

Odd-Parity Topological Superconductors: Theory and Application to $\text{Cu}_x\text{Bi}_2\text{Se}_3$

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Topological superconductors have been theoretically predicted as a new class of time-reversal-invariant superconductors which are fully gapped in the bulk but have protected gapless surface Andreev bound states. In this work, we provide a simple criterion that directly identifies this topological phase in *odd-parity* superconductors. We next propose a two-orbital $U - V$ pairing model for the newly discovered superconductor $\text{Cu}_x\text{Bi}_2\text{Se}_3$. Due to its peculiar three-dimensional Dirac band structure, we find that an inter-orbital triplet pairing with odd-parity is favored in a significant part of the phase diagram, and therefore gives rise to a topological superconductor phase. Finally we propose sharp experimental tests of such a pairing symmetry.

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The search of topological phases of matter with time-reversal symmetry has been an active field in condensed matter physics[1]. In the last few years, a new phase of matter called topological insulators[2, 3] has been predicted[4] and soon experimentally observed in a number of materials[5, 6]. More recently, a new class of time-reversal-invariant (TRI) superconductors has been predicted by a topological classification of Bogoliubov-de Gennes (BdG) Hamiltonians[7, 8]. As a close cousin of topological insulators, the so-called “topological superconductor” is fully gapped in the bulk but has gapless surface Andreev bound states hosting Bogoliubov quasiparticles[7, 9, 10]. Now the challenge is to theoretically propose candidate materials for this new phase.

In this work, we first provide a simple criterion which can be directly used to establish the topological superconductor phase in *centrosymmetric* materials with *odd-parity* pairing symmetry. This criterion applies to superconductors with spin-orbit coupling. We next study the possibility of odd-parity pairing in the newly discovered superconductor $\text{Cu}_x\text{Bi}_2\text{Se}_3$ [11], which has a 3D Dirac band structure due to strong SOC. We propose a phenomenological model for $\text{Cu}_x\text{Bi}_2\text{Se}_3$ with short-range interactions. Thanks to the peculiar Dirac band structure, we find a specific odd-parity triplet pairing is favored in a wide parameter range, giving rise to a topological superconductor. We propose an unusual flux quantization in Josephson interferometry as a sharp test of such a pairing symmetry. We also explicitly demonstrate the existence of gapless surface Andreev bound states in the resulting topological phase.

We start by introducing Nambu notation $\xi_{\mathbf{k}}^{\dagger} \equiv [c_{\mathbf{k},a\alpha}^{\dagger}, c_{-\mathbf{k},a\beta}^T(is_y)_{\beta\alpha}]$, where $\alpha, \beta = \uparrow, \downarrow$ label electron's spin and a labels the orbital basis for cell-periodic Bloch wave-functions. The BCS mean-field Hamiltonian $H = \int_{BZ} d\mathbf{k} \xi_{\mathbf{k}}^{\dagger} \mathcal{H}(\mathbf{k}) \xi_{\mathbf{k}}$ uniquely defines a BdG Hamiltonian

$$\mathcal{H}(\mathbf{k}) = [H_0(\mathbf{k}) - \mu]\tau_z + \hat{\Delta}(\mathbf{k})\tau_x, \quad (1)$$

where H_0 describes the band structure of normal metal, μ is chemical potential, and $\hat{\Delta}$ is pairing potential. For TRI

superconductors, $\Theta\mathcal{H}(\mathbf{k})\Theta^{-1} = \mathcal{H}(-\mathbf{k})$ where $\Theta = is_yK$ is time reversal operation.

The BdG Hamiltonian $\mathcal{H}(\mathbf{k})$ of a fully gapped superconductor, which describes Bogoliubov quasi-particle spectrum, formally resembles the Bloch Hamiltonian of an insulator. An important difference, however, is that $\mathcal{H}(\mathbf{k})$ has particle-hole symmetry inherited from the doubling of degrees of freedom in Nambu space: $\Xi\mathcal{H}(\mathbf{k})\Xi = -\mathcal{H}(-\mathbf{k})$ with $\Xi \equiv s_y\tau_yK$. Because of this extra symmetry, Schnyder, Ryu, Furusaki and Ludwig[7] and Kitaev[8] have shown that 3D TRI superconductors are mathematically classified by an integer invariant n instead of Z_2 invariants for insulators[2, 3]. Despite this difference, since $\mathcal{H}(\mathbf{k})$ belongs to a subset of TRI Hamiltonians, we observe that $\nu \equiv n \bmod 2$ is nothing but its own Z_2 invariant as explicitly defined in Ref.[13]. It then follows that $\nu = 1$ implies a nonzero n and is sufficient (though not necessary) to establish a topological superconductor phase.

A powerful “parity criterion” has been advanced by Fu and Kane to evaluate ν efficiently for materials with inversion symmetry[4]. This motivates us to study topological superconductors in centrosymmetric materials, for which the pairing symmetry can be either even or odd under inversion. It follows from the explicit formula for n [7] that even-parity ones cannot be topological superconductors. In this work we focus on odd-parity superconductors satisfying $PH_0(\mathbf{k})P = H_0(-\mathbf{k})$ and $P\hat{\Delta}(\mathbf{k})P = -\hat{\Delta}(-\mathbf{k})$, where P is inversion operator. We now provide a simple criterion for odd-parity topological superconductors:

Criterion: a fully gapped TRI superconductor with odd-parity pairing is a topological superconductor, if its Fermi surface encloses an odd number of TRI momenta in the Brillouin zone.

A special case of this criterion has been proved[12] for certain triplet superconductors in which $H_0(\mathbf{k}) = H_0(-\mathbf{k})$ and $\hat{\Delta}(\mathbf{k}) = -\hat{\Delta}(-\mathbf{k})$, i.e., inversion simplifies to an identity operator $P = I$. Here we generalize the proof to all odd-parity superconductors, as needed later. *Proof:* Since $P\mathcal{H}(\mathbf{k})P \neq \mathcal{H}(-\mathbf{k})$, the parity criterion of

Ref.[4] does not apply directly. Instead, because $\hat{\Delta}\tau_x$ anticommutes with τ_z , $\mathcal{H}(\mathbf{k})$ satisfy:

$$\tilde{P}\mathcal{H}(\mathbf{k})\tilde{P} = \mathcal{H}(-\mathbf{k}), \quad \tilde{P} \equiv P\tau_z. \quad (2)$$

Since the operator \tilde{P} defined here satisfies $\tilde{P}^2 = 1$ and $[\tilde{P}, \Theta] = 0$, \tilde{P} can be used in place of P as an inversion operator for odd-parity superconductors. The corresponding parity criterion with \tilde{P} reads

$$(-1)^\nu = \prod_{\alpha,m} \xi_{2m}(\Gamma_\alpha). \quad (3)$$

Here Γ_α 's ($\alpha = 1, \dots, 8$) are eight TRI momenta in 3D Brillouin zone satisfying $\Gamma_\alpha = -\Gamma_\alpha$ up to a reciprocal lattice vector. $\xi_{2m}(\Gamma_\alpha) = \pm 1$ is the \tilde{P} eigenvalue of the $2m$ -th negative energy band at Γ_α , which shares the same value $\xi_{2m}(\Gamma_\alpha) = \xi_{2m+1}(\Gamma_\alpha)$ as its Kramers degenerate partner. The product over m in (3) includes all negative energy bands of $\mathcal{H}(\mathbf{k})$. The physical meaning of (3) becomes transparent in weak-coupling superconductors, for which the pairing potential is a small perturbation to H_0 . As long as the bands $\varepsilon_n(\Gamma_\alpha)$ of $H_0(\Gamma_\alpha)$ stay away from the Fermi energy (which is generically true), pairing-induced mixing between electrons and holes in the eigenstates $\psi_m(\Gamma_\alpha)$ of $\mathcal{H}(\Gamma_\alpha)$ can be safely neglected. So we have $\xi_{2m}(\Gamma_\alpha) = p_{2m}(\Gamma_\alpha) \times \tau_{2m}(\Gamma_\alpha)$ with p and τ being the eigenvalues of P and τ_z separately. (3) then factorizes into two products over p and τ . Now the key observation is that the set of all negative energy eigenstates of \mathcal{H} corresponds to the set of *all* energy bands of H_0 (both above and below μ), which form a complete basis of H_0 . So we find $\prod_m p_{2m}(\Gamma_\alpha) = \text{Det}[P] = \pm 1$ independent of Γ_α , and thus $\prod_{\alpha,m} p_{2m}(\Gamma_\alpha) = 1$. (3) then simplifies to

$$(-1)^\nu = \prod_{\alpha,m} \tau_{2m}(\Gamma_\alpha) = \prod_{\alpha} (-1)^{N(\Gamma_\alpha)}. \quad (4)$$

Here $N(\Gamma_\alpha)$ is defined as the number of unoccupied bands at Γ_α in the normal state. (4) now has a simple geometrical interpretation: $\nu = 0$ or 1 if the Fermi surface of H_0 encloses an even or odd number of TRI momenta, respectively[24]. The latter case corresponds to a topological superconductor.

A well-known example of odd-parity pairing is superfluid He-3[14]. In particular, the TRI and fully-gapped B -phase has been recently identified as a topological superfluid [7, 9, 10], in agreement with the above criterion. This identification explains the topological origin of its gapless surface Andreev bound states theoretically predicted before[15]. Odd-parity pairing in superconductors is less well established. A famous example is Sr_2RuO_4 , as shown by phase-sensitive tests of pairing symmetry[16]. However, the observed signatures of spontaneous time reversal symmetry breaking[17] seem to prevent Sr_2RuO_4 from being a TRI topological superconductor.

In the search for odd-parity superconductors, we turn our attention to the newly discovered superconductor

$\text{Cu}_x\text{Bi}_2\text{Se}_3$ —a doped semiconductor with low electron density and $T_c = 3.8\text{K}$ [11]. A most recent angle-resolved photoemission spectroscopy experiment[18] found that the dispersion $\varepsilon_{\mathbf{k}}$ near center of the Brillouin zone Γ strikingly resembles a massive 3D Dirac fermion, being quadratic near the band bottom, and linear at higher energy. Upon doping with Cu, the Fermi energy moves into the conduction band, about 0.25eV above the band bottom in the “relativistic” linear regime[18]. To the best of our knowledge, this is the first discovery of superconductivity in a 3D Dirac material, which motivates us to study its pairing symmetry.

The Dirac band structure in the parent compound Bi_2Se_3 originates from strong inter-band SOC and can be understood from $k \cdot p$ theory[19]. Since the (lowest) conduction and (highest) valence band at Γ have opposite parity, general symmetry considerations show that the $k \cdot p$ Hamiltonian $H_0(\mathbf{k})$ to first order in k takes the form of a four-component Dirac Hamiltonian[20]:

$$H_0(\mathbf{k}) = m\Gamma_0 + v(k_x\Gamma_1 + k_y\Gamma_2) + v_z k_z\Gamma_3, \quad (5)$$

where Γ_i 's ($i = 0, \dots, 3$) are 4×4 Dirac Gamma matrices. The four components arise from electron's orbital (σ) and spin (s). As shown by first-principle calculations[5, 19], the conduction and valence bands of Bi_2Se_3 mainly consist of two orbitals: the top and bottom Se p_z -orbital in the five-layer unit cell, each mixed with its neighboring Bi p_z -orbital (z is along c axis). The two orbitals transform into each other under inversion and we label them by $\sigma_z = \pm 1$. The Gamma matrices in H_0 are then expressed as follows: $\{\Gamma_0, \Gamma_1, \Gamma_2, \Gamma_3\} \equiv \{\sigma_x, \sigma_z \otimes s_y, -\sigma_z \otimes s_x, \sigma_y\}$.

To study superconductivity in $\text{Cu}_x\text{Bi}_2\text{Se}_3$, we consider the following phenomenological effective Hamiltonian with short-range density-density interactions:

$$H_{\text{eff}} = c^\dagger(H_0 - \mu)c - \int dx \left[U \sum_{a=1,2} n_a^2 + 2Vn_1n_2 \right], \quad (6)$$

where $n_a(x) = \sum_{\alpha=\uparrow,\downarrow} c_{a\alpha}^\dagger(x)c_{a\alpha}(x)$ is electron density in orbital a . U and V are intra-orbital and inter-orbital interactions, respectively. All other local interaction terms, such as $(c^\dagger\sigma_x c)^2$ and $(c^\dagger\sigma_x \bar{s}c)^2$, are neglected[23]. H_{eff} is to be thought of as an effective low-energy Hamiltonian, which includes the effects of both Coulomb and electron-phonon interactions. We will assume that at least one of them is positive, giving rise to pairing. Since U and V are difficult to estimate from a microscopic theory, we will treat them as phenomenological parameters. Naively, one would expect that the intra-orbital effective phonon-mediated attraction would be stronger than the inter-orbital one. However, since the same is true for the Coulomb repulsion, it is possible that the overall effective interactions satisfy, e.g., $0 < V < U$.

To determine the pairing symmetry of the $U-V$ model, we take advantage of two facts: a) near T_c , $\hat{\Delta}$ forms

$\hat{\Delta}$:	$\Delta_1 I + \Delta'_1 \Gamma_0$	$\Delta_2 \Gamma_{50}$	$\Delta_3 \Gamma_{30}$	$\Delta_4 (\Gamma_{10}, \Gamma_{20})$
Θ	+	+	+	(+, +)
P	+	-	-	(-, -)
C_3	z	z	z	(x, y)
M	+	-	+	(-, +)

TABLE I: Pairing potential in mean-field BdG Hamiltonian of $U - V$ model, and their transformation rules.

an irreducible representation of crystal point group; b) the mean-field pairing potential is local in x and thus k -independent. The form of all such pairing potentials $\hat{\Delta}$ are listed in Table II, where $\Gamma_5 \equiv \Gamma_0 \Gamma_1 \Gamma_2 \Gamma_3 = \sigma_z s_z$ and $\Gamma_{jk} \equiv i\Gamma_j \Gamma_k$. Also shown are transformation rules of $\hat{\Delta}$'s under the following symmetry operations of Bi_2Se_3 : inversion $P = -\Gamma_0 = -\sigma_x$, threefold rotation around the c axis $C_3 = \exp(i\Gamma_{12}\pi/3) = \exp(-is_z\pi/3)$, and mirror about yz plane $M = -i\Gamma_{15} = -is_x$. We find that $\hat{\Delta}_1, \dots, \hat{\Delta}_4$ correspond to A_{1g}, A_{1u}, A_{2u} and E_u representations of point group D_{3d} respectively. The three A representations are one-dimensional so that the corresponding phases are non-degenerate. Among them, $c^T \hat{\Delta}_1(is_y)c \propto \Delta_1 c_{1\uparrow} c_{1\downarrow} + \Delta'_1 c_{1\uparrow} c_{2\downarrow} + (1 \leftrightarrow 2)$ is spin-singlet pairing with mixed intra- and inter-orbital (orbital triplet) components, which is invariant under all crystal symmetries; $c^T \hat{\Delta}_2(is_y)c \propto (c_{1\uparrow} c_{2\downarrow} + c_{1\downarrow} c_{2\uparrow})$ is inter-orbital (orbital singlet) spin-triplet pairing; $c^T \hat{\Delta}_3(is_y)c \propto (c_{1\uparrow} c_{1\downarrow} - c_{2\uparrow} c_{2\downarrow})$ is intra-orbital spin-singlet pairing. The E_u representation is two-dimensional with $c^T \hat{\Delta}_4(is_y)c \propto \alpha c_{1\uparrow} c_{2\uparrow} + \beta c_{1\downarrow} c_{2\downarrow}$, where α and β are arbitrary coefficients, leading to a $SU(2)$ degenerate manifold at T_c . Of these phases, the $\hat{\Delta}_2$ pairing phase is odd-parity, TRI, and fully gapped, with a Bogoliubov spectrum given by

$$E_{\pm, k} = \sqrt{\varepsilon_k^2 + \mu^2 + \Delta_2^2 \pm 2\mu \sqrt{\varepsilon_k^2 + \left(\frac{m}{\mu}\right)^2 \Delta_2^2}}, \quad (7)$$

where $\varepsilon_k = \sqrt{m^2 + v^2(k_x^2 + k_y^2) + v_z^2 k_z^2}$. Since the Fermi surface only encloses the Γ point, according to our earlier criterion $\hat{\Delta}_2$ pairing gives rise to a topological superconductor phase in the $U - V$ model for $\text{Cu}_x\text{Bi}_2\text{Se}_3$.

We now solve the linearized gap equation for T_c of the various pairing channels to obtain the phase diagram. For purely inter-orbital pairing $\hat{\Delta}_2$ and $\hat{\Delta}_4$, the gap equation reads $V\chi_{2,4}(T_c) = 1$. For purely intra-orbital pairing $\hat{\Delta}_3$, it reads $U\chi_3(T_c) = 1$. Here $\chi_i(T)$ is the finite temperature superconducting susceptibility in pairing channel $\hat{\Delta}_i$. A straight-forward calculation shows that

$$\chi_2 = \chi_0 \int d\mathbf{k} \delta(\varepsilon_{\mathbf{k}} - \mu) \text{Tr}[\Gamma_{50} \text{P}_{\mathbf{k}}]^2 / (2D_0). \quad (8)$$

Here $\chi_0 \equiv D_0 \int_0^W d\varepsilon \tanh\left(\frac{\varepsilon}{2T}\right) / \varepsilon$, where D_0 is density of states at Fermi energy and W is high-energy cutoff. The

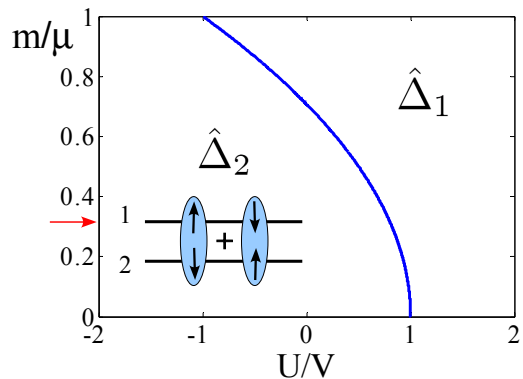


FIG. 1: Phase diagram of the $U - V$ model, showing the highest T_c phase as a function of m/μ and U/V (assuming $V > 0$). The arrow shows the experimental estimate for m/μ , which is about $\frac{1}{3}$ [18]. Two phases $\hat{\Delta}_1$ and $\hat{\Delta}_2$ appear, which are even and odd under parity respectively (see Table I). The insets show schematically the structure of the Cooper pair wavefunction in the $\hat{\Delta}_2$ phase, consisting of two electrons localized on the top (1) and bottom (2) of the five-atom unit cell.

projection operator $\text{P}_{\mathbf{k}} \equiv \sum_{\lambda=1,2} |\phi_{\lambda, \mathbf{k}}\rangle \langle \phi_{\lambda, \mathbf{k}}|$ is defined by the two degenerate Bloch states at \mathbf{k} . As we will see, the integral over the Fermi surface in (8), which takes into account the interplay between pairing potential and band structure effects in a *multi-orbital* system, will play a key role in favoring $\hat{\Delta}_2$ pairing. The other two susceptibilities χ_3 and χ_4 can be obtained simply by replacing Γ_{50} in (8) with Γ_{30} and Γ_{10} respectively. Using $\text{P}_{\mathbf{k}} = \frac{1}{2}(1 + \sum_{\nu=0}^3 n_{\mathbf{k}}^{\nu} \Gamma_{\nu})$ and $n_{\mathbf{k}} = (m, vk_x, vk_y, vk_z) / \varepsilon_{\mathbf{k}}$ for Dirac Hamiltonian H_0 , we obtain $\chi_2 = \chi_0(1 - m^2/\mu^2)$, $\chi_3 = \chi_4 = 2\chi_2/3$. The gap equation for the intra- and inter-orbital mixed pairing $\hat{\Delta}_1$ is:

$$\det \left[\begin{pmatrix} U\chi_0 & U\chi_0 C_1 \\ V\chi_0 C_1 & V\chi_0 C_2 \end{pmatrix} - I \right] = 0, \quad (9)$$

where $C_n = (m/\mu)^n$ for $n = 1, 2$. From (8) and (9), we now deduce the phase diagram. Since $\chi_3 < \chi_0$ and $\chi_4 < \chi_2$, $\hat{\Delta}_3$ and $\hat{\Delta}_4$ always have a lower T_c than their counterparts $\hat{\Delta}_1$ and $\hat{\Delta}_2$, respectively. Only the latter two phases appear in the phase diagram. By equating their T_c 's, we obtain the phase boundary:

$$U/V = 1 - 2m^2/\mu^2. \quad (10)$$

Fig.1 shows the highest T_c phase as a function of U/V and m/μ , for positive (attractive) V . The $\hat{\Delta}_2$ pairing phase dominates in a significant part of the phase diagram. Note that experimentally, it has been estimated that $m/\mu \approx \frac{1}{3}$ [18]. When $V < 0$ the $\hat{\Delta}_1$ phase is stable for $U > m^2/\mu^2|V|$, whereas for smaller U the system is non-superconducting. The fact that the phase boundary starts at the point $U = V$ and $m = 0$ is not accidental: at this point the Hamiltonian (6) has an enlarged $U(1)$

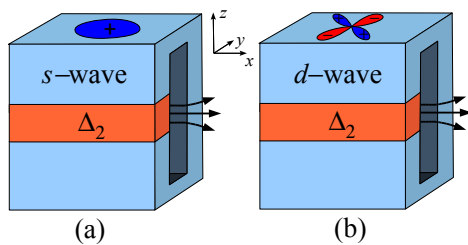


FIG. 2: Phase sensitive experiments to test Δ_2 pairing, which is odd under both inversion ($\mathbf{r} \rightarrow -\mathbf{r}$) and reflection about the yz plane ($x \rightarrow -x$). A superconducting ring made of either an s -wave (a) or d -wave (b) superconductor contains a segment of a Δ_2 superconductor. The flux through the ring is $nh/4e$ (a) or $(n + \frac{1}{2})h/2e$ (b), where n is an integer.

chiral symmetry: $c \rightarrow \exp(i\theta\Gamma_{50})c$. Under the unitary transformation $\exp(i\pi\Gamma_{50}/4)$, the two pairing potentials $c^T(is_y)c$ and $c^T\Gamma_{50}(is_y)c$ transform into each other[25].

From now on, we focus on the topologically non-trivial $\hat{\Delta}_2$ phase. To obtain the surface Andreev bound state spectrum, we solve the BdG Hamiltonian in a semi-infinite geometry $z < 0$:

$$\mathcal{H}(k_x, k_y) = (-iv_z\Gamma_3\partial_z + m\Gamma_0 - \mu)\tau_z + \Delta_2\Gamma_{50}\tau_x + v(k_x\Gamma_1 + k_y\Gamma_2). \quad (11)$$

The continuum Hamiltonian (11) must be supplemented with a boundary condition at $z = 0$. For a $\text{Cu}_x\text{Bi}_2\text{Se}_3$ crystal naturally cleaved in between two five-layer unit cells, the wavefunction amplitude on the bottom layer corresponding to $\sigma_z = -1$ must vanish, so that $\sigma_z\psi = \psi|_{z=0}$ is satisfied. By solving \mathcal{H} at $k_x = k_y = 0$, we find that a Kramers pair of zero-energy surface Andreev bound states ψ_{\pm} exist for $\mu^2 > m^2 - \Delta_2^2$, i.e., as long as the bulk gap remains finite. The wavefunctions of ψ_{\pm} are particularly simple for $m = 0$ [21]:

$$\psi_{\pm}(z) = e^{-\kappa z}(\cos k_0 z|\sigma_z = 1\rangle + \sin k_0 z|\sigma_z = -1\rangle) \otimes |s_z = \pm 1, \tau_y = \mp 1\rangle, \quad (12)$$

where $\kappa = \Delta_2/v_z$ and $k_0 = \mu/v_z$. Using $k \cdot p$ theory, we obtain the low-energy Hamiltonian describing the dispersion of surface Andreev bound states at small k_x and k_y : $H_{sf} = v_s(k_x s_y - k_y s_x)$. The velocity v_s is given by $v_s = \langle \psi_- | v\Gamma_1\tau_z | \psi_+ \rangle / \langle \psi_+ | \psi_+ \rangle \simeq v\Delta_2^2/\mu^2$.

Finally, we discuss the experimental consequences of the Δ_2 state. The topologically protected surface state can be detected by scanning tunneling microscopy. In addition, the oddness of this state under parity and mirror symmetries has consequences for phase-sensitive experiments. Consider a c -axis Josephson junction between a Δ_2 superconductor and an s -wave superconductor. Since the Δ_2 state is odd under reflection about the yz plane, whereas the s -wave gap Δ_s is even, the leading order Josephson coupling between the two superconductors, $-J_1(\Delta_s^*\Delta_2 + c.c.)$, vanishes (as well as higher

odd-order terms). The second order Josephson coupling, $-J_2[(\Delta_s^*)^2\Delta_2^2 + c.c.]$, can be non-zero (as well as higher even-order terms). Therefore, the flux through a superconducting ring shown in Fig. 2a is quantized in units of $\frac{h}{4e}$ [22]. Alternatively, in a Josephson junction between a Δ_2 superconductor and a d -wave superconductor oriented as shown in Fig. 2b, the first order Josephson coupling is non-zero. The flux through the ring in Fig. 2b takes the value $\frac{h}{2e}(n + \frac{1}{2})$ (n is an integer). The same holds for an s -wave superconductor which does not have the mirror symmetry relative to the yz plane. The observation of these anomalous flux quantization relations would be a unique signature of the topological Δ_2 state.

To conclude, we present a theory of odd-parity topological superconductors and propose the newly discovered superconductor $\text{Cu}_x\text{Bi}_2\text{Se}_3$ as a potential candidate for this new phase of matter. We hope this work will bridge the study of topological phases and unconventional superconductivity, as well as stimulate the search for both in centrosymmetric materials with spin-orbit coupling.

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- [1] M. Levin and X. G. Wen, Rev. Mod. Phys. **77**, 871 (2005); M. Freedman *et al*, Ann. Phys. **310**, 428 (2004).
 - [2] L. Fu, C.L. Kane and E.J. Mele, Phys. Rev. Lett. **98**, 106803 (2007).
 - [3] J.E. Moore and L. Balents, Phys. Rev. B **75**, 121306(R) (2007).
 - [4] L. Fu and C.L. Kane, Phys. Rev. B **76**, 045302 (2007).
 - [5] D. Hsieh *et al.*, Nature (London) **452**, 970 (2008); Y. Xia *et al.*, Nat. Phys. **5**, 398 (2009). D. Hsieh *et al.*, Nature **460**, 1101 (2009).
 - [6] Y. L. Chen *et al.*, Science **325**, 5937 (2009)
 - [7] A. Schynder, S. Ryu, A. Furusaki and A. Ludwig, Phys. Rev. B **78**, 195125 (2008)
 - [8] A. Kitaev, arXiv:0901.2686
 - [9] X. L. Qi, T. Hughes, S. Raghu and S. C. Zhang, Phys. Rev. Lett. **102**, 187001 (2009)
 - [10] R. Roy, arXiv:0803.2868 (unpublished)
 - [11] Y. S. Hor *et al*, arXiv:0909.2890
 - [12] M. Sato, Phys. Rev. B **79**, 214526 (2009)
 - [13] L. Fu and C. L. Kane, Phys. Rev. B **74**, 195312 (2006)
 - [14] A. Leggett, Rev. Mod. Phys. **47**, 331 (1975).
 - [15] Y. Nagato, M. Yamamoto, and K. Nagai, J. Low Temp. Phys. **110**, 1135 (1998)
 - [16] Nelson *et al.*, Science **306**, 1151 (2004)
 - [17] J. Xia *et al.*, Phys. Rev. Lett. **97**, 167002 (2006)
 - [18] M. Z. Hasan, unpublished data on $\text{Cu}_x\text{Bi}_2\text{Se}_3$.
 - [19] H. Zhang *et al.*, Nat. Phys. **5**, 438 (2009)
 - [20] P. A. Wolff, J. Phys. Chem. Solids, **25**, 1057 (1964).
 - [21] A similar problem has been solved in L. Fu and C. L.

- Kane, Phys. Rev. Lett. **100**, 096407 (2008).
- [22] E. Berg, E. Fradkin and S. Kivelson, Nature Physics **5**, 830(2009).
- [23] Microscopically, these additional terms are proportional to the square of the wavefunction overlap of orbitals localized on the top and bottom of the five-atom unit cell, about 9\AA apart. Therefore they are expected to be small.
- [24] Strictly speaking, this relation between ν and Fermi surface topology only holds for weak-coupling superconductors.
- [25] For $m = 0$ and arbitrary U/V , a Z_2 symmetry $c \rightarrow \Gamma_{50}c$ forbids mixing between intra- and inter-orbital components in $\hat{\Delta}_1$ pairing.