Odd-Parity Topological Superconductors: Theory and Application to $Cu_xBi_2Se_3$

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Topological superconductors have a full pairing gap in the bulk and gapless surface Andreev bound states. In this Letter, we provide a sufficient criterion for realizing time-reversal-invariant topological superconductors in centrosymmetric superconductors with *odd-parity* pairing. We next study the pairing symmetry of the newly discovered superconductor $Cu_xBi_2Se_3$ within a two-orbital model, and find that a novel spin-triplet pairing with odd parity is favored by strong spin-orbit coupling. Based on our criterion, we propose that $Cu_xBi_2Se_3$ is a good candidate for a topological superconductor. We close by discussing experimental signatures of this new topological phase.

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The search for topological phases of matter with time-reversal symmetry has been an exciting field in condensed matter physics [1,2]. The recent theoretical prediction and experimental observation of topological insulators in a number of materials [3–5] have attracted great interest in this subject. Soon afterwards, a class of time-reversal-invariant (TRI) topological superconductors [6,7] was theoretically predicted based on a mathematical classification of Bogoliubov–de Gennes (BdG) Hamiltonians [6,8]. Closely related to topological insulators, topological superconductors are fully gapped in the bulk but have gapless surface Andreev bound states. The prediction of topological superconductors has raised great interest. Now the challenge is to find candidate materials for this new topological phase of matter.

In this Letter, we first provide a sufficient criterion for TRI topological superconductors in *centrosymmetric* materials with *odd-parity* pairing symmetry. This criterion applies to superconductors with spin-orbit coupling, which belong to the symmetry class DIII [9]. Next we study the pairing symmetry of the newly discovered superconductor $Cu_xBi_2Se_3$ [10] within a two-orbital model for its band structure. We find a novel spin-triplet pairing with odd parity is favored by strong spin-orbit coupling. According to our criterion, the resulting state realizes a topological superconductor. We explicitly calculate the hallmark surface Andreev bound state spectrum. Finally, we propose experimental signatures of this possible topological superconductor phase in $Cu_xBi_2Se_3$.

Criterion.—A time-reversal-invariant centrosymmetric superconductor is a topological superconductor if (1) it has odd-parity pairing symmetry with a full superconducting gap *and* (2) its Fermi surface encloses an odd number of TRI momenta Γ_α (which satisfy $\Gamma_\alpha = -\Gamma_\alpha$ up to a reciprocal lattice vector) in the Brillouin zone.

The above criterion directly relate the topological class of a superconductor to its pairing symmetry and Fermi surface topology, both of which are accessible experimentally (by phase-sensitive measurements and angle-resolved photoemission). Therefore, we hope our criterion will be useful in the material search for topological superconductors.

To prove the criterion, we start from the connection between the mathematical classification of superconductors in class DIII [6,8] and that of insulators in class AII [11,12]. The connection becomes explicit when we write the mean-field (MF) Hamiltonian for superconductors in the BdG formalism:

$$\begin{aligned} H_{\mathrm{MF}} &= \int d\mathbf{k}\, \xi_{\mathbf{k}}^\dagger \mathcal{H}(\mathbf{k}) \xi_{\mathbf{k}}, \\ \xi_{\mathbf{k}}^\dagger &\equiv (c_{\mathbf{k}\uparrow}^\dagger, c_{\mathbf{k}\downarrow}^\dagger, c_{-\mathbf{k}\downarrow}^T, -c_{-\mathbf{k}\uparrow}^T), \\ \mathcal{H}(\mathbf{k}) &= [H_0(\mathbf{k}) - \mu]\tau_z + \hat{\Delta}(\mathbf{k})\tau_x. \end{aligned} \tag{1}$$

Here $\mathbf{k}$ is crystal momentum in the Brillouin zone, $\uparrow$, $\downarrow$ are the electron's spin index, $\tau_{x,z}$ are Pauli matrices in Nambu space. $c^\dagger$ and c also carry an orbital index (not shown explicitly), which labels a basis for cell-periodic Bloch wave functions. The BdG Hamiltonian $\mathcal{H}$ includes the kinetic energy specified by the band structure H_0, chemical potential μ, and the pairing potential $\hat{\Delta}$. A TRI superconductor satisfies $\Theta \mathcal{H}(\mathbf{k}) \Theta^{-1} = \mathcal{H}(-\mathbf{k})$, where $\Theta \equiv i s_y K$ is the time-reversal transformation (s_y is a spin Pauli matrix and K is complex conjugation). Since Θ takes the same form for both the BdG Hamiltonian of superconductors and the Bloch Hamiltonian of band insulators, the previously defined Z_2 topological invariant ν of an insulator [11,12] applies to superconductors as well. In particular, $\nu = 1$ is sufficient (though not necessary) to establish a topological superconductor phase [13].

We now evaluate ν for inversion symmetric superconductors with odd-parity pairing. The band structure and pairing potential of such superconductors satisfy $PH_0(\mathbf{k})P = H_0(-\mathbf{k})$ and $P\hat{\Delta}(\mathbf{k})P = -\hat{\Delta}(-\mathbf{k})$, respectively, where P is an inversion operator acting on the orbitals within a unit cell. For a single-orbital superconductor, P reduces to the identity operator and odd-parity pairing is equivalent to spin-triplet pairing. A criterion for a topological superconductor in this special case has been proved by Sato [14]. Our criterion applies to odd-parity superconductors in general. This will be necessary for the purpose of studying the multiorbital superconductor $Cu_xBi_2Se_3$ later.

From the definition (1), we see that the BdG Hamiltonian $\mathcal{H}(\mathbf{k})$ of an odd-parity superconductor has the following Z_2 symmetry:

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

This novel Z_2 symmetry will play a key role below. At TRI momenta $\Gamma_\alpha = -\Gamma_\alpha$, $[\tilde{P}, \mathcal{H}(\Gamma_\alpha)] = 0$, so that the BdG eigenstates $|\psi_m(\Gamma_\alpha)\rangle$ of $\mathcal{H}$ satisfy $\tilde{P}|\psi_m(\Gamma_\alpha)\rangle = \xi_m(\Gamma_\alpha)|\psi_m(\Gamma_\alpha)\rangle$ with eigenvalues $\xi_m = \pm 1$. Since $\tilde{P}$ and Θ commute, Kramers partners share the same $\tilde{P}$ eigenvalue: $\xi_{2m}(\Gamma_\alpha) = \xi_{2m+1}(\Gamma_\alpha)$. In the presence of such a Z_2 symmetry (2), Fu and Kane found a simple formula for the Z_2 invariant ν [11]:

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

The product over m includes one member of each negative-energy Kramers pair. We now examine the physical meaning of ξ_m for weak-coupling superconductors, whose pairing gap is small compared to Fermi energy. Generically, the point Γ_α is far from the Fermi surface. Then BdG eigenstates $|\psi(\Gamma_\alpha)\rangle$ can be approximated by Bloch eigenstates $|\phi(\Gamma_\alpha)\rangle$ of H_0. In particular, a negative-energy BdG eigenstate either derives from an occupied band $|\phi^o\rangle \otimes |\tau_z = 1\rangle$ below Fermi energy or an unoccupied band $|\phi^u\rangle \otimes |\tau_z = -1\rangle$ above Fermi energy. Therefore,

$$\xi_m(\Gamma_\alpha) = p_m(\Gamma_\alpha)\tau_m(\Gamma_\alpha), \tag{4}$$

where $p = \pm 1$ is the eigenvalue of the inversion operator P and $\tau = \pm 1$ is the eigenvalue of the particle-hole operator τ_z. Substituting (4) into (3), we find

$$\begin{aligned}(-1)^\nu &= \prod_{\alpha,i} p_{2i}(\Gamma_\alpha)\,\mathrm{sgn}[\mu - \varepsilon_{2i}(\Gamma_\alpha)] \\ &= \prod_{\alpha,i} \mathrm{sgn}[\mu - \varepsilon_{2i}(\Gamma_\alpha)] = \prod_\alpha (-1)^{N(\Gamma_\alpha)},\end{aligned} \tag{5}$$

where i labels the *complete* set of energy bands of H_0, with corresponding energies $\varepsilon_i(\mathbf{k})$. In the second equality of (5), we have used the identity $\prod_i p_{2i}(\Gamma_\alpha) = \det[P]$ (independent of Γ_α), so that $\prod_{\alpha=1}^{2^d} \det[P] = 1$ (2^d is the number of TRI momenta in spatial dimensions $d = 1, 2, 3$). In the last equality of (5), $N(\Gamma_\alpha)$ is defined as the number of unoccupied bands at Γ_α in the normal state. Now Eq. (5) has a simple geometrical meaning: the Z_2 topological invariant $\nu = 0\,(1)$ if the Fermi surface of H_0 encloses an even (odd) number of TRI momenta. This completes the proof of our criterion for odd-parity topological superconductors.

A classic example of odd-parity pairing is superfluid He-3. In particular, the TRI B phase has been recently identified as a topological superfluid [6,7,15]. Odd-parity pairing in superconductors is less well established. A famous example is Sr_2RuO_4, in which odd-parity pairing is established by phase-sensitive measurements [16]. However, the observed spontaneous time-reversal breaking signatures [17] seem to disqualify Sr_2RuO_4 as a TRI topological superconductor.

In the search for odd-parity pairing, we turn our attention to the newly discovered superconductor $Cu_xBi_2Se_3$, which is a doped semiconductor and becomes superconducting at 3.8 K [10]. Its pairing symmetry is unknown at present. We now show theoretically that a novel odd-parity pairing is favored by strong spin-orbit coupling in this material. If realized, such a pairing symmetry will lead to a topological superconductor phase.

To study superconductivity in $Cu_xBi_2Se_3$ requires the knowledge of its band structure and pairing mechanism. As shown by a very recent angle-resolved photoemission spectroscopy study [18], the band structure of $Cu_xBi_2Se_3$ is similar to its parent compound Bi_2Se_3: the conduction and valence bands are separated by a small band gap about 0.3 eV at $\mathbf{k} = \mathbf{0}$. According to first-principles calculations on Bi_2Se_3 [19], these two bands are predominantly superpositions of Se p_z orbitals on the top and bottom layer of the unit cell (each is mixed with its neighboring Bi p_z orbital). Keeping these two orbitals only, the band dispersion near $\mathbf{k} = \mathbf{0}$ is well described by the following continuum $k \cdot p$ Hamiltonian [19]:

$$H_0(\mathbf{k}) = m\sigma_x + v(k_x\sigma_z s_y - k_y\sigma_z s_x) + v_z k_z \sigma_y, \tag{6}$$

where $\sigma_z = \pm 1$ denotes the two orbitals and $s_z = \pm 1$ denotes electron spin parallel (antiparallel) to the z direction (c axis). As for the pairing mechanism, very little is known so far. For simplicity we consider short-range electron density-density interactions:

$$H_{\mathrm{int}}(\mathbf{x}) = -U[n_1^2(\mathbf{x}) + n_2^2(\mathbf{x})] - 2Vn_1(\mathbf{x})n_2(\mathbf{x}), \tag{7}$$

where $n_i(\mathbf{x}) = \sum_{\alpha=\uparrow,\downarrow} c_{i\alpha}^\dagger(\mathbf{x})c_{i\alpha}(\mathbf{x})$ is electron density in orbital i. U and V are intraorbital and interorbital interactions, respectively. We assume that at least one of them is attractive, responsible for superconductivity. Taking the band structure and pairing interaction together, we introduce the following two-orbital U-V model for $Cu_xBi_2Se_3$:

$$H = \int d\mathbf{k}\, c_\mathbf{k}^\dagger[H_0(\mathbf{k}) - \mu]c_\mathbf{k} + \int d\mathbf{x}\, H_{\mathrm{int}}(\mathbf{x}). \tag{8}$$

Because of Cu doping, the Fermi energy μ lies in the conduction band approximately 0.4 eV above the middle of the band gap [18], which leads to a small Fermi surface.

We now determine the superconducting mean-field phase diagram of the U-V model. Since the pairing interaction involves two orbitals and is local in $\mathbf{x}$, the mean-field pairing potential is orbital dependent but $\mathbf{k}$ independent. In Table I, we classify all possible pairing potentials according to the representation of the $Cu_xBi_2Se_3$ crystal point group D_{3d}. The basic symmetry transformations of the D_{3d} group are inversion operation P, threefold rotation around the z axis C_3, and mirror reflection about the yz plane M. Their actions on spin and orbital are represented by unitary operators shown in the left-hand column in Table I . We find four different pairing symmetries in the A_{1g}, A_{1u}, A_{2u}, and E_u representations of the D_{3d} group. The three A representations are one dimensional and the E representation is two dimensional. The form of the corresponding pairing order parameter $\hat{\Delta}_i$, $i = 1, \ldots, 4$, is listed in the BdG formalism in Table I and shown explicitly:

$$\begin{aligned} &\hat{\Delta}_1\colon\ c_{1\uparrow}c_{1\downarrow} + c_{2\uparrow}c_{2\downarrow} \text{ and } c_{1\uparrow}c_{2\downarrow} - c_{1\downarrow}c_{2\uparrow}, \\ &\hat{\Delta}_2\colon\ c_{1\uparrow}c_{2\downarrow} + c_{1\downarrow}c_{2\uparrow}, \\ &\hat{\Delta}_3\colon\ c_{1\uparrow}c_{1\downarrow} - c_{2\uparrow}c_{2\downarrow}, \\ &\hat{\Delta}_4\colon\ (c_{1\uparrow}c_{2\uparrow}, c_{1\downarrow}c_{2\downarrow}). \end{aligned} \tag{9}$$

The symmetry properties of $\hat{\Delta}_i$ are shown in Table I. We pay particular attention to inversion symmetry that interchanges orbitals 1 and 2. The spin-singlet pairing $\hat{\Delta}_1$, which has both intraorbital and interorbital components, is invariant under all crystal symmetries. The other three pairings are odd under inversion. $\hat{\Delta}_3$ is spin-singlet, whereas $\hat{\Delta}_2$ and $\hat{\Delta}_4$ are interorbital spin-triplet. Among the odd-parity phases, only the $\hat{\Delta}_2$ phase is TRI *and* fully gapped. In addition, the Fermi surface of $Cu_xBi_2Se_3$ only encloses *one* TRI momentum $\mathbf{k} = \mathbf{0}$. So according to our earlier criterion, the $\hat{\Delta}_2$ pairing in the U-V model for $Cu_xBi_2Se_3$ realizes a topological superconductor phase.

To obtain the phase diagram, we solve the following linearized gap equations for T_c in each pairing channel:

$$\begin{aligned} &\hat{\Delta}_1\colon\ \det\left[\begin{pmatrix} U\chi_0(T_c) & U\chi_{01}(T_c) \\ V\chi_{01}(T_c) & V\chi_1(T_c) \end{pmatrix} - I\right] = 0, \\ &\hat{\Delta}_{2,4}\colon\ V\chi_{2,4}(T_c) = 1, \qquad \hat{\Delta}_3\colon\ U\chi_3(T_c) = 1. \end{aligned} \tag{10}$$

Here, various χ's are finite temperature superconducting susceptibilities in different pairing channels. $\chi_0 \equiv D_0 \int d\varepsilon \tanh(\frac{\varepsilon}{2T})/\varepsilon$ is the standard superconducting susceptibility, where D_0 is density of states at the Fermi energy. The other susceptibilities $\chi_1, \ldots, \chi_4$ are reduced from χ_0 by various form factors due to the orbital dependence of pairing potentials and Bloch wave functions. These form factors are crucial for determining T_c of the competing superconducting channels. A straightforward calculation shows that

$$\frac{\chi_1}{\chi_0} = \int d\mathbf{k}\, \delta(\varepsilon_{\mathbf{k}} - \mu)\, \mathrm{Tr}[\sigma_x \mathcal{P}_{\mathbf{k}}]^2/(2D_0), \tag{11}$$

TABLE I. Classification of all k-independent pairing potentials of the two-orbital U-V model according to the representations of D_{3d} point group

$\hat{\Delta}$	I and σ_x	$\sigma_y s_z$	σ_z	$(\sigma_y s_x, \sigma_y s_y)$
Representation	A_{1g}	A_{1u}	A_{2u}	E_u
$P = \sigma_x$	$+$	$-$	$-$	$(-, -)$
$C_3 = e^{-is_z\pi/3}$	z	z	z	(x, y)
$M = -is_x$	$+$	$-$	$+$	$(+, -)$

where $\mathcal{P}_{\mathbf{k}} \equiv \sum_{\lambda=1,2} |\phi_{\lambda,\mathbf{k}}\rangle\langle\phi_{\lambda,\mathbf{k}}|$ is the projection operator onto the Hilbert space of two degenerate Bloch states at $\mathbf{k}$. Similarly, χ_2, χ_3, and χ_4 are obtained by replacing σ_x in (11) by their corresponding pairing potentials $\sigma_y s_z$, σ_z, and $\sigma_y s_x$ (or $\sigma_y s_y$). Using the band structure H_0, we obtain the values of χ's: $\chi_{01} = \chi_0 m/\mu$, $\chi_1 = \chi_0(m/\mu)^2$, $\chi_2 = \chi_0(1 - m^2/\mu^2)$, $\chi_3 = \chi_4 = 2\chi_2/3$. Because $\chi_3 < \chi_0$ and $\chi_4 < \chi_2$, we find that $\hat{\Delta}_3$ always has a lower T_c than $\hat{\Delta}_1$, and $\hat{\Delta}_4$ lower than $\hat{\Delta}_2$. Only the $\hat{\Delta}_1$ and $\hat{\Delta}_2$ phases appear in the phase diagram. By calculating their T_c's from (10), we obtain the phase boundary:

$$U/V = 1 - 2m^2/\mu^2. \tag{12}$$

Figure 1 shows the highest T_c phase as a function of $\frac{U}{V}$ 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 $m/\mu \approx 1/3$ [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 nonsuperconducting. Note that for $U = V$ and $m = 0$ the Hamiltonian (8) has an enlarged U(1) chiral symmetry: $c \to \exp(i\theta\sigma_x s_z)c$. The transformation at $\theta = \pi/4$ transforms $\hat{\Delta}_1$ into $\hat{\Delta}_2$, explaining their degeneracy.

As the phase diagram shows, the spin-triplet Δ_2 phase wins as soon as the interorbital attraction exceeds over the intraorbital one ($V > U$), contrary to the naive expectation that a repulsive interaction is required. This arises from the specific form of spin-orbit coupling in the band structure (6), which favors Δ_2 pairing. The realistic values of U and V for $Cu_xBi_2Se_3$ are difficult to estimate. Nonetheless, if superconductivity is phonon driven, the residual electron repulsion renormalizes the bare values of U and V. Therefore it is possible that the weaker interorbital repulsion leads to $V > U$.

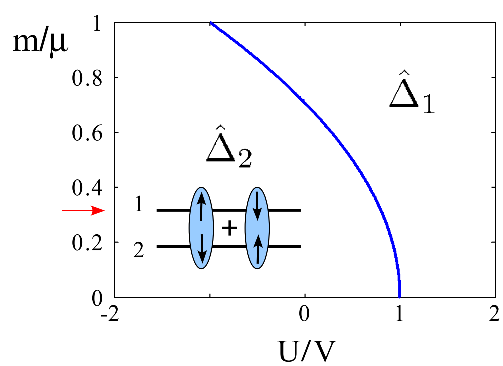

FIG. 1 (color online). Phase diagram of the two-orbital U-V model, showing the highest T_c phase as a function of m/μ and U/V. The arrow shows the experimental estimate for $m/\mu \simeq 1/3$ [18]. The two phases $\hat{\Delta}_1$ and $\hat{\Delta}_2$ are even and odd under inversion, respectively. The insets shows schematically that the Cooper pair wave function in the $\hat{\Delta}_2$ phase consists of two electrons on the top (1) and bottom (2) of the five-atom unit cell.

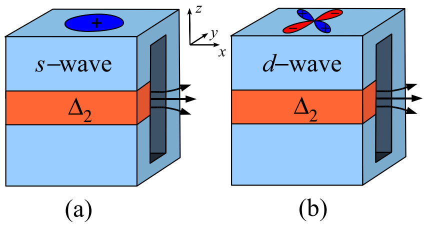

FIG. 2 (color online). Phase-sensitive experiments to test Δ_2 pairing, which is odd under both inversion ($\mathbf{r} \to -\mathbf{r}$) and reflection about the yz plane ($x \to -x$). A superconducting ring made of either an s-wave (a) or d-wave (b) superconductor contains a segment of a Δ_2 superconductor.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

From now on, we focus on the topologically nontrivial $\hat{\Delta}_2$ phase. To obtain the surface Andreev bound state spectrum, we solve the BdG Hamiltonian in a semi-infinite geometry $z < 0$ by replacing k_z by $-i\partial_z$ in $\mathcal{H}(k_x, k_y, k_z)$. The boundary condition at $z = 0$ should be chosen carefully. The natural cleavage plane for $Cu_xBi_2Se_3$ crystal is in between two five-layer unit cells. For such a surface termination, the wave function amplitude on the bottom layer vanishes. So we impose $\sigma_z \psi = \psi|_{z=0}$. By solving the semi-infinite problem at $k_x = k_y = 0$, we find that a Kramers pair of zero-energy surface Andreev bound states $\psi_\pm$ exists as long as the bulk gap is finite. The wave functions of $\psi_\pm$ are particularly simple for $m = 0$ [20]:

$$\psi_\pm(z) = e^{-\kappa z}(\cos k_0 z|\sigma_z = 1\rangle + \sin k_0 z|\sigma_z = -1\rangle) \otimes |s_z = \pm 1, \tau_y = \mp 1\rangle, \tag{13}$$

where $\kappa = \Delta_2/v_z$ and $k_0 = \mu/v_z$. Using $k \cdot p$ theory, we obtain the low-energy Hamiltonian for surface Andreev bound states: $H_{sf} = v_s(k_x s_y - k_y s_x)$, with $v_s \simeq v\Delta_2^2/\mu^2$.

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 inversion and mirror symmetries can be directly tested by 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 state Δ_s is even, the leading order Josephson coupling between the two superconductors, $-J_1(\Delta_s^*\Delta_2 + \text{c.c.})$, vanishes. The second order Josephson coupling, $-J_2[(\Delta_s^*)^2\Delta_2^2 + \text{c.c.}]$, can be nonzero. Therefore, the flux through a superconducting ring shown in Fig. 2(a) is quantized in units of $\frac{h}{4e}$ [21,22]. Alternatively, in a Josephson junction between a Δ_2 superconductor and a d-wave superconductor oriented as shown in Fig. 2(b), the first order Josephson coupling is allowed. The Josephson ring then becomes a π junction: the flux enclosed takes the value $\frac{h}{2e}(n + \frac{1}{2})$. The observation of these anomalous flux quantization relations would be a unique signature of the topological Δ_2 state.

To conclude, we present a criterion of odd-parity topological superconductors and propose the newly discovered superconductor $Cu_xBi_2Se_3$ as a potential candidate. 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 [23].

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Note add in proof.—Recently, we learned of Ref. [24], which obtained a similar criterion for odd-parity topological superconductors.

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