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Topological states in A15 superconductors

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Abstract

Superconductors with the A15 structure are prototypical type-II *s*-wave superconductors which have generated considerable interest in early superconducting material history. However, the topological nature of the electronic structure remains unnoticed so far. Here, using first-principles band structure calculations based on density functional theory, we show that the A15 superconductors (Ta₃Sb, Ta₃Sn, and Ta₃Pb) have nontrivial band topology in the bulk electronic band structures, leading to the formation of topological surface states near the Fermi energy. Due to the bulk superconductivity, the proximity effect in the topological surface states would induce topological superconductivity even without heterostructure of a topological insulator and an *s*-wave superconductor. Our results indicate that the A15 superconductors are promising candidates for the realization of the topological superconductivity and the Majorana fermion.

I. INTRODUCTION

Topological phase of a matter has been a central theme of recent condensed matter physics^{1,2}. An intriguing aspect of the topological states is that they are promising platforms to realize novel excitations such as Majorana fermions in condensed matter systems whereas they are elusive in high-energy physics^{3–12}. One of the propositions to realize Majorana fermions is making heterostructures between strong topological insulators and *s*-wave superconductors, where the proximity-induced superconductivity in the topological surface states is analogous to that in a spinless $p_x + ip_y$ superconductor that is expected to have Majorana bound states at the vortices^{4,5}. A straightforward extension of the idea would be to search for conventional *s*-wave superconductors which also have topological surface states^{13–17}. The realization of topological superconductivity in a single material is advantageous considering the possible complexity at the interfaces of heterostructures.

A natural strategy for the search in this direction would be to examine existing superconductor material families in view of topological band theory. In conventional Bardeen-Cooper-Schrieffer (BCS) superconductors, the band structure in the normal phase is metallic and sizable density-of-states exists at the Fermi level. In contrast, the topological characterization of the band structure requires a band gap in order to define a topological invariant of the occupied band manifold since the band topology is defined using continuous deformation of the Hamiltonian without closing a gap. However, we note that it is still possible to define the band topology as long as there is a gap in the energy spectrum at each k -point (i.e., separate band manifolds). While the band structure of the superconductor would have metallic bands at the Fermi level, it is possible to have topological surface states in part of the Brillouin zone (BZ) where the metallic bulk bands do not overlap with them for appropriate surface termination. Thus, if we find a superconductor which has gaps at every k -point in the BZ with nontrivial band topology, it would be a potential candidate for the topological superconductor.

Here, we show that superconductors with the A15 structure, which are representative metal-based superconductors mostly discovered from 1950's to 1970's^{18–20}, are promising candidates for topological superconductors. Specifically, Ta₃Sb, Ta₃Sn, and Ta₃Pb are shown to have topological bulk band structures characterized by nontrivial \mathbb{Z}_2 invariants²¹. We find that the topological surface bands appear near the Fermi energy as dictated by the bulk-

boundary correspondence¹. Interestingly, since we have lower symmetry in the [001] surface, the topological surface states show non-helical spin texture unlike, e.g., Bi₂Se₃^{22,23}. We also discuss the electronic band structures of Nb compounds in the A15 family.

Compared with recently discovered FeSe_xTe_{1-x}¹⁴⁻¹⁶, the A15 superconductor has the following differences and advantages. First, the spin configuration of the surface states in the A15 superconductor has more generalized form (see below for details). In the realization of the time-reversal symmetric proximity-induced surface topological superconductor, the minus sign required by Fermi statistics comes from π Berry phase. Hence, in principle, any spin texture with π Berry phase can be utilized. However, only helical spin configurations have been reported so far, including FeSe_xTe_{1-x}. Second, the energy window where surface states reside without overlap with bulk bands is relatively larger. In FeSe_xTe_{1-x}, the spin-orbit coupling (SOC) gap is reported to be about 10 meV where the Dirac-cone-type surface states lie. In Ta₃Sb, for example, along $\bar{X}-\bar{\Gamma}$ of the surface BZ, direct bulk energy gap at each k -point is at least about 76 meV, which makes it easier to resolve the surface states using angle-resolved photoemission spectroscopy (ARPES). Third, the A15 superconductors are stoichiometric compounds which would have better material quality. Fourth, the pairing mechanism in the A15 superconductor is known to be conventional BCS type, thus it is conceptually straightforward to understand the underlying physics.

II. THEORETICAL METHODS

We performed first-principles electronic structure calculations based on density functional theory as implemented in Vienna *ab initio* simulation package (VASP)^{24,25}. We employed the projector augmented-wave method²⁶, and for the exchange correlation functional we adopted Perdew-Burke-Ernzerhof revised for solid (PBEsol)²⁷. We used a plane-wave basis set with the energy cutoff of 325 eV, and $10 \times 10 \times 10$ k -point meshes were exploited. The experimental lattice constants were used²⁸⁻³¹ except for the case where we could not find an experimental value. For the surface state calculations, we used 21-layer-thick slab models in the [001] direction with sufficiently large vacuum regions ($\gtrsim 23$ Å) to prevent the spurious interactions between the periodic images. The electronic structure was also checked and the symmetry property was analyzed using Quantum espresso package³².

III. RESULTS AND DISCUSSIONS

The superconductors with the A15 structure have cubic symmetry with the space group $Pm\bar{3}n$ #223 (Fig. 1c). They are intermetallic compounds with chemical formulae A_3B where A atoms lie at the cube face of the unit cell forming mutually orthogonal one-dimensional chains along edges, and B atoms constitute a bcc lattice. The crystal structure belongs to a nonsymmorphic space group where for instance we have a symmetry operation involving a screw axis,

$$\begin{pmatrix} x \\ y \\ z \end{pmatrix} \rightarrow \begin{pmatrix} \frac{1}{2} - y \\ \frac{1}{2} + x \\ \frac{1}{2} + z \end{pmatrix} = \begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x \\ y - \frac{1}{2} \\ z \end{pmatrix} + \begin{pmatrix} 0 \\ \frac{1}{2} \\ \frac{1}{2} \end{pmatrix}, \quad (1)$$

with the lattice constant set to 1 for simplicity. This operation is a 4-fold rotation around z axis with respect to $(0, 1/2, 0)$ followed by a fractional translation along z direction. Accordingly, we have 4-fold rotational symmetry in the bulk electronic band structure although we do not have the strict 4-fold rotation in the crystal structure.

The electronic band structure of the representative superconductor Ta_3Sb shows metallic feature with separate band manifolds, i.e., separation of the “valence” and the “conduction” bands in the whole BZ as shown in Fig. 1a. We find that SOC is essential to have the separation of the band manifolds (Fig. 1a, b). The bands near the Fermi energy mostly have Ta d character. Since the crystal structure possesses the spatial inversion symmetry, the band topology of the valence bands can be calculated from the parities of the wavefunctions at the time-reversal invariant momenta (TRIM)³³. The parity products are $+, +, -, \text{ and } +$ for Γ , $3X$, $3M$, and R , respectively, which results in a strong topological phase with $(\nu_0; \nu_1\nu_2\nu_3) = (1; 000)$ where ν_0 is the strong \mathbb{Z}_2 index and ν_1, ν_2, ν_3 are the weak ones (Fig. 1d). Here, the strong index is determined from the product of the parities at all 8 TRIM, and the weak indices from the product at 4 TRIM in $k_i = \pi$ ($i = x, y, z$) planes with the lattice constant set to 1. We also check the electronic band structure with modified Becke-Johnson (MBJ) potential which gives more accurate results for the band energy and the band gap^{34,35} (see the appendix for the MBJ band structure). We confirm that the band structure does not change qualitatively, and the band topology remains the same.

One of the direct consequences of the nontrivial bulk band topology is the existence of the topological surface bands. In the $[001]$ surface of Ta_3Sb , we indeed find topological surface

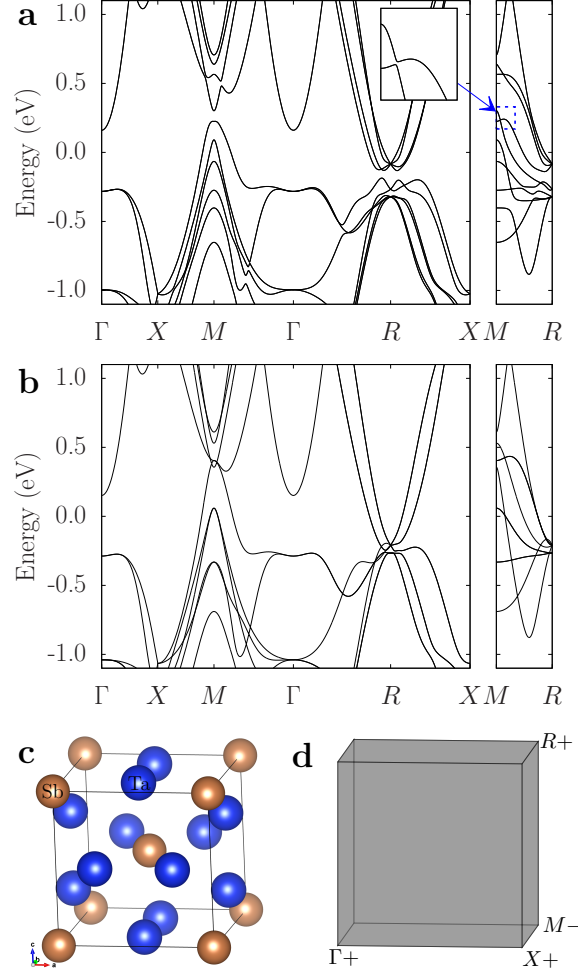


FIG. 1. Electronic band structure and atomic structure of Ta₃Sb. The band structure along high-symmetry paths in the BZ (a) with and (b) without SOC. (c) The atomic structure of Ta₃Sb. (d) The parity products in the BZ. The Fermi energy is set to 0.

states as shown in Fig. 2a. The number (mod 2) of crossings between the surface states and a line connecting two TRIM of the surface BZ in the gaps is dictated by the projected parity products. For example, since we have different parities at $\bar{\Gamma}$ and \bar{X} (i.e., + at $\bar{\Gamma}$ and - at \bar{X}), an odd number of crossings occurs along $\bar{\Gamma}$ - \bar{X} (Fig. 2a), which characterizes topological surface states. This confirms the bulk-boundary correspondence between the bulk topological invariants and the surface state configurations.

The spin-polarized surface states have non-helical spin structure (as opposed to typical helical surface states, e.g., in Bi₂Se₃) due to the reduced symmetry at the [001] surface (Fig 2). In general, topological surface states are spin-polarized due to the SOC and the breaking of

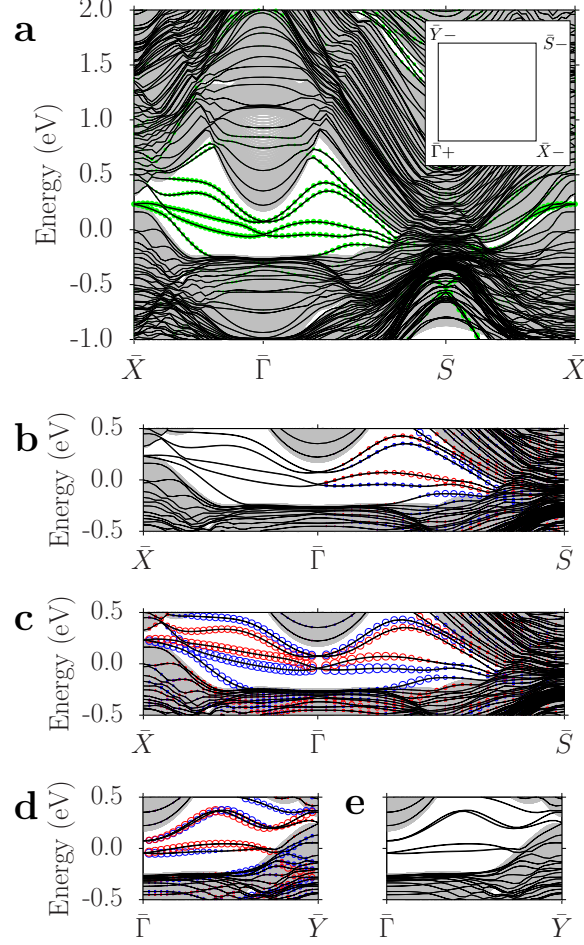


FIG. 2. Surface states of Ta₃Sb in the [001] surface. (a) Electronic band structure along high-symmetry paths in the surface BZ. Green circles denote the surface contribution. The inset shows the projected parity products at TRIM. (b), (d) x -component of the spin angular momentum. (c), (e) y -component of the spin angular momentum. The red and blue circles denote the positive and negative values, respectively. The grey regions correspond to the projected bulk states.

the inversion symmetry at the surface. The specific spin configuration is determined by the relevant symmetry of the terminated surface. Whereas we have the 4-fold symmetry in the bulk electronic bands, we have only 2-fold symmetry in the [001] surface since the symmetry involving the fractional translation is broken. The symmetry reduction at the surface is important for the qualitative understanding of the spin configuration. To see this, we consider the effective Hamiltonian $H_{\text{eff}} = \mathcal{A}k_y\sigma_x - \mathcal{B}k_x\sigma_y$ which is the general form under C_{2v} (the relevant symmetry of the surface states near $\bar{\Gamma}$) and the time-reversal symmetry up to linear order in k . Here, σ 's are Pauli matrices that describe the spin degree of freedom. H_{eff} gives

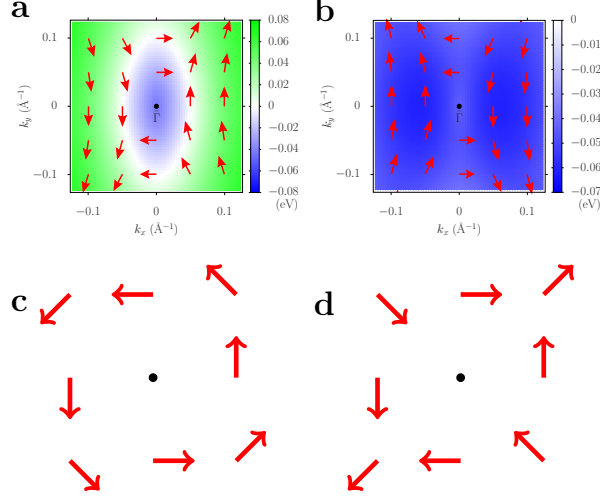


FIG. 3. Spin angular momentum texture of surface states near $\bar{\Gamma}$ in the [001] surface of Ta_3Sb . The spin texture of the (a) lower and (b) upper bands. Green and blue colors represent the band energy with respect to the Fermi level as indicated in the color bar. The schematic illustration of (c) helical (Rashba-type) spin texture and (d) linear Dresselhaus-type one.

an anisotropic Dirac cone with the energy eigenvalues $E = \pm|\mathbf{k}|\sqrt{\mathcal{A}^2 \sin^2 \theta_{\mathbf{k}} + \mathcal{B}^2 \cos^2 \theta_{\mathbf{k}}}$, in which $\cos \theta_{\mathbf{k}} = k_x/|\mathbf{k}|$ and $\sin \theta_{\mathbf{k}} = k_y/|\mathbf{k}|$. When the local k axis is rotated by $\pi/4$, the Hamiltonian takes the form $\alpha_R(k_y\sigma_x - k_x\sigma_y) + \alpha_D(k_x\sigma_x - k_y\sigma_y)$ with $\alpha_R = (\mathcal{A} + \mathcal{B})/2$ and $\alpha_D = (\mathcal{A} - \mathcal{B})/2$. Here, the α_R term gives rise to helical (Rashba-type) spin texture (Fig. 3c), and the α_D term leads to linear Dresselhaus-type one (Fig. 3d)^{36,37}. Indeed, our first-principles calculations show that the resulting spin configuration of the surface states near the Fermi energy around $\bar{\Gamma}$ is a mixture of the two types of spin textures (Fig. 3a). Note that under higher symmetry C_{4v} or C_{3v} we should have $\mathcal{A} = \mathcal{B}$, i.e., only the α_R (helical) term survives. If the screw rotation is changed to conventional rotation, the [001] surface would have C_{4v} symmetry, allowing only helical spin configuration.

Now we discuss the proximity induced superconductivity in the surface states. Here, we consider the simplest case under the C_{2v} symmetry and the time-reversal symmetry, where we have a single Dirac cone at the $\bar{\Gamma}$ point. If we substitute $k'_x = \frac{\mathcal{B}}{v}k_x$ and $k'_y = \frac{\mathcal{A}}{v}k_y$ with $v = \sqrt{\mathcal{A}^2 + \mathcal{B}^2}$ in the effective Hamiltonian, the Hamiltonian becomes mathematically analogous to the isotropic helical Dirac cone described by $v(k'_y\sigma_x - k'_x\sigma_y)$. The analysis can be given in a similar way with Ref.⁵ except for the spin helicity. We consider the Cooper pairs tunneling into the surface states due to the proximity effect by introducing

$H_p = \Delta\psi_{\uparrow}^{\dagger}\psi_{\downarrow}^{\dagger} + \text{H.c.}$ with $\Delta = \Delta_0 e^{i\phi}$. Then the Bogoliubov–de Gennes (BdG) Hamiltonian is given by $H_{BdG} = \frac{1}{2}\Psi^{\dagger}\mathcal{H}_{BdG}\Psi$ where

$$\mathcal{H}_{BdG} = \begin{pmatrix} -iv(\sigma_x\partial_y - \sigma_y\partial_x) - \mu & \Delta \\ \Delta^* & iv(\sigma_x\partial_y - \sigma_y\partial_x) + \mu \end{pmatrix}, \quad (2)$$

and $\Psi = (\psi_{\uparrow}, \psi_{\downarrow}, \psi_{\downarrow}^{\dagger}, -\psi_{\uparrow}^{\dagger})^T$ with μ being the chemical potential. By solving the BdG equation $\mathcal{H}_{BdG}\zeta = E\zeta$ for a vortex-like condition $\Delta = \Delta_0(r)e^{i\theta}$ in polar coordinates, the zero energy bound states can be found. The solution for $\mu = 0$ case is simple and can be written as

$$\zeta(r, \theta) = \begin{pmatrix} 1 \\ 0 \\ 0 \\ -1 \end{pmatrix} \exp\left(-\int_0^r ds \frac{\Delta_0(s)}{v}\right), \quad (3)$$

which represents the Majorana zero mode localized at the vortex.

Although our model assumed the simple surface band structure with a single anisotropic Dirac cone, the surface band structure from our DFT calculation is more complicated having accidental surface bands as well as topological ones. The accidental surface states can be removed from the Fermi energy by changing the surface potential whereas the topological ones are guaranteed to remain gapless by the nontrivial bulk topological order. In principle, if we change the surface potential properly, it could be possible to have simpler surface band structure having only a single time-reversal pair of surface bands at the Fermi level.

The electronic band structure of Ta₃Sn shows qualitatively the same band topology. Since we substitute Sb (Group VA in the periodic table) with Sn (Group IVA), the Fermi energy moves downwards below the surface states (Fig. 4). The experimental superconducting transition temperatures (T_c) of Ta₃Sb and Ta₃Sn are 0.7K and 8.3K, respectively¹⁸. We also find nontrivial band topology in Ta₃Pb (Pb also belongs to Group IVA) which has $T_c = 17\text{K}$ ¹⁹. The compounds with Sn or Pb have the advantage that they have higher T_c while electron doping would be needed to adjust the Fermi level in the surface. The manipulation of the Fermi level in the surface layers could be possible using chemical substitution or liquid gating^{38,39}.

Another variation of the composition would be the substitution of Ta with Nb since they belong to the same group in the periodic table. However, we find that the valence and the

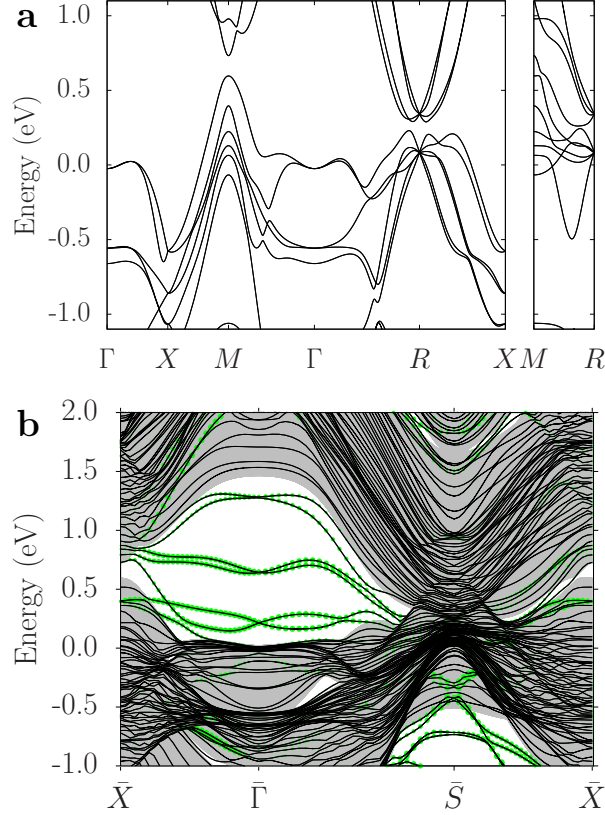


FIG. 4. Electronic structure of Ta₃Sn. (a) Bulk band structure along high-symmetry paths in Ta₃Sn. (b) Band structure of the [001] surface. Green circles denote the surface contribution. The Fermi level is set to 0.

conduction bands in Nb₃Sb and Nb₃Sn are not separated unlike the Ta compounds probably due to the weaker SOC strength of Nb. Thus, the \mathbb{Z}_2 bulk band topology is not properly defined in the Nb compounds.

IV. CONCLUSION

In conclusion, we reported hitherto unnoticed topological phases in A15 superconductors, Ta₃Sb, Ta₃Sn, and Ta₃Pb. The topological band structure was characterized by the nontrivial strong \mathbb{Z}_2 topological invariant $\nu_0 = 1$. Corresponding topological surface states appear in the [001] surface, and they show non-helical spin texture due to the reduced symmetry at the surface. The proximity induced superconductivity at the surface would give rise to the Majorana zero mode. The topological surface bands of the proposed compounds could be experimentally verified using ARPES^{1,40}. Our study shows that the A15 superconduct-

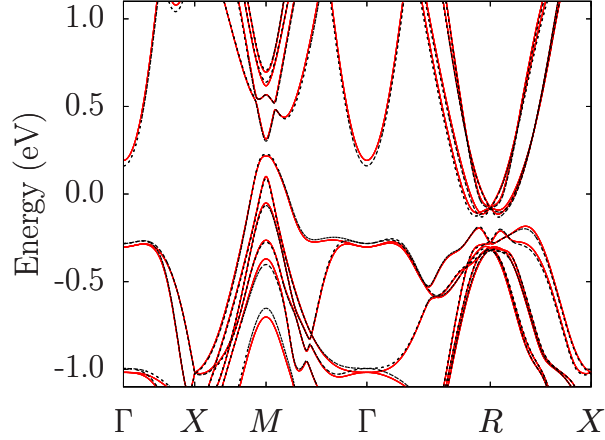


FIG. 5. Electronic band structure of Ta_3Sb using modified Becke-Johnson (MBJ) potential. The red solid and black dotted lines show the band structures with the MBJ and PBEsol, respectively.

tors are promising candidates for the realization of the topological superconductivity and Majorana fermions, and potentially useful for topological quantum computation.

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Appendix A: Electronic band structure with the MBJ potential

The electronic band structure of Ta_3Sb using MBJ potential is presented in Fig. 5.

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