy. We have conducted a theoretical analysis that shows, based on a 1D-Kitaev-chain model as discussed in the Supplemental Materials, that indeed the 4π periodicity could be projected to the Little-Parks effect when it is expected for the fractional Josephson effect.

In summary, we have discovered novel non-2π periodicities of the Little-Parks effect in epitaxial rings of β-Bi_2Pd, a TSC with triplet pairing. The conventional, exclusively 2π-periodic Little-Parks oscillation never manifests in epitaxial β-Bi_2Pd, as would be expected for any other superconductors. Even for β-Bi_2Pd, the unconventional periodicities occur only in epitaxial and not in polycrystalline samples. Having excluded trivial causes, the experimental findings call for new mechanisms to account for the unexpected quantizations.

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Figure Captions

Fig. 1. Experimental setup. (a) Relation between the effective charge and the quantization periodicity. (b) A scanning electron microscope image of a representative 800 nm × 800 nm ring device. (c) Scanning electron microscopic images of various ring device designs. The scale bars mark the length of the side of the square devices or the diameter of the round device. (d) Temperature regime of the Little-Parks effect with respect to the superconducting phase transition, indicated by the blue and red shaded areas in the normalized resistance versus temperature curves for ring devices of polycrystalline β-Bi_2Pd/Si [18] and epitaxial β-Bi_2Pd/$SrTiO_3$(001) (ring type-IV, Device A), respectively. (e) Resistance versus temperature curves for Device B (type-I, β-Bi_2Pd/MgO) and Device C (type-VI, β-Bi_2Pd/$SrTiO_3$). (f) Upper panel: the raw data observed in Device A at 2.7 K. The dashed line indicates the aperiodic background. Lower panel: the Little-Parks oscillation obtained after subtracting the background.

Fig. 2. Little-Parks effect in Nb, polycrystalline and epitaxial β-Bi_2Pd rings. Left: the Little-Parks effect of (a) polycrystalline Nb, (b) polycrystalline and (c) epitaxial β-Bi_2Pd (Device A) rings. Right: The fast Fourier transform (FFT) spectra of the Little-Parks oscillations. The yellow triangle marks where to expect the peak for the 2π periodicity. The experimental data shown in (a-c) are collected at 5.7 K for Nb, 2.6 K for polycrystalline β-Bi_2Pd, and 2.7 K for epitaxial β-Bi_2Pd/$SrTiO_3$(001) (Device A), respectively. The Little-Parks oscillations of polycrystalline Nb and β-Bi_2Pd [(a) and (b)] are reproduced from Ref. [18].

Fig. 3. The non-2π periodicities. The Little-Parks oscillations (a) and the Fourier transform analyses (b) of Device B, a type-I ring device of epitaxial β-Bi_2Pd/MgO(001), plotted to Φ_0-period of 116 Oe (102 Oe expected from the design geometry). The yellow triangle marks the position of the 2π periodicity. (c) to (f): the Little-Parks effect (c and e) and the Fourier transform spectra (d and f) of Devices C and D, respectively. Device C is a type-VI ring device of β-Bi_2Pd/$SrTiO_3$(001) which expects Φ_0-period of 25.5 Oe. (c) and (d) are plotted to the observed Φ_0-period of 27.6 Oe. Device D is a type-III ring device of β-Bi_2Pd/$SrTiO_3$(001) with expected Φ_0-period of 57.4 Oe. (e) and (f) are plotted to the observed Φ_0-period of 60.0 Oe.

Fig. 4. Summary of observed periodicities. (a) Determination of the Φ_0-period. Squares: Φ_0-periods of 11 polycrystalline β-Bi_2Pd/Si ring devices [18]. Triangles: Φ_0-periods of 6 polycrystalline α-BiPd//$SrTiO_3$ ring devices [26]. Circles: Φ_0-periods of epitaxial β-Bi_2Pd rings, Devices A-D (this work). The curves present calculated correct Φ_0-period and other two erroneously periods. Yellow: Φ_0-period, $H_{2\pi} = \frac{\Phi_0}{\mu_0 L^2}$. Green: $2\Phi_0$-period, $H_{2\Phi_0} = \frac{hc}{e\mu_0 L^2}$. Blue: $\frac{1}{2}\Phi_0$-period,

$H_{\frac{1}{2}\phi_0} = \frac{hc}{4e\mu_0 L^2}$. (b) The graph summarizes the occurrence of different periodicities observed from a total number of 30 ring devices made of 70 nm-thick β-Bi_2Pd thin films epitaxially grown on $SrTiO_3$(001) and MgO(001) substrates with various device design geometries.

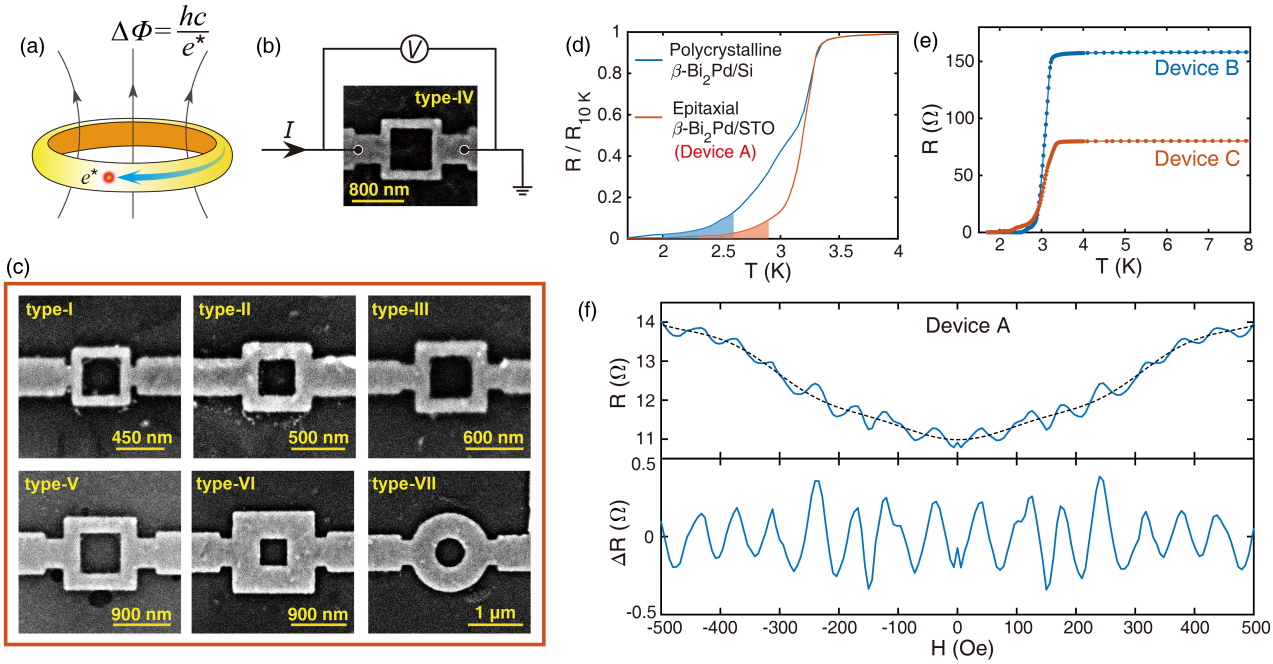


FIG. 1. **Experimental setup.**

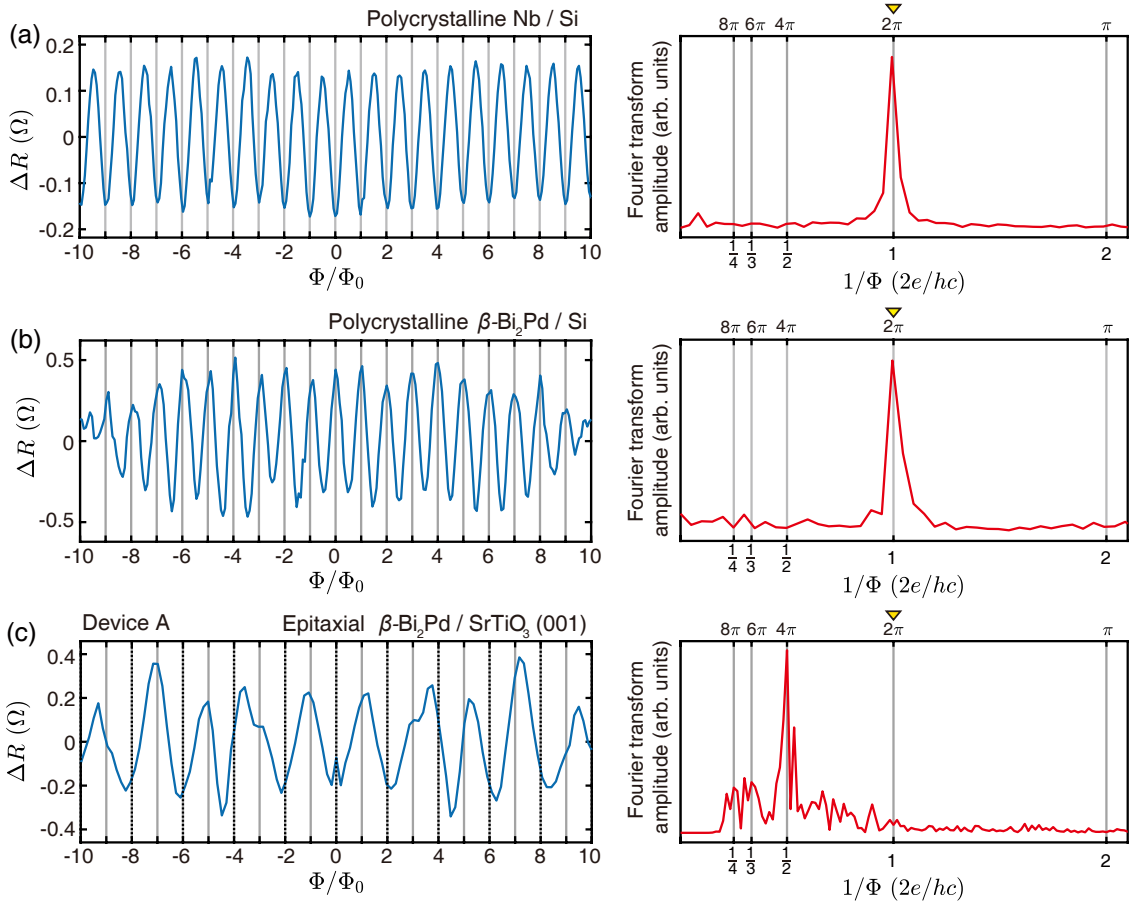


FIG. 2. **Little-Parks effect in Nb, polycrystalline and epitaxial β-Bi_2Pd rings.**

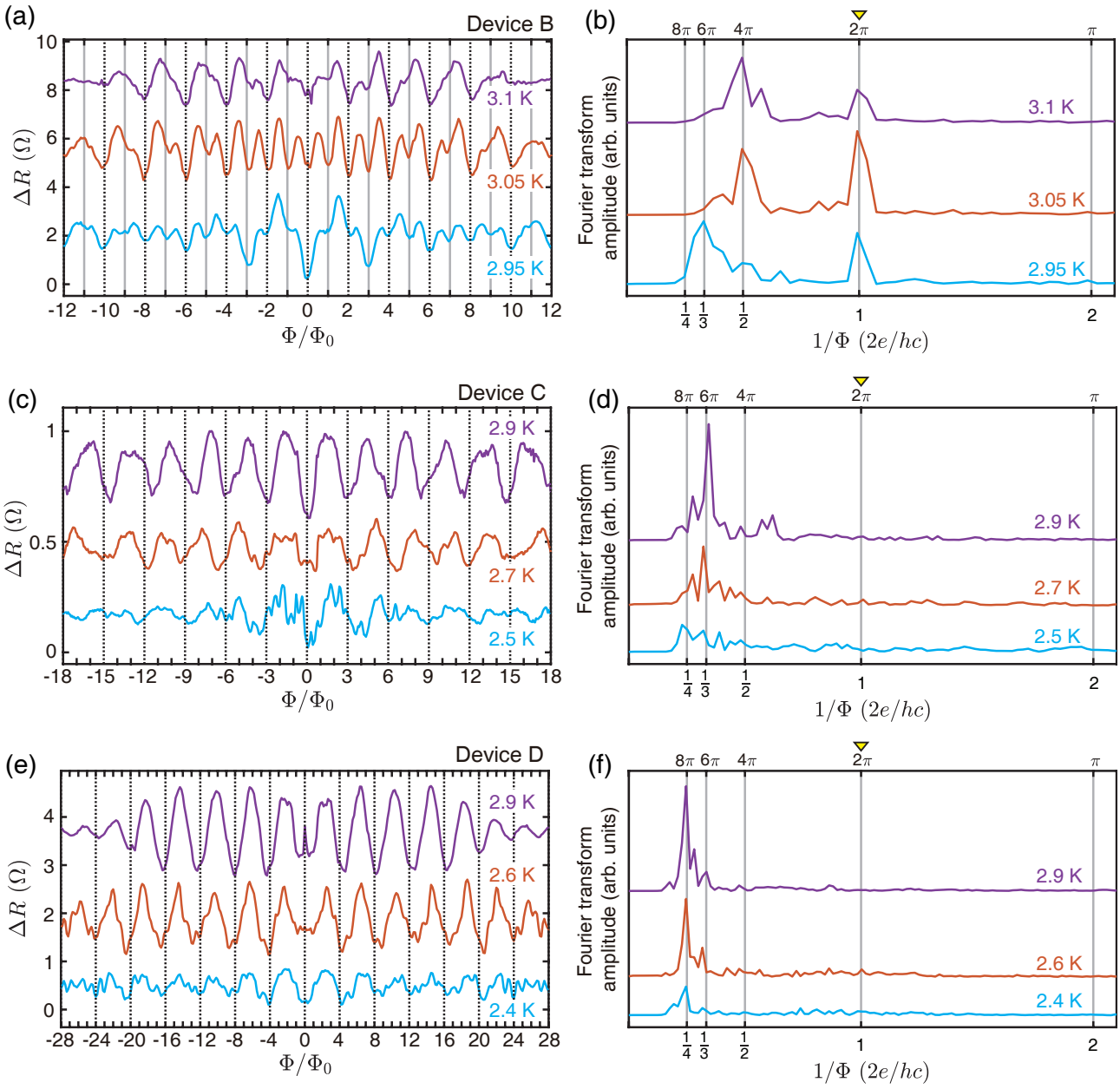


FIG. 3. **The non-2π periodicities.**

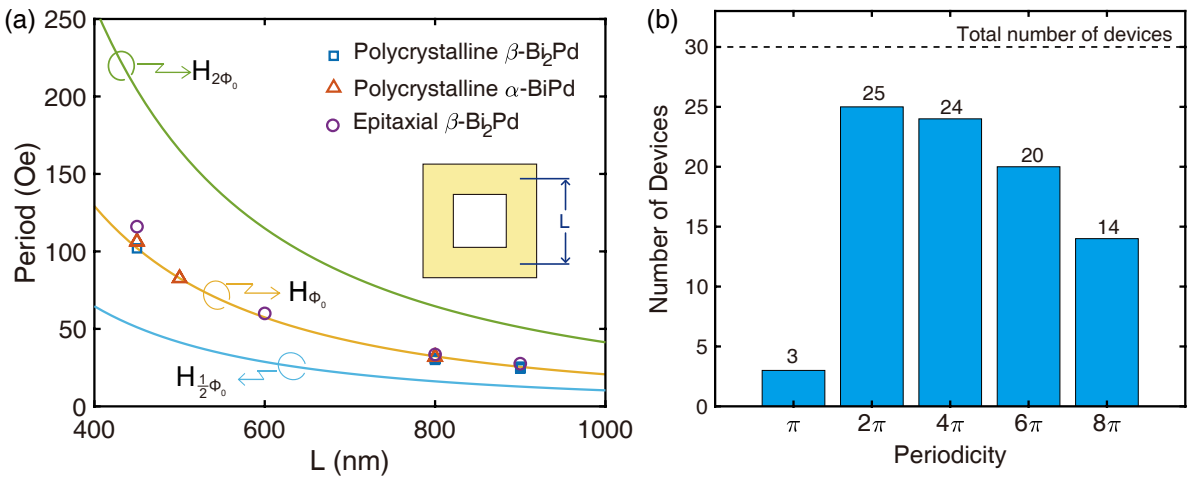


FIG. 4. **Summary of observed periodicities.**