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Odd-Parity Pairing and Topological Superconductivity in a Strongly Spin-Orbit Coupled Semiconductor

Satoshi Sasaki,1 Zhi Ren,1 A. A. Taskin,1 Kouji Segawa,1 Liang Fu,2,* and Yoichi Ando1,†

1Institute of Scientific and Industrial Research, Osaka University, Ibaraki, Osaka 567-0047, Japan
2Department of Physics, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, USA

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The existence of topological superconductors preserving time-reversal symmetry was recently predicted, and they are expected to provide a solid-state realization of itinerant massless Majorana fermions and a route to topological quantum computation. Their first likely example, CuBi2Se3, was discovered last year, but the search for new materials has so far been hindered by the lack of a guiding principle. Here, we report point-contact spectroscopy experiments suggesting that the low-carrier-density superconductor Sn1−xInxTe is accompanied by surface Andreev bound states which, with the help of theoretical analysis, would give evidence for odd-parity pairing and topological superconductivity. The present and previous finding of possible topological superconductivity in Sn1−xInxTe and CuBi2Se3 suggests that odd-parity pairing favored by strong spin-orbit coupling is likely to be a common underlying mechanism for materializing topological superconductivity.

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Topological superconductors (TSCs) have become a research frontier in the study of topologically ordered electronic states of matter [1–4]. As a superconducting (SC) cousin of topological insulators [5,6], a TSC supports gapless surface quasiparticle states consisting of massless Majorana fermions as its distinctive characteristic. Majorana fermions are peculiar in that particles are their own antiparticles [7], and they are currently attracting significant interest because of their potential for fault-tolerant topological quantum computing [8]. The p-wave superconductor Sr2RuO4 has been widely discussed [9] to be an example of a chiral TSC associated with spontaneous time-reversal symmetry breaking [10]. More recently, time-reversal-invariant TSCs were theorized and attracted much attention [6]. Lately, the CuBi2Se3 superconductor [11] has been theoretically proposed [4] and experimentally identified [12] as the first likely example of such a TSC. However, CuBi2Se3 crystals are intrinsically inhomogeneous [13] and it has been difficult to elucidate the nature of the surface Majorana fermions. Naturally, discoveries of new TSC materials are strongly called for. In this context, CuBi2Se3 is peculiar in that it is a superconductor obtained by doping a topological insulator, and such materials are few and far between; consequently, the prospect of finding new TSC materials in doped topological insulators is not very bright.

Nevertheless, the discovery of possible topological superconductivity in CuBi2Se3 suggested that other TSCs might also be found in low-carrier-density semiconductors whose Fermi surface is centered around time-reversal-invariant momenta [14–16]. This motivated us to look for signatures of topological superconductivity in In-doped SnTe (denoted Sn1−xInxTe) [17,18] whose Fermi surface depicted in Fig. 1(a) satisfies the above criteria. In this Letter, by performing point-contact spectroscopy on Sn1−xInxTe single crystals, we found evidence for the existence of a surface Andreev bound state (ABS), which is a hallmark of an unconventional superconductivity [19]. Knowing that the symmetry and low-energy physics of this material [20] allows only three types of superconducting gap functions and that all possible unconventional states are topological, it is possible to conclude that Sn1−xInxTe is likely to be a TSC. This discovery not only enriches the family of possible TSC materials for their detailed investigations, but also points to a common mechanism for topological superconductivity, providing a guiding principle for the search of TSCs.

It is known that In in Sn1−xInxTe acts as an acceptor and suppresses the ferroelectric structural phase transition (SPT) in SnTe. Above \( x \approx 0.04 \) the SPT is completely suppressed and the system becomes a robust superconductor whose \( T_c \) gradually increases with \( x \) up to \( \sim 2 \text{K} \) at \( x \approx 0.10 \) [18]. Specific-heat measurements have confirmed bulk superconductivity with possibly a strong pairing interaction for \( x = 0.044 \) (where \( T_c = 1.0 \text{K} \)) [18], but no experiment to detect the surface ABS has been carried out so far. In this Letter, we focus on samples with \( x = 0.045 \) to avoid complications associated with the SPT.

SnTe crystallizes in the rocksalt structure (space group \( Fm\overline{3}m \)) and hence possesses the \( O_3 \) point-group symmetry. Our In-doped single crystals were grown by a vapor transport method. High-purity elements of Sn (99.99%), Te (99.999%), and In (99.99%) were used as starting materials. The In concentration was measured with inductively coupled plasma atomic emission spectroscopy and was confirmed to be consistent with the observed \( T_c \) [18]. The crystallographic orientation of the surface plane was confirmed by the x-ray Laue analysis to be (001).
FIG. 1 (color online). SnTe and the soft point-contact spectroscopy. (a) The Fermi surfaces of \( p \)-type SnTe are centered around the four equivalent \( L \) points, which belong to the time-reversal-invariant momenta, in the bulk Brillouin zone of the cubic NaCl structure with fcc Bravais lattice. (b) Schematic picture of the soft point-contact spectroscopy experiment. (c) Atomic force microscope picture of an as-grown faceted surface of \( \text{Sn}_{1-x}\text{In}_x\text{Te} \) single crystal and its height profile. (d) Atomic force microscope picture of the Ag particles on the measured surface after the gold wire is removed. (e) Temperature dependence of the resistivity of the measured sample \((x = 0.045)\), showing no sign of structural phase transition. Lower inset shows a magnified view near the SC transition at 1.2 K. Upper inset shows the magnetic-field dependence of the Hall resistivity \( \rho_{xy} \) showing completely \( B \)-linear behavior, which indicates that the second valence band maxima, even if slightly populated, plays little role in our sample; the slope gives the carrier density of \( 8 \times 10^{25} \text{ cm}^{-3} \).

The resistivity and the Hall resistivity were measured in the Hall-bar geometry with a six-probe method on the same crystal [Fig. 1(e)]. The Quantum Design Physical Properties Measurement System was used as a platform to cool the samples down to 0.37 K and apply magnetic fields up to 9 T. The upper critical field \( H_{c2} \) defined by a sharp resistivity onset was 0.3 T at 0.37 K [Fig. 2(e)].

We performed conductance spectroscopy on the faceted \((001)\) as-grown surface [Fig. 1(e)] of \( \text{Sn}_{1-x}\text{In}_x\text{Te} \) single crystals with \( x = 0.045 \) \([T_c = 1.2 \text{ K}, \text{see Fig. 1(e)}]\) using a soft point-contact technique [21] [Fig. 1(b)] which was successfully applied to \( \text{Cu}_3\text{Bi}_2\text{Se}_3 \) [12] to reveal its possible TSC nature. The soft point contacts were prepared by putting a tiny drop of silver paste below a 30-\( \mu \text{m} \)-diameter gold wire [Fig. 1(b)]; an atomic force microscope image of the silver nanoparticles on a measured surface is shown in Fig. 1(d). The \( dI/dV \) spectra were measured with a lock-in technique by sweeping a dc current that is superimposed with a small amplitude \( 1.8 \mu \text{A (rms)} \), corresponding to 0.7 \( \text{A/cm}^2 \) ac current, and a quasi-four-probe configuration was employed to read the voltage between a normal metal (silver paste) and the sample (see Ref. [12] for details). We show in the Supplemental Material [22] that this technique yields ordinary Andreev reflection spectra [23] when applied to the conventional \( s \)-wave superconductor Sn.

When applied to \( \text{Sn}_{1-x}\text{In}_x\text{Te} \), this technique allowed us to observe an intriguing signature of ABS [24] [Figs. 2(a) and 2(b)] rather than the ordinary Andreev reflection; namely, the bias-voltage dependence of the differential conductance \( dI/dV \) presents a pronounced peak at zero voltage (i.e., Fermi level) accompanied by dips on its sides at the energy scale of the SC gap \((\pm 0.1 \text{ meV})\). In the case of the ordinary Andreev reflection [23], as one can see in Fig. S1 of the Supplemental Material [22], two peaks, rather than dips, should be observed at the SC gap energy at low enough temperatures. Moreover, in our data for \( \text{Sn}_{1-x}\text{In}_x\text{Te} \), the point-contact conductance at zero energy, \( G_{PC} \), in the SC state becomes more than twice the normal-state value [Figs. 2(c) and 2(d)], which is impossible for Andreev reflections [23] and points to the existence of ABS on the surface [19,24].

The large magnitude of the observed zero-bias conductance peak (ZBCP) is already a strong indication that it is due to an ABS, but it is prudent to examine the possible relevance of other origins of the ZBCP, such as heating effect [25], reflectionless tunneling [26], and magnetic Kondo scattering [27]. In this respect, the magnetic-field dependence of the spectra [Fig. 2(b)] gives evidence...
against those other possibilities (see the Supplemental Material [22] for details) and one can conclude with reasonable confidence that the observed ZBCP is caused by an inherent surface ABS. This conclusion points to an unconventional SC state in Sn$_{1-x}$In$_x$Te.

To identify the nature of the SC state in Sn$_{1-x}$In$_x$Te, we first note that the Fermi surface in the normal state consists of four ellipsoids centered at four $L$ points of the fcc Brillouin zone. The conduction and valence bands in the vicinity of each $L$ point are described by the $k \cdot p$ Hamiltonian [20]:

$$H(k) = m \sigma_z + v \sigma_y (k_1 s_2 - k_2 s_1) + v s_3 \sigma_y,$$

(1)

Here $k_3$ is the momentum along the threefold axis $\Gamma L$; $k_2$ is along the twofold axis $L K$. $s_1$ and $\sigma_i$ are Pauli matrices associated with spin and orbital degrees of freedom, respectively. Specifically, the two orbitals labeled by $\sigma_2 = \pm 1$ are mainly derived from the $p$ orbitals of Sn and Te atoms, respectively. We emphasize that at $L$ points these two types of $p$ orbitals have opposite parity and do not mix. The four-band Hamiltonian (1) of Sn$_{1-x}$In$_x$Te at the $L$ points of the fcc lattice is essentially equivalent to that of Cu$_2$Bi$_2$Se$_3$ at the $\Gamma$ point of the rhombohedral lattice [14], both of which are dictated by the underlying $D_{3d}$ point group symmetry.

We now discuss the possible pairing symmetries. Since the four $L$ points are invariant under the inversion of crystal momentum $k \rightarrow -k$, superconducting order parameters with zero total momentum correspond to pairing within each Fermi pocket, and therefore consist of four components on the four Fermi pockets: $\tilde{\Delta} = (\Delta_1, \Delta_2, \Delta_3, \Delta_4)$. Each $\Delta_j$ can be classified by the representations of $D_{3d}$, a subgroup of the $O_h$ point group for In-doped SnTe that leaves $L_j$ invariant. For the Hamiltonian (1) at a given $L_j$, there are four types of momentum-independent gap functions $\Delta_j$ with different internal spin and orbital structures, corresponding to the $A_{1g}$, $A_{1u}$, $A_{2u}$, and $E_u$ representations of $D_{3d}$ [4]. Furthermore, depending on the relative phases between $\Delta_1, \ldots, \Delta_4$, $\tilde{\Delta}$ belong to different representations of the $O_h$ point group. It is beyond the scope of this Letter to exhaust all possibilities. Instead, we consider those superconducting states that do not spontaneously break any lattice symmetry, in accordance with all experimental facts known so far. There are three such states corresponding to the following one-dimensional representations of $O_h$ point group: $A_{1g}$, $A_{1u}$, and $A_{2u}$. The $E_u$ state breaks the threefold rotation symmetry around (111) axis.

Among these three states, $A_{1g}$ is even parity and fully gapped, which corresponds to an $s$-wave superconductor and does not have a surface ABS. Both $A_{1u}$ and $A_{2u}$ states are unconventional superconductors with odd-parity pairing. The $A_{1u}$ state is fully gapped and realizes an odd-parity TSC. The topological invariant is given by $N = \sum_j N_j$, where $|N_j| = 1$ is the invariant associated with each Fermi surface and its sign is given by $\text{sgn}(\Delta_j)$ [15]. Importantly, the four components $\Delta_1, \ldots, \Delta_4$ are related by rotation symmetry and have the same sign in the $A_{1u}$ state. As a result, the $A_{1u}$ state of In-doped SnTe is a TSC with $|N| = 4$, which supports topologically protected surface ABS.

The odd-parity $A_{2u}$ state has point nodes at the intersection of each Fermi pocket with the $\Gamma L$ line. These nodes are protected by the mirror symmetry of the fcc crystal structure. While it is impossible to define a 3D topological invariant for a gapless phase, one can still define “weak” topological invariants associated with 2D time-reversal-invariant planes in the Brillouin zone [28,29] that are fully gapped. For the $A_{2u}$ state in In-doped SnTe, any plane that passes a single $L$ point and avoids the nodes satisfies the criterion for 2D odd-parity TSC [4,30] and has a nonzero weak topological invariant. As a result, the $A_{2u}$ state has topologically protected ABS, similar to those in the $A_{2u}$ state of Cu$_2$Bi$_2$Se$_3$ theoretically demonstrated earlier [12].

From the above analysis, we conclude that the two odd-parity states $A_{1u}$ and $A_{2u}$ are topologically nontrivial and support ABS that can naturally give rise to the observed ZBCP. We further propose an electron-phonon mechanism for odd-parity pairing in Sn$_{1-x}$In$_x$Te. First, we note that SnTe has a soft TO phonon at $q = 0$, which couples strongly to interband electronic excitations [31]. This phonon mode corresponds to the displacement of Sn and Te sublattices relative to each other. It becomes unstable and leads to the SPT at low temperature. The SPT temperature is suppressed by In doping [18]. As one can see in Fig. 1(e), the temperature dependence of the resistivity shows no kink down to $T_c$, which indicates that the SPT is completely suppressed in our sample; according to the phase diagram [18], this is reasonable for $x = 0.045$. This suggests that the TO phonon remains stable. Moreover, proximity to the SPT suggests that the tendency toward ferroelectricity is strong, which naturally points to an attractive interaction between Sn and Te $p$ orbitals.

Assuming that such an interorbital attraction from electron-phonon coupling is the origin for superconductivity, we can now theoretically deduce the pairing symmetry of Sn$_{1-x}$In$_x$Te by following a similar analysis as was done for Cu$_2$Bi$_2$Se$_3$ [4]. Essentially, the spin-orbit coupled band structure (1) cooperates with the above attractive interaction to favor the pairing between Sn and Te orbitals. Because the two orbitals have opposite parity, as mentioned earlier, one may conclude that the pairing symmetry in Sn$_{1-x}$In$_x$Te is most likely odd parity. A detailed theory of the pairing mechanism and a full determination of the type of odd-parity pairing is beyond the scope of this Letter and will be presented elsewhere [32]. In any case, since the even-parity state does not produce a surface ABS but both odd-parity states in Sn$_{1-x}$In$_x$Te do, our experimental observation strongly suggests that the odd-parity pairing is realized in this material, which agrees with the above theoretical consideration for the pairing mechanism. Given that the two possible odd-parity states are both topological
as already discussed, the present observation leads to the conclusion that Sn$_{1-x}$In$_x$Te is likely to be a TSC. Note that the similarities in both band structure and pairing symmetry between Cu$_2$Bi$_2$Se$_3$ and Sn$_{1-x}$In$_x$Te naturally suggest that the calculations of the surface ABS performed for Cu$_2$Bi$_2$Se$_3$ [12,14,33,34] should also hold qualitatively for Sn$_{1-x}$In$_x$Te. This means that the observed ZBCP is exactly what is theoretically expected for this type of TSC.

In passing, it is useful to note that, in the conductance spectra of previously known candidate TSCs (Sr$_2$RuO$_4$ [35] and Cu$_2$Bi$_2$Se$_3$ [12]), the unusual dip at the SC gap energy scale has been consistently observed, bearing strongly similar to the present spectra.

Finally, we have also studied a similar superconducting material Pb$_{1-x}$Tl$_x$Te with the same point-contact technique [36]. Both Sn$_{1-x}$In$_x$Te and Pb$_{1-x}$Tl$_x$Te superconduct at 1–2 K [37], crystallize in rocksalt structure, and have similar band structures. Nevertheless, we found no evidence for a TSC state in Pb$_{1-x}$Tl$_x$Te (Fig. 3); the observed data are consistent with the Andreev reflection spectra of conventional SC state with a low contact transparency (close to the tunneling limit). The occurrence of the conventional SC state here is probably because the pairing interaction in Pb$_{1-x}$Tl$_x$Te is dominated by the charge Kondo mechanism [37] which leads to ordinary s-wave pairing. This comparison seems to indicate the importance of the TO phonon for TSC in this class of materials.

The discovery of possible topological superconductivity in Sn$_{1-x}$In$_x$Te reported here is instructive for further explorations of new TSCs: It gives us a guiding principle to look for semiconductors with strong spin-orbit coupling and having Fermi surfaces surrounding time-reversal-invariant momenta, because the likely occurrence of TSC in both Cu$_2$Bi$_2$Se$_3$ and Sn$_{1-x}$In$_x$Te strongly suggests a common mechanism. In addition, this discovery has practical importance: While the previously discovered candidate material Cu$_2$Bi$_2$Se$_3$ suffers a problem of intrinsic inhomogeneity [13] which hindered detailed studies, high-quality single crystals of Sn$_{1-x}$In$_x$Te with 100% SC volume fraction are readily available. Hence, Sn$_{1-x}$In$_x$Te would make it possible to explore the new topological state of matter, the time-reversal-invariant TSC, on a robust platform for the first time.

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*liangfu@mit.edu
†y_ando@sanken.osaka-u.ac.jp

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Pb$_{1-x}$Tl$_x$Te single crystals were grown by a vapor transport method using high-purity elements of Pb (99.998%), Te (99.999%), and Tl (99.999%). The Tl concentration was measured with inductively coupled plasma atomic emission spectroscopy and was consistent with the $T_c$ value [37]. For the point-contact experiments, Pb$_{1-x}$Tl$_x$Te crystals were cleaved at room temperature in air to obtain a good (001) surface.