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<th>Citation</th>
<th>Fu, Liang. “Odd-Parity Topological Superconductor with Nematic Order: Application to Cu$_x$ Bi$_2$ Se$_3$.” Phys. Rev. B 90, no. 10 (September 2014). © 2014 American Physical Society</th>
</tr>
</thead>
<tbody>
<tr>
<td>As Published</td>
<td><a href="http://dx.doi.org/10.1103/PhysRevB.90.100509">http://dx.doi.org/10.1103/PhysRevB.90.100509</a></td>
</tr>
<tr>
<td>Publisher</td>
<td>American Physical Society</td>
</tr>
<tr>
<td>Version</td>
<td>Final published version</td>
</tr>
<tr>
<td>Accessed</td>
<td>Sat Mar 02 09:09:21 EST 2019</td>
</tr>
<tr>
<td>Citable Link</td>
<td><a href="http://hdl.handle.net/1721.1/90431">http://hdl.handle.net/1721.1/90431</a></td>
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**ODS**
Odd-parity topological superconductor with nematic order: Application to Cu$_x$Bi$_2$Se$_3$

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(Received 7 August 2014; revised manuscript received 25 August 2014; published 26 September 2014)

Cu$_x$Bi$_2$Se$_3$ was recently proposed as a promising candidate for time-reversal-invariant topological superconductors. In this work, we argue that the unusual anisotropy of the Knight shift observed by Zheng and co-workers (unpublished), taken together with specific heat measurements, provides strong support for an unconventional odd-parity pairing in the two-dimensional $E_u$ representation of the $D_{3d}$ crystal point group, which spontaneously breaks the threefold rotational symmetry of the crystal, leading to a subsidiary nematic order. We predict that the spin-orbit interaction associated with hexagonal warping plays a crucial role in pinning the two-component order parameter and makes the superconducting state generically fully gapped, leading to a topological superconductor. Experimental signatures of the $E_u$ pairing related to the nematic order are discussed.

DOI: 10.1103/PhysRevB.90.100509

Time-reversal-invariant ($T$-invariant) topological superconductors in two and three dimensions are a new class of unconventional superconductors which exhibit a full superconducting gap in the bulk and gapless helical quasiparticles on the boundary [1–3]. Because these quasiparticles do not possess conserved charge or spin quantum numbers, they cannot be distinguished from their antiparticles and hence are regarded as itinerant Majorana fermions.

There is currently intensive effort in finding $T$-invariant topological superconductors in real materials [4–9]. Recent theoretical works [10,11] have established that the key requirement for topological superconductivity in inversion-symmetric systems is odd-parity pairing symmetry. Only a few odd-parity superconductors are known to date. Two prime examples are Sr$_2$RuO$_4$ and UPt$_3$. However, both materials seem to have nodes and/or spontaneously break time-reversal symmetry, and hence do not qualify as $T$-invariant topological superconductors.

Recently, the doped topological insulator Cu$_x$Bi$_2$Se$_3$, which is superconducting with a maximum $T_c$ of 3.8 K [12], was proposed as a candidate topological superconductor with odd-parity pairing [10]. Since then this material has been intensively studied. Specific heat measurements down to 0.3 K found a full superconducting gap [13]. The upper critical field appears to exceed the Pauli limit, which is interpreted as consistent with triplet pairing [14]. Much interest is sparked by the observation of a zero-bias conductance peak in a point-contact spectroscopy experiment on Cu$_{0.3}$Bi$_2$Se$_3$ [15], which is attributed to the putative Majorana fermion surface states from topological superconductivity. However, a later scanning tunneling spectroscopy measurement on Cu$_{0.2}$Bi$_2$Se$_3$ found a full gap in the tunneling spectrum at very lower temperature, without any sign of in-gap states [16]. The discrepancy between these two surface sensitive experiments has led to considerable debate and controversy about the nature of superconductivity in Cu$_x$Bi$_2$Se$_3$ [17–22]. In view of the current status, direct probes of the pairing symmetry in the bulk are much needed.

In a very recent nuclear magnetic resonance (NMR) study of Cu$_{0.3}$Bi$_2$Se$_3$, Zheng’s group discovered an unusual anisotropy in the Knight shift as a small applied field is rotated within the $ab$ plane [23]. The Knight shift is isotropic above $T_c$, and decreases in the superconducting state. Remarkably, the change in the Knight shift is largest when the field is parallel to a particular crystal axis. This uniaxial anisotropy does not conform with the threefold rotational symmetry of the crystal, and thus provides a direct evidence of spontaneous crystal symmetry breaking associated with unconventional superconductivity in Cu$_x$Bi$_2$Se$_3$.

In this Rapid Communication, we identify the pairing symmetry of Cu$_x$Bi$_2$Se$_3$ from the existing NMR and specific heat measurements, theoretically establish a fully gapped topological superconductor phase, and predict experimental signatures for further study. Our main finding is that among all possible pairing symmetries, only the odd-parity pairing in the two-dimensional (2D) $E_u$ representation, first introduced in Ref. [10], is compatible with the rotational symmetry breaking observed in NMR measurements [23] and the full superconducting gap found in specific heat measurement [13]. Since this $E_u$ pairing generates a subsidiary nematic order, we call the resulting state a “nematic superconductor.”

The fully gapped nature of the $E_u$ superconducting state found here is remarkable, considering that previous works invariably found nodes in the gap [10,15,24]. Moreover, a full gap is required for topological superconductivity. While previous works are based on a rotationally invariant Dirac fermion model for the bulk band structure of Cu$_x$Bi$_2$Se$_3$, we find that crystalline anisotropy plays an indispensable role in the odd-parity $E_u$ state. We show by general argument and model study that the spin-orbit interaction associated with hexagonal warping [25] pins the direction of the two-component $E_u$ order parameter to a twofold axis of the crystal, consistent with the Knight-shift anisotropy, and makes the superconducting state generically fully gapped.

Pairing symmetry. It was recognized at the outset that strong spin-orbit coupling must be taken into consideration in discussing the pairing symmetry of Cu$_x$Bi$_2$Se$_3$ [10]. Indeed, the importance of spin-orbit coupling becomes manifest in the Knight-shift measurement of the electron’s spin susceptibility. If spin-orbit coupling were absent, the Knight shift would be fully isotropic for spin-singlet as well as triplet pairing, in the latter case because the triplet $d$ vector would be free to rotate with the applied magnetic field. In contrast, in the presence of spin-orbit coupling, the notion of spin-singlet or triplet pairing is, strictly speaking, not well defined. Instead, pairing symmetries are classified according to the...
representations of the crystalline symmetry group $D_{3d}$ \cite{10}, which acts simultaneously on spatial coordinates and the electron’s spin. The consequence is that the spin structure of the superconducting order parameter is locked to the crystal axis, generically resulting in an anisotropic spin susceptibility.

Among the six irreducible representations of $D_{3d}$ ($A_{1g}$, $A_{1u}$, $A_{2g}$, $A_{2u}$, $E_u$, and $E_g$), only the $E_u$ and $E_g$ representations are multidimensional and hence potentially compatible with the spontaneous rotational symmetry breaking observed in the Knight-shift measurement. In order to determine which one of the two is the pairing symmetry of Cu$_2$B$_2$Se$_3$, we first consider Ginzburg-Landau theory for the $E_u$ and $E_g$ superconducting states. The $D_{3d}$ point group symmetry dictates that up to the fourth order, the Landau free energy in both cases must take the form

$$ F = r(|\Psi_1|^2 + |\Psi_2|^2) + u_1(|\Psi_1|^2 + |\Psi_2|^2)^2 + u_2|\Psi_1|^2 + |\Psi_2|^2, $$

(1)

where $r \propto (T - T_c)$. Here $\Psi = (\Psi_1, \Psi_2)$ is the two-component order parameter, which transforms as a vector under the threefold rotation. The same form of the free energy also applies to other crystal systems \cite{26–28}. Importantly, the nature of the superconducting state below $T_c$ depends on the sign of $u_2$. For $u_2 > 0$, a $T$-breaking chiral superconducting state with a complex order parameter $\Psi \propto (\vec{z} \times \vec{r})$, arises, which is isotropic within the $ab$ plane. For $u_2 < 0$, a $T$-invariant state with a real order parameter $\Psi \propto (\cos \theta, \sin \theta)$ arises. This superconducting state spontaneously breaks the rotational symmetry, and possesses a subsidiary nematic order parameter $Q$:

$$ Q = (|\Psi_1|^2 - |\Psi_2|^2, \Psi_1^* \Psi_2 + \Psi_2^* \Psi_1). $$

(2)

The two components of $Q$ transform as $x^2 - y^2$ and $xy$, respectively. Such a nematic superconductor with uniaxial anisotropy is consistent with the Knight-shift measurement, whereas the isotropic chiral state is not.

We now show that the nematic state with $E_g$ pairing and the one with $E_u$ pairing can be experimentally distinguished by their qualitatively different gap structures, because of the difference in the parity of the order parameter: $E_u$ is even parity and $E_g$ is odd parity. To analyze the gap structure, it is convenient to express the pair potential $\Delta(k)$ in the band basis.

Since the superconducting gap is much smaller than the Fermi energy, due to the presence of both time-reversal and inversion symmetry, the energy bands are twofold degenerate at every $k$, which we label by a "pseudospin" index $\alpha$. Because of spin-orbit coupling, $\alpha = 1, 2$ does not correspond to the electron’s spin. The pair potential thus reduces to a $2 \times 2$ matrix over the Fermi surface, the gap function $\Delta_{\alpha\alpha}(k)$.

Depending on the parity of the order parameter, the gap function of a $T$-invariant superconductor takes two different forms:

$$ \Delta^e(k) = \Delta(k) \cdot I, \quad \text{where} \quad \Delta(k) = \Delta(-k), $$

(3)

$$ \Delta^o(k) = \vec{d}(k) \cdot \vec{\sigma}, \quad \text{where} \quad \vec{d}(k) = -\vec{d}(-k). $$

(4)

The even-parity gap function $\Delta^e(k)$ is a real scalar, while the odd-parity gap function $\Delta^o(k)$ is parametrized by a real vector field $\vec{d}(k)$, the $d$ vector. The superconducting gaps $\delta(k)$ in the two cases are given by $|\Delta(k)|$ and $|\vec{d}(k)|$, respectively.

The scalar nature of the even-parity gap function (3) dictates that the $T$-invariant $E_g$ state of Cu$_2$B$_2$Se$_3$ must have line nodes. To see this, let us recall that for any non-$s$-wave pairing, the gap function integrated over the Fermi surface must be zero:

$$ \int_{k_{FS}} d|k \Delta(k)| = 0. $$

(5)

As shown by angle-resolved photoemission spectroscopy experiments \cite{18,29}, Cu$_2$B$_2$Se$_3$ has a connected Fermi surface enclosing $k = 0$. It then follows from Eq. (5) that $\Delta(k)$ must change sign somewhere on such a Fermi surface, resulting in unavoidable line nodes. As an explicit example, the $E_g$ gap function $\Delta(k) \propto k_x k_y k_z$, considered in Ref. [24] has lines of nodes on the $k_z = 0$ and $k_x, k_y = 0$ planes. The existence of line nodes conflicts with the specific heat measurement \cite{13}. This seems sufficient to rule out the $E_g$ pairing in Cu$_2$B$_2$Se$_3$. In contrast, we will show below that the $E_u$ states generically have a full superconducting gap.

**Superconducting gap.** For the sake of concreteness, we first derive the superconducting gap of the $E_u$ state within a two-orbital model for Cu$_2$B$_2$Se$_3$. Later, we will show that the presence or absence of nodes is a robust property that depends only on symmetry, not microscopic details.

The band structure of Cu$_2$B$_2$Se$_3$ at low energy is described by a $k \cdot p$ Hamiltonian at $\Gamma$, which to first order in $k$ takes the following form \cite{10}:

$$ H_0 = \sum_k c_{k1}^\dagger (v(k_x s_y - k_y s_x) \sigma_x + v_z k_z \sigma_y + m \sigma_x - \mu) c_k, $$

where $c_{k1} = (c_{1\uparrow}, c_{1\downarrow}, c_{2\uparrow}, c_{2\downarrow})$ consists of two orbitals hereafter denoted as 1 and 2, in addition to the electron’s spin. Here $\sigma$ and $s$ are two sets of Pauli matrices associated with orbital and spin, respectively. It is worth pointing out that spin-orbit coupling in time-reversal and inversion-symmetric systems necessarily involves more than one orbital, as shown in the two-orbital Hamiltonian here. The physical origin of $H_0$ is elucidated in Ref. [30]. The chemical potential $\mu$ lies in the conduction band due to Cu doping.

In this two-orbital model, the $E_u$ pairing arises when electrons in the two orbitals within a unit cell pair up to form a spin triplet, with zero total spin along an in-plane direction $n = (n_x, n_y)$. The corresponding pair potential, $V_n = n_x V_x + n_y V_y$, is a superposition of two independent basis functions given in Ref. [10] (therein called "$\Delta_n$ pairing"):

$$ V_x = i \Delta_0 ( c_{1\uparrow}^\dagger c_{2\uparrow} - c_{1\downarrow} c_{2\downarrow}^\dagger), $$

$$ V_y = \Delta_0 ( c_{1\uparrow}^\dagger c_{2\downarrow} + c_{1\downarrow}^\dagger c_{2\uparrow}). $$

(6)

$V_n$ is $T$-invariant and rotational symmetry breaking. $n$ should be regarded as a nematic director (a headless vector), because the superconducting order parameters $V_n$ and $V_{-n}$ only differ by sign and correspond to the same physical state.

We can directly obtain the superconducting gap $\delta_n(k)$ by diagonalizing the BCS mean-field Hamiltonian $H_{sc} = H_0 + V_n$. Alternatively, we can derive the gap function $\Delta(k)$ by rewriting $V_n$, defined by (6) in spin and orbital basis, in terms of
band eigenstates of $H_0$ at the Fermi energy, as done in Ref. [24]. To leading order in $\Delta_0/\mu$, the two approaches yield identical results for the superconducting gap on the Fermi surface: $\delta_0(k) = \Delta \sqrt{k_x^2 + (k \cdot n)^2}$, where $\Delta = \Delta_0 \sqrt{1 - m^2/\mu^2}$. Here we have introduced a rescaled momentum $\tilde{k}$ to parametrize the Fermi surface:
\[
\tilde{k} = (v k_x, v k_y, v k_z)/\sqrt{\mu^2 - m^2}.
\]

$\tilde{k}$ maps the ellipsoidal Fermi surface of the Hamiltonian $H_0$ to a unit sphere. The gap $\delta_0(k)$ vanishes at two points on the equator of the Fermi surface: $\pm k_0 = \pm k_F \hat{z} \times n$. Hence, based on this model, previous works concluded that the $E_u$ states in Cu$_2$Bi$_2$Se$_3$ have point nodes.

However, we note that $H_0$ is fully rotationally invariant around the $\hat{z}$ axis. This is an artifact of the first-order $k \cdot p$ theory, which does not include any effect of crystalline anisotropy. In reality, the crystal of Cu$_2$Bi$_2$Se$_3$ only has a discrete threefold symmetry, and this crystalline anisotropy is solely responsible for pinning the direction of the $E_u$ order parameter $n$. This motivates us to take crystalline anisotropy into account and reexamine the gap structure of $E_u$ pairing.

We find that the gap structure depends on the orientation of the order parameter $n$ relative to the crystal axes: The point nodes remain present when $n$ is parallel to twofold axes, whereas they become lifted for $n$ in all other directions, resulting in a full superconducting gap. To illustrate this node lifting explicitly, we add a “hexagonal warping” term of third order in $n$ to the Hamiltonian, which is allowed by the $D_{3d}$ point group symmetry of Cu$_2$Bi$_2$Se$_3$:
\[
H = H_0 + \lambda \sum_k (k_x^4 + k_y^4) c_k \sigma_x c_k, \quad k_\pm \equiv k_x \pm i k_y.
\]

Here $x$ is along a twofold axis, or equivalently, normal to a mirror plane, as shown in Fig. 1. This hexagonal warping term arises from the spin-orbit interaction associated with crystalline anisotropy and can be regarded as the bulk counterpart of the warping term for topological insulator surface states [25,31]. For $\lambda \neq 0$, the Fermi surface becomes hexagonally deformed, and more important, the orbital-resolved spin polarization of Bloch states in $k$ space becomes modified.

By solving the mean-field Hamiltonian $H_{sc} = H + V_n$ with a single pair potential as before, we find the superconducting gap in the presence of hexagonal warping,
\[
\delta_0(k) = \Delta \sqrt{1 - |\tilde{k} \cdot (\hat{z} \times n)|^2},
\]
where $\tilde{k}$ is still defined by Eq. (7), but $k$ now lives on a new Fermi surface determined by
\[
\sqrt{m^2 + v^2 (k_x^2 + k_y^2) + \lambda^2 (k_y^4 + k_x^4) + v^2 k_z^2} = \mu.
\]

It is clear from (9) that the gap $\delta_0(k)$ goes to zero only where $|n \cdot (\hat{k} \times \hat{z})| = 1$. Importantly, we note that for $\lambda \neq 0$, $|k \times \hat{z}|$ is less than 1 everywhere on the warped Fermi surface, except at six corners of the hexagon on the $k_z = 0$ plane (see Fig. 1): $\pm k = k_F \hat{y}$ and the star of $\pm k$ obtained by threefold rotation, where $|\hat{k} \times \hat{z}| = 1$. As a result, the zero-gap condition $|\tilde{k} \cdot (\hat{z} \times n)| = 1$ is satisfied only when the nematic director $n$ is parallel to one of the three twofold axes, such as $n = \pm \hat{x}$. In this case, the nodes found previously remain present. In contrast, for $n = (\cos \theta, \sin \theta)$ in all other directions, $\theta \neq 0, \pm \pi/3, or \pm 2\pi/3$, the nodes are lifted by hexagonal warping, resulting in a full gap.

We plot in Fig. 1 the superconducting gaps over the equator of a hexagonlike Fermi surface, for two $E_u$ pairings with $n = \hat{x}$ and $\hat{y}$, respectively, which are representative of the two contrasting cases. It should be said that the quantitative gap structures are model specific. For example, the gap anisotropy depends on the amount of warping and the microscopic pairing interaction. Nonetheless, the presence of nodes for $n = \hat{x}$ and a full gap for $n = \hat{y}$, which we have explicitly shown using the Hamiltonian (8) and the pair potential (6), are robust and model-independent properties of the $E_u$ superconducting state in Cu$_2$Bi$_2$Se$_3$, as we will show below.

Stable nodes have a deep origin in the symmetry and topology of the gap function. In a $T$-invariant odd-parity superconductor, a node in the gap occurs where the $d$ vector is zero. Importantly, we observe that when strong spin-orbit coupling is present, as in Cu$_2$Bi$_2$Se$_3$, the $d$ vector $d(k)$ (whose direction depends on the choice of pseudospin basis at $k$) is generically a three-component vector field in $k$ space, instead of collinear or planar. This is simply because a crystalline symmetry group alone is generally insufficient to make any component of the $d$ vector vanish everywhere in $k$ space. Since $d(k) = 0$ requires satisfying three equations, it is vanishingly improbable to find a solution on the two-dimensional Fermi surface [32]. This implies that stable nodes in $T$-invariant odd-parity superconductors are unlikely to occur in the presence of...
spin-orbit coupling, unless there is special crystal symmetry protecting their existence.

An example of protected nodes arises when there is a reflection symmetry with respect to a mirror plane, e.g., \( x \rightarrow -x \), and the odd-parity order parameter is invariant under this reflection. In this case, \( d(k_x = 0, k_y, k_z) \) and \( d(k_x = \pi/a, k_y, k_z) \) must be parallel to the normal of the mirror plane, due to its pseudovector nature. Such a two-dimensional uniaxial \( d \)-vector field on the \( k_x = 0, \pi/a \) plane is allowed to have lines of zeros, whose intersection with the Fermi surface will generate stable point nodes in the superconducting gap [32].

The general argument presented above explains the gap structures of different \( E_n \) states of \( \text{Cu}_2\text{Bi}_2\text{Se}_3 \) found in our model studies. The rotationally invariant model \( H_0 \) has the artifact of being symmetric with respect to any vertical plane, thus resulting in point nodes regardless of the nematic director \( n \) [33]. However, the crystal of \( \text{Cu}_2\text{Bi}_2\text{Se}_3 \) has only three mirror planes that are 120° apart from each other, which is correctly captured in the refined model (8) with hexagonal warping. For \( n \) normal to a mirror plane such as \( n = \pm \hat{x} \), the corresponding order parameter \( V_n \) is invariant under the reflection \( x \rightarrow -x \); hence the nodes located on the \( k_x = 0 \) plane are protected by this mirror symmetry. For \( n \) in all other directions, however, the order parameter is not invariant under any reflection; hence nodes are absent [34].

To capture the important effect of crystalline anisotropy in Ginzburg-Landau theory, we must include higher-order terms in the free energy (1), which start at the sixth order,

\[
F_6 = \kappa [(\Psi_+^* \Psi_- - (\Psi_+ \Psi_-^*)^2)], \quad \Psi_\pm \equiv \Psi_1 \pm i \Psi_2.
\]

Depending on \( \kappa > 0 \) or \( \kappa < 0 \), \( n \) is pinned either parallel or perpendicular to one of the three mirror planes, e.g., along the \( \hat{y} \) or \( \hat{x} \) axis. It is natural to expect that the fully gapped state with \( n = \hat{y} \) has a lower free energy below \( T_c \) than the nodal state with \( n = \hat{x} \). The nematic state with \( n = \hat{y} \) has two degenerate gap minima at \( \pm k_y \hat{x} \), and spontaneously lowers the point group symmetry from \( D_{4d} \) (rhombohedral) to \( C_{2h} \) (orthorhombic). This crystal symmetry breaking naturally leads to an anisotropic spin susceptibility. Importantly, the \( C_{2h} \) point group in the symmetry breaking phase has only one principal axis—the twofold axis \( \hat{x} \) that lies within the \( ab \) plane. It is exactly along this axis that the change in Knight shift was found to be largest in the NMR experiment [23]. This agreement lends additional support to the \( E_n \) pairing symmetry we have identified. A quantitative calculation of spin susceptibility in the anisotropic \( E_n \) state depends on microscopic details, which we leave to future study.

The anisotropic \( E_n \) state found here is a remarkable realization of odd-parity pairing with a full gap, with no known counterpart. For comparison, among the various phases of superfluid \( ^3\text{He} \), the \( T \)-invariant \( B \) phase is isotropic, while the anisotropic \( A \) phase is \( T \) breaking. Perhaps the closest analog to \( \text{Cu}_2\text{Bi}_2\text{Se}_3 \) is the \( A \) phase of \( \text{UPT}_3 \) [35], whose order parameter is real and breaks the sixfold crystal rotational symmetry [36]; however, this phase is known to have nodes.

**Topological superconductivity.** With an odd-parity pairing symmetry and a full gap, the \( E_n \) superconducting state in \( \text{Cu}_2\text{Bi}_2\text{Se}_3 \) satisfies all the requirements for \( T \)-invariant topological superconductivity stated in Ref. [10]. The exact topology depends further on the nature of the Fermi surface. At low doping, the normal state has an ellipsoidal Fermi pocket centered at \( \Gamma \), which under \( E_n \) pairing will become a three-dimensional (3D) topological superconductor, with Majorana fermion surface states on all crystal faces. At high doping, the Fermi surface is most likely open and cylinderlike, as indicated by recent photoemission [18] and de Haas–van Alphen measurements [37,38]. If this is the case, the \( E_n \) pairing will give rise to a quasi-two-dimensional topological superconductor, which is equivalent to stacked layers of 2D topological superconductors along the \( c \) axis, corresponding to \( v_z = 0 \) in our model (8). Side surfaces of this state host an even number of 2D massless Majorana fermions. The top and bottom surfaces are fully gapped, but a step edge on these surfaces hosts 1D helical Majorana fermions. It has been noted in a related context [18] that the scenario of quasi-2D topological superconductivity may explain both the point-contact and scanning tunneling spectroscopy measurements. In either the 3D or quasi-2D case, more direct evidence of Majorana fermions would be desirable.

**Experimental signatures.** The \( ab \)-plane gap anisotropy of the \( E_n \) pairing can be directly probed by directional-dependent thermal conductivity [39] or tunneling spectra. Here we focus on testing the \( E_n \) pairing symmetry in \( \text{Cu}_2\text{Bi}_2\text{Se}_3 \) via the subsidiary nematic order. Symmetry dictates a linear coupling between a uniaxial strain \( \epsilon_{ij} \) in the \( ab \) plane and the superconducting order parameter:

\[
F_5 = g \left[ \frac{\epsilon_{xx} - \epsilon_{yy}}{2} (|\Psi_1|^2 - |\Psi_2|^2) + \epsilon_{xy} (\Psi_1^* \Psi_2 + \Psi_2^* \Psi_1) \right].
\]

As a result of this coupling, an uniaxial strain in the \( ab \) plane acts as a symmetry breaking field for the nematic order, which should be able to align the nematic director of the superconducting order parameter near \( T_c \), thereby changing the pattern of the anisotropic Knight shift. In addition, a small uniaxial strain should enhance the superconducting transition temperature, irrespectively of its direction. The investigation of such strain-related effects on superconductivity seems within experimental reach [40] and may shed light on the pairing symmetry of \( \text{Cu}_2\text{Bi}_2\text{Se}_3 \). Furthermore, the nematic order parameter allows for half-integer disclination, around which the superconducting order parameter changes sign. Hence these disclinations may trap a half-integer flux quantum (\( h/4e \)). Finally, it would be interesting to consider whether the nematic order or other orders related to the \( E_n \) pairing can emerge prior to the onset of superconductivity, similar to such phenomena in other systems [41–44].

I thank Guo-qing Zheng for showing me the NMR data prior to publication. This work is supported by DOE Office of Basic Energy Sciences, Division of Materials Sciences and Engineering under Award No. DE-SC0010526.
[34] We have checked that nodes are absent both on and near the Fermi surface.