

CONDENSED MATTER PHYSICS

Beyond triplet: Unconventional superconductivity in a spin-3/2 topological semimetal

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In all known fermionic superfluids, Cooper pairs are composed of spin-1/2 quasi-particles that pair to form either spin-singlet or spin-triplet bound states. The “spin” of a Bloch electron, however, is fixed by the symmetries of the crystal and the atomic orbitals from which it is derived and, in some cases, can behave as if it were a spin-3/2 particle. The superconducting state of such a system allows pairing beyond spin-triplet, with higher spin quasi-particles combining to form quintet or septet pairs. We report evidence of unconventional superconductivity emerging from a spin-3/2 quasi-particle electronic structure in the half-Heusler semimetal YPtBi, a low-carrier density noncentrosymmetric cubic material with a high symmetry that preserves the p -like $j = 3/2$ manifold in the Bi-based Γ_8 band in the presence of strong spin-orbit coupling. With a striking linear temperature dependence of the London penetration depth, the existence of line nodes in the superconducting order parameter Δ is directly explained by a mixed-parity Cooper pairing model with high total angular momentum, consistent with a high-spin fermionic superfluid state. We propose a $\mathbf{k} \cdot \mathbf{p}$ model of the $j = 3/2$ fermions to explain how a dominant $J = 3$ septet pairing state is the simplest solution that naturally produces nodes in the mixed even-odd parity gap. Together with the underlying topologically nontrivial band structure, the unconventional pairing in this system represents a truly novel form of superfluidity that has strong potential for leading the development of a new series of topological superconductors.

INTRODUCTION

When spin-orbit coupling (SOC) is strong enough to rearrange the order of electronic energy bands, various topological phases arise, and the interplay between superconductivity and the topologically ordered phase is of particular interest. The noncentrosymmetric half-Heusler compounds containing heavy metallic elements exhibit strong SOC, which can invert the Bi-derived s -like Γ_6 and p -like Γ_8 bands, giving a semimetal system with nontrivial topological electronic structure (1–3). The observation of superconductivity in the RTBi (where R = rare earth and T = Pt or Pd) (4, 5) has added a new richness to these materials that compounds topological aspects of normal-state band structure, superconductivity, and even magnetic order (6). In the superconducting state wave function, nontrivial topologies can arise both in fully gapped superconductors (7) and unconventional superconductors with point or line nodes, particularly in Weyl and noncentrosymmetric superconductors (8). In the latter, the lack of parity symmetry can lead to mixed even-odd parity pairing states on spin-split Fermi surfaces due to antisymmetric SOC (ASOC) (9).

The situation in these materials is further enriched by the $j = 3/2$ total angular momentum index of the states in the Γ_8 electronic band near the chemical potential. This arises from the strong atomic SOC of the $s = 1/2$ spin and the $l = 1$ orbital angular momenta in the p atomic states of Bi. The high crystal symmetry and the relatively simple band structure conspire to preserve the $j = 3/2$ character of the low-energy electronic

states, permitting Cooper pairs with angular momentum beyond the usual spin-singlet or spin-triplet states. In particular, as demonstrated schematically in Fig. 1, high-angular momentum pairing components with quintet ($J = 2$) and septet ($J = 3$) states are possible through the pairing combinations of spin-1/2 and spin-3/2 quasi-particles, giving rise to the possibility of the high-spin superfluidity (10–12). Such an unprecedented exotic pairing state arises from new $j = 3/2$ interactions that do not appear for the spin-1/2 case, allowing new opportunities for topological superconducting states (13).

Here, we focus on the archetype topological half-Heusler YPtBi, a clean limit superconductor with an extremely small electronic density of states at the Fermi level (4, 14), corresponding to a tiny carrier density $n \approx 2 \times 10^{18} \text{ cm}^{-3}$ (4) that rivals that of the record holder SrTiO₃ (15). The superconducting phase transition at $T_c \approx 0.8 \text{ K}$ (4) cannot be explained within the Bardeen-Cooper-Schrieffer (BCS) theory framework, which would require a carrier density nearly three orders of magnitude larger to explain the superconducting phase temperature (16), and the upper critical field $H_{c2}(0) = 1.5 \text{ T}$ exceeds the orbital pair-breaking limit for a conventional s -wave pairing state (4, 17). The linear temperature dependence of the upper critical field over the entire superconducting temperature range (4, 17) resembles that seen in the topological superconductors, such as Cu_xBi₂Se₃ (18) and Bi₂Se₃ under pressure (19).

RESULTS

To establish a proper pairing model for YPtBi, understanding the electronic structure is essential. Generally, the crystal electric field in a face-centered cubic crystal structure splits the degenerate atomic energy levels into twofold degenerate conduction band and two- and fourfold degenerate valence bands at the Γ -point as shown in Fig. 2A (left). As the atomic SOC of Bi becomes stronger, the valence bands push each other. In YPtBi, the SOC is sufficiently strong to invert the order of the bands, pushing the p -like Γ_8 band above the s -orbital-derived Γ_6 band.

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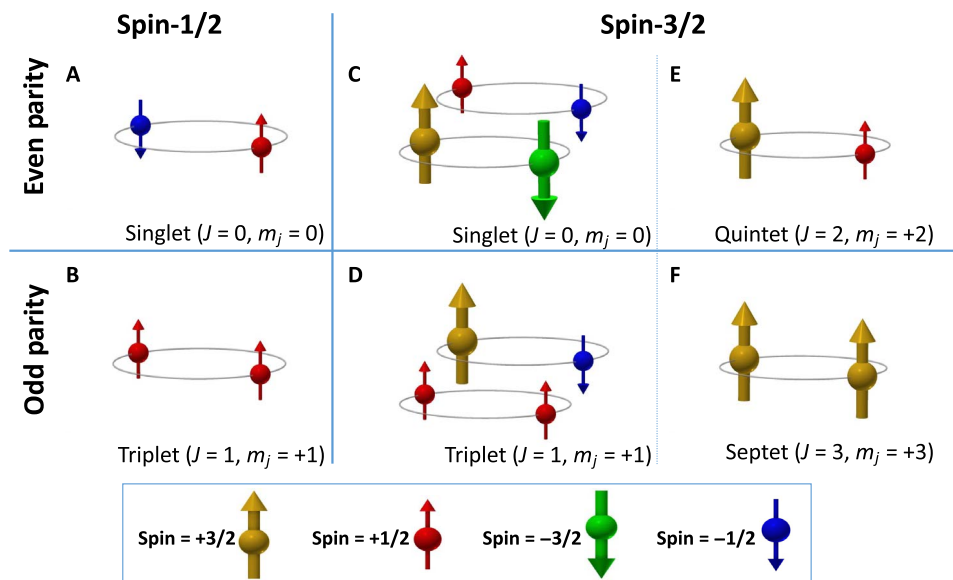


Fig. 1. High-spin Cooper pairing. In conventional spin 1/2 systems, there exists four pairing channels among the spin $-1/2$ and $1/2$ states: one spin-singlet state (with total angular momentum given by $J = 0$ and with the z component of angular momentum, J_z , given by $m_j = 0$) and three spin-triplet states, with $J = 1$ and $m_j = -1, 0$, and 1 . The Pauli exclusion principle requires the antisymmetric even-valued J states to have even spatial parity and the symmetric odd-valued J states to have odd spatial parity. The spin-singlet $J = 0, m_j = 0$ Cooper pair is depicted in (A), whereas the spin-triplet $J = 1, m_j = 1$ Cooper pair is depicted in (B). For the spin 3/2 systems, there exist 16 pairing channels among the spin $-3/2, -1/2, 1/2$, and $3/2$ states: one spin-singlet state with $J = 0$ and $m_j = 0$; three spin-triplet states with $J = 1$ and $m_j = -1, 0$, and 1 ; five spin-quintet states with $J = 2$ and $m_j = -2, -1, 0, 1$, and 2 ; and seven spin-septet states with $J = 3$ and $m_j = -3, -2, -1, 0, 1, 2$, and 3 (see the Supplementary Materials for complete listing). The highest m_j state for each J is depicted in (C) to (F). In (C), the $J = 0, m_j = 0$ spin-singlet pair is a quantum superposition of two Cooper pairs, with one pair made from spins $-1/2$ and $1/2$ and the other pair made from spins $-3/2$ and $3/2$. In (D), the $J = 1, m_j = 1$ spin-triplet pair is a quantum superposition of two Cooper pairs, with one made from two paired spin $1/2$ states and the other from pairing spin $3/2$ with spin $-1/2$. (E) and (F) show the $J = 2, m_j = 2$ and $J = 3, m_j = 3$ states, respectively.

This produces a topological semimetal where the low-energy states have spin-3/2 character.

To characterize the band structure in YPtBi, we use density functional theory (DFT) calculations. The calculated bands near the Fermi level along the high symmetry points are shown in Fig. 2B, confirming the topological band inversion of s -like Γ_6 and p -like Γ_8 bands as shown previously (20, 21). Lacking inversion symmetry splits the spin-degenerate band (22). A maximum spin splitting near the chemical potential is observed along $[111]$ (Γ -L) and zero-splitting degeneracy along $[100]$ (Γ -X). The theoretical chemical potential lies on the band touching point. However, experimental chemical potentials are located at -35 and -300 meV determined by quantum oscillation (4) and angle-resolved photoemission spectroscopy (ARPES) (23, 24) experiments, respectively (see the Supplementary Materials for details).

The most interesting aspect of the band inversion and the position of the experimental chemical potential in the Γ_8 band arise due to the $j = 3/2$ total angular momentum, which comes from the SOC of spin $s = 1/2$ electrons in the $l = 1$ p orbitals of Bi. Near the Fermi energy, we model the Γ_8 bands by a $j = 3/2$ $\mathbf{k} \cdot \mathbf{p}$ theory (25). Up to quadratic order in \mathbf{k} , the single-particle Hamiltonian is

$$H = \alpha k^2 + \beta \sum_i k_i^2 \check{J}_i^2 + \gamma \sum_{i \neq j} k_i k_j \check{J}_i \check{J}_j + \delta \sum_i k_i (\check{J}_{i+1} \check{J}_i \check{J}_{i+1} - \check{J}_{i+2} \check{J}_i \check{J}_{i+2}) \quad (1)$$

where $i = x, y$, and z and $i + 1 = y$ if $i = x$, etc., and \check{J}_i are 4×4 matrix representations of the $j = 3/2$ angular momentum operators. The first line of Eq. 1 is the Luttinger-Kohn model, whereas the second line is the

ASOC due to the broken inversion symmetry in YPtBi. The parameters α, β, γ , and δ are chosen by fitting to our ab initio calculations adjusted against ARPES results by matching the bulk bands Γ_6 and Γ_7 (see fig. S1 for details), which yield $\alpha = 20.5 \text{ eV}^2/\pi^2$, $\beta = -18.5 \text{ eV}^2/\pi^2$, $\gamma = -12.7 \text{ eV}^2/\pi^2$, and $\delta = 0.06 \text{ eV}^2/\pi^2$ by fixing the chemical potential at $u = -35$ meV, estimated by using quantum oscillation frequency $F = 46$ T with a parabolic band (see the Supplementary Materials for details). Here, a is the lattice constant taken from the study by Haase *et al.* (26). The observed low density of hole carriers is consistent with a Fermi energy lying close to the top of the hole bands, yielding typical Fermi surfaces shown in Fig. 2C.

The Hamiltonian Eq. 1 has two major implications for the superconductivity in YPtBi. First, because the quasi-particles in the Γ_8 band have intrinsic angular momentum $j = 3/2$, they can form Cooper pairs with higher intrinsic angular momentum than allowed in the conventional theory of $j = 1/2$ quasi-particle pairing; specifically, in addition to the familiar singlet ($J = 0$) and triplet ($J = 1$) states, we must also consider quintet ($J = 2$) and septet ($J = 3$) pairing (see the Supplementary Materials for full set of states). Second, the absence of inversion symmetry (manifested by ASOC) implies that a stable superconducting state will be dominated by pairing between quasi-particles in time-reversed states near the Fermi energy (9). As detailed in the Supplementary Materials, this condition is generically satisfied by a mixture of conventional s -wave singlet pairing with an unconventional p -wave septet pairing state (13). We emphasize that this unconventional superconducting state cannot occur for Cooper pairs made from pairing usual $j = 1/2$ states. The proposed superconducting states do not depend on the details of the band structure, for example, local density approximation (LDA) or modified Becke-Johnson LDA (MBJLDA). The key

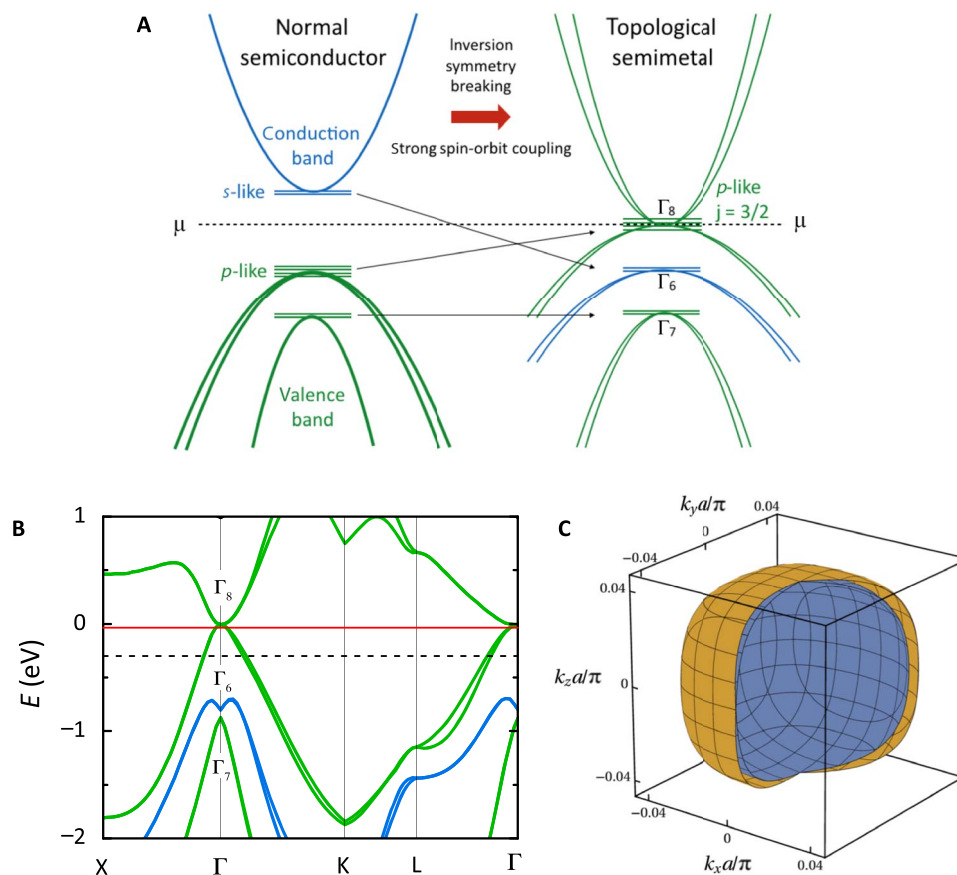


Fig. 2. Topological band structure and spin-split Fermi surface of YPtBi. The effect of strong SOC on a normal semiconductor band structure acts to produce a topological semimetal, which retains the spin-3/2 character of the original p -like band. As shown schematically in (A), as SOC is increased, the s -like conduction band is pushed below the chemical potential μ , whereas the fourfold-degenerate p -like valence band at the Γ -point is pushed up to the chemical potential forming spin $j = 3/2$ p -like conduction band. The absence of parity symmetry in the YPtBi crystal structure generally causes further splitting of the bands away from the Γ -point. Because of the high symmetry of the cubic crystal structure of the half-Heusler material YPtBi, its MBJLDA electronic structure (see main text), shown in (B), retains the fourfold degeneracy of the p -like $j = 3/2$ states at the Γ -point. The solid and dashed horizontal lines represent μ determined by quantum oscillation and angle-ARPES experiments, respectively. (C) Theoretical spin-split Fermi surfaces obtained by fitting the $j = 3/2 \mathbf{k} \cdot \mathbf{p}$ theory in Eq. 1 to the ab initio results by fixing the chemical potential at $\mu = -35$ meV (see main text).

requirement is only that the bands stem from a $j = 3/2$ representation at the Γ -point, and the nontrivial pairing states with nodes exist for all band structures as demonstrated in the study by Brydon *et al.* (13).

To determine the spin splitting of the true bulk Fermi surface, the angle-dependent Shubnikov–de Haas (SdH) effect was studied. First, we examine the magnetoresistance derivative, dR_{xx}/dB , to access directly to the oscillatory component. Figure 3A shows dR_{xx}/dB versus B at various in-plane angles ϕ defined from the crystallographic [010] direction, measured at $T = 2$ K. A node-like feature of beating oscillations, observable near 7 T for $\phi \leq 10^\circ$, moves in the magnetic field as the angle increases away from the highest symmetry direction. Angle-dependent SdH frequency (F), which is proportional to the cross-sectional area of Fermi surface maxima, was determined at the representative angles by using the fast Fourier transform (FFT) technique. The symmetrized plot of F versus ϕ is presented in Fig. 3B based on actual data with $0^\circ \leq \phi \leq 90^\circ$. At first glance, the SdH frequency is almost constant around $F = 46$ T (red line), which is consistent with a nearly spherical Fermi surface. Clear split peak was observed when $H \parallel [010]$, that is, $\phi = 0^\circ$, with two frequencies of 39 and 50 T. The observed two frequencies correspond, respectively, to the inner and outer orbits of spin-split Fermi surfaces. To understand the nature of the Fermi surfaces associated with

the two frequencies, we determined the temperature-dependent amplitude of the FFT spectra as shown in Fig. 3C. As temperature rises, the split-peak feature is no longer visible above $T = 10$ K due to thermal broadening of the corresponding Landau levels. A representative effective mass $m^* = 0.11m_e$ by using the Lifshitz-Kosevich theory for both frequencies. The angle-dependent SdH data strongly support the theoretical spin-split Fermi surfaces.

To further constrain the pairing model, we focus on measurements of the temperature-dependent London penetration depth $\Delta\lambda(T)$, which is intimately related to the superconducting order parameter Δ (27). This approach is particularly useful in the case of YPtBi, where thermodynamic signatures of the superconducting state are difficult to measure, because λ^2 is inversely proportional to $N(0)$. The absolute value of the zero-temperature $\lambda(0)$ is $1.6 \mu\text{m}$ (28), about two orders of magnitude greater than that found in conventional superconductors with $T_c \sim 1$ K, such as zinc or aluminum.

As shown in Fig. 4A, a sharp and single superconducting transition at $T_c \approx 0.8$ K is observed, implying high quality of single crystal YPtBi. The transition temperature is consistent with transport measurements (4, 17). We compare the low-temperature behavior of $\Delta\lambda(T)$ in YPtBi to that of KFe_2As_2 (29), an unconventional superconductor with line

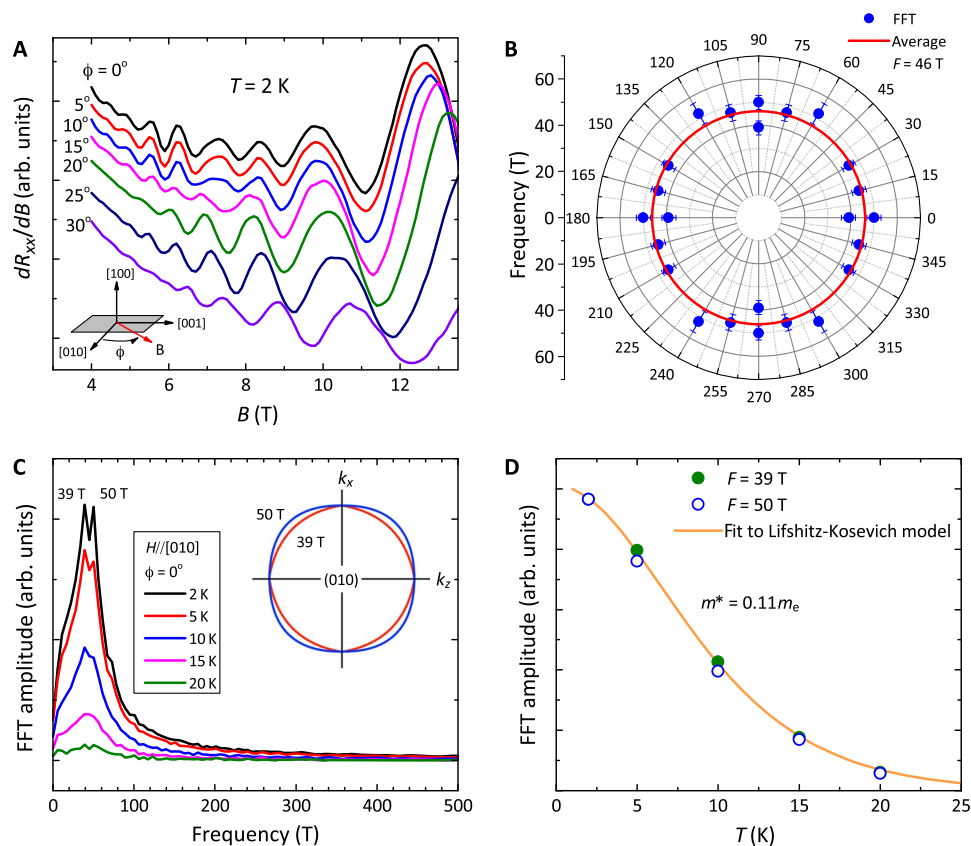


Fig. 3. Angle-dependent quantum oscillations in YPtBi. SdH oscillations were used to demonstrate the geometry of the spin-split Fermi surfaces. (A) dR_{xx}/dB versus B at $T = 2$ K is presented, measured at various in-plane angles ϕ defined from crystallographic [010] direction. A node of beating oscillation is observable near 7 T for $\phi \leq 10^\circ$. The beating pattern changes as the angle is increased away from the high-symmetry direction. Actual magnetoresistance data R_{xx} are presented in the Supplementary Materials. (B) Angle-dependent frequency (F) was determined by using the FFT method on background subtracted oscillations (see the Supplementary Materials for details). The quantum oscillation frequency is nearly independent on the field orientation, and two frequencies are resolved when the field is applied with $\phi = 0^\circ$, for example, $H \parallel [010]$. The red solid line is an averaged frequency, 46 T. The error bar is the frequency resolution of FFT. (C) Temperature-dependent FFT spectrum of SdH oscillations at $\phi = 0^\circ$. The two frequencies, which are responsible for the beating pattern observed at $\phi \leq 10^\circ$, are resolved to be 39 and 50 T, which correspond, respectively, to the inner and outer spin-split Fermi surfaces as shown in the inset. (D) The temperature-dependent amplitude of the FFT spectra is nearly identical for both spin-split Fermi surfaces as expected. A representative effective mass $m^* = 0.11m_e$ was determined by using the Lifshitz-Kosevich theory to both Fermi surfaces.

nodes (29), and the anisotropic s -wave superconductor CaPd_2As_2 (30), both taken using an identical experimental setup. The contrast is striking, with $\Delta\lambda(T)$ in YPtBi being nearly identical to that of KFe_2As_2 and completely different from that of CaPd_2As_2 . In a fully gapped s -wave superconductor, the thermally activated quasi-particles are responsible for the expected exponential temperature dependence of $\Delta\lambda(T)$ at low temperatures (see the Supplementary Materials for details), whereas power laws are clear signatures of nodes or zeroes in the superconducting order parameter (27). In a gap structure with line nodes, the penetration depth varies linearly with temperature at sufficiently low temperatures ($T < 0.3T_c$) in a clean sample (see the Supplementary Materials for details) (31), as observed in the prototypical d -wave superconductor $\text{YBa}_2\text{Cu}_3\text{O}_{6.95}$ (YBCO) (32) and in the mixed-parity noncentrosymmetric superconductors CePt_3Si (33) and $\text{Li}_2\text{Pt}_3\text{B}$ (34).

In YPtBi, we obtained the best least squares fitting for $\Delta\lambda(T)$ to a power-law function $\Delta\lambda = AT^n$ was obtained with $n = 1.20 \pm 0.02$ and $A = 1.98 \pm 0.08 \mu\text{m}/\text{K}^{1.2}$ in a temperature range that spans above $0.2T_c$. This nearly T -linear behavior is consistent with the expectation for a line-nodal superconductor. The observed small deviation from linearity is likely due to moderate impurity scattering, quantified by modifying the temperature dependence $\Delta\lambda(T) = bT^2/(T + T^*)$ (35) with scattering rate

parameter $T^* = 0.07T_c$, indicating an exceptionally clean sample. The extraordinarily large power-law prefactor A in YPtBi is consistent with the London theory expectation $\lambda(0) \propto n^{-2}$ given the small carrier density of this material.

DISCUSSION

Line nodes could, in principle, arise from a large number of different pairing states. However, the cubic symmetry of YPtBi imposes severe constraints on the pairing: For example, the pure d -wave state realized in YBCO is very unlikely here, because it would be difficult to avoid mixing with another degenerate d -wave state. Although symmetry permits line nodes due to an extended s -wave state, this requires significant fine-tuning due to the small, nearly spherical Fermi surface of the material. Generic models for a nodal order parameter in YPtBi are concerned in a mixture of even-odd parity states, for example, singlet-triplet mixture. For T_d symmetry, the lowest orbital angular momentum A_1 triplet state is f -wave, which for small k gives gap functions on the two spin-split $j = 1/2$ Fermi surfaces (13). This state exhibits line nodes if the f -wave triplet gap Δ_f is larger than the s -wave singlet gap Δ_s . However, dominant f -wave symmetry of the Cooper pairs is highly unlikely if quasi-local interactions

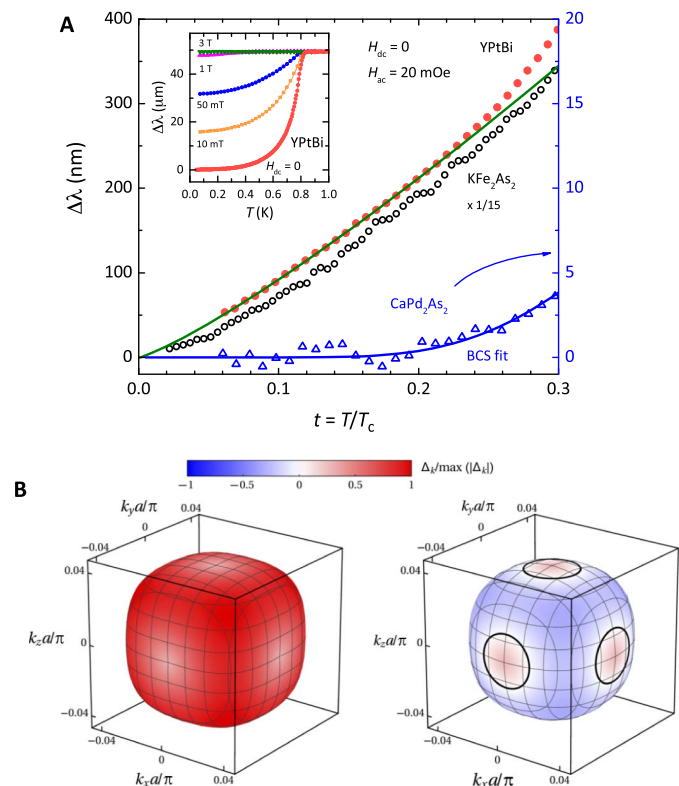


Fig. 4. Evidence for line nodes and spin-3/2 singlet-septet mixed parity pairing model. (A) The London penetration depth $\Delta\lambda(T)$ of YPtBi (solid circles) measured in zero dc field (20 mOe ac field) is compared in (A) with that of KFe_2As_2 (open circles; $T_c = 3.4$ K), an unconventional superconductor with line nodes (29), and the anisotropic s -wave superconductor CaPd_2As_2 (open triangles; $T_c = 1.3$ K) (30), both taken by using an identical experimental setup. The nearly linear variation of $\Delta\lambda(T)$ is in contrast with the full-gap BCS superconductor CaPd_2As_2 data (blue line), constraining any possible pairing model to one that yields line nodes. Inset shows $\Delta\lambda$ in YPtBi under finite magnetic fields. Because of the high intrinsic angular momentum of the Γ_8 band quasiparticles involved in Cooper pairing in YPtBi, our $j = 3/2 \mathbf{k} \cdot \mathbf{p}$ model yields a manifold of possible pairing states with intrinsic angular momenta up to $J = 3$. Incorporating the lack of inversion symmetry, the singlet-septet pairing state is the simplest even-odd parity mixture with line nodes in the pairing gap that arise from the dominant $J = 3$ septet component (see main text). The gap sign and magnitudes are depicted in (B) for the two spin-dependent Fermi surfaces of YPtBi, showing the presence of line of zero-gap nodes (black lines) situated on one of the spin-dependent surfaces.

give rise to superconductivity (36); these interactions would more plausibly give rise to a p -wave state. The simplest and most generic scenarios for the nodal superconductivity in YPtBi are provided by a dominant $J = 3$ (septet) p -wave gap with a subdominant $J = 0$ (singlet) s -wave gap, as allowed by the noncentrosymmetric crystal structure.

As shown in Fig. 4B, the gap structure resulting from this mixed singlet-septet state displays ring-shaped line nodes on one of the spin-split Fermi surfaces. These line nodes are protected by a topological winding number and lead to nondegenerate surface zero-energy flat bands (see the Supplementary Materials for details) (8, 37), which are of immense interest in the context of topological excitations. The mixed singlet-septet state is a natural generalization of the theory of $j = 1/2$ noncentrosymmetric superconductors. As discussed further in the Supplementary Materials however, the observation of gap line nodes and the broken inversion symmetry may be consistent with other exotic pairing states (13). Furthermore, with a conventional Eliashberg theory

unapplicable to such a low-carrier density system, one must consider other pairing instabilities such as parity fluctuations (38) and instabilities due to apolar optical phonon (39) as possible mechanisms of superconductivity in the half-Heusler system. Studying the pairing mechanism of these exotic high-angular momentum pairing states, as well as their interplay with other symmetry-breaking orders (5), will elucidate the complexity and richness of this family of multifaceted topological materials.

METHODS

YPtBi single crystals were grown out of molten Bi with starting composition Y/Pt/Bi = 1:1:20 (atomic ratio). The starting materials Y ingot (99.5%), Pt powder (99.95%), and Bi chunk (99.999%) were put into an alumina crucible, and the crucible was sealed inside an evacuated quartz ampule. The ampule was heated slowly to 1150°C, kept for 10 hours, and then cooled down to 500°C at a 3°C/hour rate, where the excess of molten Bi was decanted by centrifugation.

The calculated band structure of YPtBi was obtained using the WIEN2k implementation of the full potential linearized augmented plane-wave method with the Tran-Blaha modified Becke-Johnson exchange-correlation potential (MBJLDA) (40), with SOC included in the calculation. The k -point mesh was taken to be $11 \times 11 \times 11$, and cubic lattice constant $a = 664.0(1)$ pm was obtained from the study by Haase *et al.* (26).

The temperature variation of London penetration depth $\Delta\lambda(T)$ was measured in a commercial dilution refrigerator by using a tunnel diode resonator technique. The single-crystal sample with dimensions $0.29 \text{ mm} \times 0.69 \text{ mm} \times 0.24 \text{ mm}$ was mounted on a sapphire rod and inserted into a 2-mm inner diameter copper coil that produces radio frequency excitation field with empty-resonator frequency of 22 MHz with amplitude $H_{ac} \approx 20$ mOe. The shift of the resonant frequency (in centimeter gram second units) is $\Delta f(T) = -G4\pi\chi(T)$, where $\chi(T)$ is the differential magnetic susceptibility, $G = f_0 V_s / 2V_c(1 - N)$ is a constant, N is the demagnetization factor, V_s is the sample volume, and V_c is the coil volume. The constant G was determined from the full frequency change by physically pulling the sample out of the coil. With the characteristic sample size, R , $4\pi\chi = (\lambda/R)\tanh(R/\lambda) - 1$, from which $\Delta\lambda$ can be obtained (27).

Magnetic field-dependent magnetoresistance was determined on samples by using a standard four-probe technique. Contacts were made by using high-purity silver wires and conducting epoxy, and measurements were performed in a commercial cryostat with a single-axis rotator in magnetic fields up to 14 T at temperatures as low as 2 K.

SUPPLEMENTARY MATERIALS

Supplementary material for this article is available at <http://advances.sciencemag.org/cgi/content/full/4/4/eaao4513/DC1>

- fig. S1. Band structure of YPtBi
- fig. S2. Photon-dependent ARPES of Bi-terminated YPtBi(111).
- fig. S3. Normalized magnitude of each gap along high symmetry points.
- fig. S4. Superfluid density in YPtBi and other well-known superconductors.
- fig. S5. Angle-dependent magnetoresistance in YPtBi.
- fig. S6. Angle-dependent frequency of Shubnikov-de Haas quantum oscillation in YPtBi.
- fig. S7. Temperature-dependent quantum oscillations with $\theta = 90^\circ$ and $\phi = 0^\circ$.

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