The combination of a topological phase with a superconductor can lead to exotic quantum phenomena, such as a topological superconductor (TSC) that hosts Majorana fermions. Unfortunately, all the known TSCs to date have a very low transition temperature, which severely limits the experimental measurement of Majorana fermions. Here we discover the existence of a topological Dirac-nodal-line (DNL) state in a well-known conventional high-temperature superconductor MgB$_2$. First-principles calculations show that the DNL structure in MgB$_2$ exhibits unique characteristic one-dimensional dispersive DNL, protected by spatial-inversion and time-reversal symmetry, which connects the electron and hole Dirac states. More interestingly, we show that topological zero modes bound to vortices can exist on the surfaces of MgB$_2$ of different orientations, which can be made behaving as a 3D TSC to host surface Majorana modes. Our discovery may enable the experimental measurement of Majorana fermions at an unprecedented high temperature.

Superconducting and topological states are among the most fascinating quantum phenomena in nature. The entanglement of these two states in a solid material into a topological superconducting state will give rise to even more exotic quantum phenomena, such as Majorana fermions. Recently, much effort has been devoted to searching for topological superconductors (TSCs). The first way to realize a TSC phase is by proximity effect via formation of a heterojunction between a topological material and a SC [1–4]. Cooper pairs can tunnel into a topological surface state (TSS), forming a localized state that hosts Majorana bound states at magnetic vortices [1–3], or into a spin-polarized TSS leading to half-integer quantized conductance [4]. Secondly, TSCs can be made by realizing superconductivity in a topological material [5–11] or conversely by identifying topological phase in a SC [12–15]. Broadly speaking, it is preferred to work with one single material, because interfacing two materials may suffer from interface reaction and lattice mismatch. Regardless of which approach to create a TSC, however, a common challenge is that all the known TSCs to date has a very low transition temperature. Up to now, a few superconducting/topological heterostructures are realized with low critical temperature ($T_c \sim 4$ K) [8]. The superconducting transition induced by doping and/or pressurizing a few topological insulators has a $T_c$ of $4 \sim 9$ K [5–11], while the $T_c$ for some materials where topological and superconducting phases coexist is $< 7$ K [12–14]. High-temperature two-dimensional (2D) SC FeSe on SrTiO$_3$ substrate has recently been shown to also host a 2D topological insulating phase with hole doping, whereas its superconducting phases requires electron doping [15].

Here, we discover the existence of a topological phase in a conventional SC of MgB$_2$ with a $T_c$ of $\sim 40$ K, the highest transition temperature known for a bulk BCS SC. Based on density-functional theory (DFT) calculations, we demonstrate a topological Dirac nodal line (DNL) [16–18] structure in MgB$_2$, exhibiting a unique combination of topological and superconducting properties. The characteristic 1D dispersive DNL is shown to be protected by both spatial-inversion and time-reversal symmetry, which connects the electron and hole Dirac states. TSSs of (010) surface of MgB$_2$ shows a highly anisotropic band dispersion, crossing the Fermi level within the superconducting gap. The essential physics of the DNL structure in MgB$_2$ is further analyzed by effective tight-binding (TB) models. The effects of superconducting transition on DNL are also studied. Most importantly, the zero modes in the induced vortex core can be realized on (001) and (010) surfaces of MgB$_2$ at high temperature, resembling a high-$T_c$ 3D TSC.

MgB$_2$ has an AlB$_2$-type centrosymmetric crystal structure with the space group P6/mmm (191). As shown in Fig. 1(a), it is a layered structure with alternating close-packed trigonal layers of Mg while B layers form a primitive honeycomb lattice like graphene. The optimized lattice constants are $a = 3.074$ Å and $c = 3.518$ Å, which agree well with the experimental [19, 20] and other theoretical results [21, 22]. The first Brillouin zone (BZ) of bulk MgB$_2$ and the projected surface BZ of (010) plane are shown in Fig. 1(b).

To reveal the electronic and topological properties of MgB$_2$, its electronic band structure is calculated with and without spin-orbit coupling (SOC) (see Supplemental Material [23]). Fig. 1(c) and (d) show the dominant bonding character of B sheet and the bulk band structure of MgB$_2$ with SOC, respectively. The band structure exhibits linear dispersions at both K and H point, which can be easily understood in terms of the B sub-
1.87 eV, while at a hole-doped Dirac band with a Dirac-point energy of \(1.91\) eV. As \(k_z\) increases, the hole-doped Dirac state changes to be electron-doped continuously, and the critical point is at \(k_z = 0.218\) where the carrier changes sign. Usually, SOC may open up gaps at the band crossing points; inversion and/or time-reversal symmetry is insufficient to protect the band crossings. But additional symmetry, like non-symmetric symmetry, can protect nodal points or lines. For MgB\(_2\), the DNL is protected by crystal symmetry and SOC may introduce a small gap leading to a topological insulating phase. However, the SOC strength of B is negligibly small (~\(\mu\)eV), even weaker than C. Consequently, the DNL of MgB\(_2\) survives by a combination of inversion, time-reversal and crystal symmetries, along with weak SOC. We note that MgB\(_2\) also has a nodal chain structure among the conduction and valence bands (see Supplemental Material [23]), but they are located far from the Fermi level.

We define two independent topological \(Z_2\) indices denoted by \(\zeta_1\) and \(\zeta_2\) [25], one on a closed loop wrapping around the NL and the other on a cylinder enclosing the whole line, respectively (Fig. S2 [23]). The expression of \(\zeta_1\) is described by the Berry phase, \(\phi = \oint d\vec{k} \cdot \vec{A}(\vec{k})\), as a line integral along a closed path,

\[
\zeta_1 = \frac{1}{\pi} \oint_C d\vec{k} \cdot \vec{A}(\vec{k}),
\]

where \(\vec{A}(\vec{k})\) is the Berry connection, \(\vec{A}(\vec{k}) = i \langle \nabla |n\rangle \). The simplest Hamiltonian near the K(K') point for the DNL of MgB\(_2\) is

\[
h(\vec{k}) = v_F (k_x \sigma_x + k_y \sigma_y) + \alpha \cos(k_z) \sigma_0,
\]

where \(\sigma_i\) are Pauli matrices. For any path in the \((k_x,k_y)\)-plane that goes around the DNL, the index \(\zeta_1\) is 1, which means the DNLs are stable against perturbations. For the topological invariant of the DNL, one can calculate \(\zeta_2\) using the flow of Wannier charge centers on a set of loops covering the enclosing manifold [26, 27]. For the DNL in MgB\(_2\), \(\zeta_2\) is 0. But the NLs cannot shrink to a point, instead, they appear in pairs and can only be annihilated in pairs [28]. Furthermore, the parities of energy states can be used to assign the \(Z_2\) invariants in topological DNL semimetals (DNLSs). We found that MgB\(_2\) is characterized by weak \(Z_2\) indices (see Table S1 [23]).

To further reveal the topological nature of the DNLS state in MgB\(_2\), we also calculated the TSSs and Fermi arcs as additional signatures of DNLS. Fig. 2 shows the calculated surface-state spectrum of Mg-terminated (010) surface using an iterative Green’s function method. We calculated the band dispersions perpendicular to the \(\Gamma-Z\) direction with four representative cuts at different \(k_{sy}\) values in the surface BZ, as indicated in Fig. 1(b). As the bulk BZ is projected onto the (010) surface BZ, one can expect that the NL is located at \(k_{sx} = 2/3\) along the symmetry line between \(\Gamma(\mathbf{Z})\) and \(\mathbf{X(U)}\). The TSSs of DNLS connect two gapless Dirac points, which are the surface projections of the nodal points in the NL [Fig. 2(a)]. Interestingly, as \(k_{sy}\) increase, the type of bulk Dirac band is changed from the hole- to electron-doped. Accordingly, the TSSs connecting two Dirac points are also changed from hole to electron type. Moreover, these TSSs are quite anisotropic: the surface band dispersion is almost flat along the \(k_{sx}\) direction, but highly dispersive along the \(k_{sy}\) direction [Fig. 2(a)-(c)]. The B-terminated surface states are shown in Fig. S3 [23].

We now discuss the Fermi surface, whose evolution is obtained from the Green’s function method for different Fermi energy \(E_F\) [Fig. 2(d)]. The Fermi surface is composed of one Fermi arc, touching at two singularity points in the same plane as \(k_z = 0\) planes, with one pocket (electron-like) coming from the antibonding and the other (hole-like) from the bonding \(p_z\) band.
doping levels. At $E = 0$, 0.15, 0.3, and 0.5 in 2D surface BZ as indicated in Fig. 1(b), respectively. (b) The surface states along the X-U direction. (c) 3D schematic plot of the electronic surface band structure near two Dirac points. The gray planes indicate the momentum locations of cuts 1 to 4 in (a). (d) Constant energy contours of Mg-terminated (010) surface at fixed energies $E_F = -0.5$, 0, 0.5 and 1.0 eV. The red dots mark two pieces of Fermi arcs connecting surface projection of bulk Dirac points.

The essential physics of the DNL structure in MgB$_2$ is further characterized by an effective TB model using B $p_z$ orbital (see supplemental Materials [23]) which gives a quite good agreement with DFT calculations [Fig. 3(a)]. Given the DNL structure of MgB$_2$, interesting features of quantum oscillation (the Shubnikov-de Hass or the de Haas-van Alphen effect) can be observed, to manifest the predicted nontrivial Berry phase [17]. In graphene, such non-zero Berry phase has been confirmed [29, 30]. Similarly, the effective model of MgB$_2$ exhibits a pseudospin vortex texture arising from the band-degeneracy point [Fig. 3(b)]. We note that the pseudospin is actually independent of $k_z$. One can clearly see the two inequivalent BZ corners (K and K') having different topologies and being characterized with opposite Berry phases. To measure the non-trivial Berry phase via Landau-fan-type analysis, the electron orbits should enclose the vortex points in a magnetic field. Fig. 3(c) shows the calculated Fermi surface at different $E_F$. For an un-doped system, the electron and hole extremum orbits in a magnetic field along $z$-direction at $E_F$ enclose the $\Gamma$ point, giving rise to a zero Berry phase. However, for a doped system, the Fermi surface topology changes for different doping levels. At $E_F = 1.0$ eV ($E_F = -1.2$ eV), the hole (electron) extremum orbit encloses the vortex point to enable a non-zero Berry phase [Fig. 3(b)-(c)]. There are three different (energy) ranges of doping characterized with different Berry phases. If $E_F$ locates in $0.29$ eV< $E_F$ < $3.25$ eV ($-3.48$ eV < $E_F$ < $-1.17$ eV), the hole (electron) extremum orbit encloses the vortex point for a non-zero Berry phase. For $-1.17$ eV < $E_F$ < $0.29$ eV, the electron (hole) extremum orbit excludes the vortex point having the zero Berry phase. Thus, to observe the non-zero Berry phase, electron or hole doping is needed. It is known that for MgB$_2$, the Mg atoms can be substituted by Al to form Mg$_{1-x}$Al$_x$B$_2$, and B can be substituted by C to form Mg(B$_{1-y}$C$_y$)$_2$ [31-33], to achieve electron doping. Using the rigid band and virtual crystal approximation, we have calculated the alloy band structures, which confirm an upward shifting of $E_F$ (Fig. S4 [23]). The non-trivial Berry phase can be measured with a doping concentration of x>0.17 or y>0.07. Moreover, the biaxial compressive strain also induces electron doping in MgB$_2$ (Fig. S5 [23]).

On the one hand, our discovery of topological state in MgB$_2$ might not appear surprising from the theoretical point of view, because of its similarity (B hexagonal plane) to graphene/graphite. One the other hand, it is quite surprising from the experimental perspective, considering the fact that MgB$_2$ has been studied for over decades but none of the experiments has detected any topological signature. This is because there
are some fundamental differences between MgB$_2$ and graphene/graphite based systems as we have revealed here. In particular, we show that in order to detect the topological signatures in MgB$_2$, one has to do experiments differently from before, e.g. by measuring angle-resolved photoemission spectroscopy on the (010) [34] instead of the commonly used (001) surface and magnetoresistance in the doped sample instead of the intrinsic one. However, our most important discovery is possibly the topological zero mode at the vortices on the surface of MgB$_2$ as we discuss below.

In general, a topological superconducting phase can be generated in two ways. One can start with a trivial simple band structure and add a momentum dependent pairing term to open a topological superconducting gap, such as a chiral $p$-wave TSC. Or one can start with a topological band, such as a Dirac band, and add a simple pairing term as in a s-wave superconductor. One interesting example of the second approach is the proximity-induced TSC proposed by Fu and Kane [1] and confirmed by experiment [35, 36]. Here we propose another example of the second approach by adding a pairing term to the topological bands of DNL in MgB$_2$. It is a rare case analogous to a 3D time-reversal invariant TSC.

MgB$_2$ is a conventional BCS SC with two superconducting gaps, $\Delta_\sigma$ and $\Delta_\pi$, which arise from the $\sigma$ and $\pi$ bands, respectively. The magnitude of the energy gap ranges from 1.5 to 3.5 meV for the $\pi$ band and 5.5 to 8 meV for the $\sigma$ band [37–43], respectively. Since the DNL in MgB$_2$ originates from the $\pi$ band, we consider the superconducting gap for the $\pi$ band which happens to have a nontrivial band topology as we discover. Considering the DNL structure with s-wave superconducting pairing, the Bogoliubov de Gennes (BdG) Hamiltonian is given by [44]

$$H_{\text{BdG}} = v_F \tau^z (k_x \sigma_x + k_y \sigma_y) + [\alpha \cos(k_z) - \mu] \tau^z \pm \Delta_\pi \tau^x,$$

with the basis $\Psi_+ = \{ \psi_{A1}^+, \psi_{B1}^+, \psi_{A2}^+, \psi_{B2}^+ \}$ and $\Psi_- = \{ \psi_{A1}^-, \psi_{B1}^-, \psi_{A2}^-, \psi_{B2}^- \}$, respectively. $\psi_{A/B,1/2}$ is the electron annihilation operator with spin up/down at sublattice A/B. $\Delta_\pi (\mu)$ is the superconducting gap of $\pi$ band (chemical potential). When $\Delta_\pi$ is spatially constant, the energy eigenvalues are solved as [23]

$$E(\vec{k}) = \pm \sqrt{\pm v_F |\vec{k}| + \alpha \cos(k_z) - \mu}^2 + \Delta_\pi^2.$$  

The low-energy spectrum with the effective Dirac equation of similar structure appears in the theory of a spinless $p_x + i p_y$ superconductor [1, 45]. The source of the Dirac type behavior is the symmetry of the $p_x + i p_y$ superconducting order parameter. Though this is similar to the proximity induced Majorana mode with Dirac surface state in s-wave SC/TI, there are several advantageous implications: (1) The superconducting gap is an intrinsic property of the superconductivity of MgB$_2$ with the highest known $T_c$. (2) The topological zero-energy state is very robust existing in a wide range of varying chemical potential (~2eV), as the effective chemical potential $\mu_{\text{eff}} = \mu - \alpha \cos(k_z)$ can be tuned with $k_z$.

Now we show that the zero mode can exist at the vortices on both the (001) and (010) surfaces of MgB$_2$, as illustrated in Fig. 4. First, we consider the (001) surface with a magnetic field perpendicular to B plane, which induces vortex lines in the bulk MgB$_2$. With a single vortex centered at $\vec{r} = 0$, the $\Delta_\pi$ becomes $\Delta_\pi (\vec{r})e^{\pm i \theta}$. The bound states at a vortex are determined by solving the BdG equation $H_{\text{BdG}}+\epsilon \Psi_+ = E \Psi_+$. By putting a four-component trial solution $\Psi_+ = (\xi_1(r, \theta)e^{-i k_z z})$, for the bound states and setting $\mu = \alpha (1 + \lambda^2 / 2)$, the BdG equation in the presence of the vortex is simplest. Then the zero energy eigenfunction $\xi_1$ and $\xi_2$ are given by $\xi_1(r, \theta) = [f(r), 0, 0, i f(r)]^T$, $\xi_2(r, \theta) = [0, i f(r), f(r), 0]^T$, respectively, where the localized function $f(r)$ is given by $f(r) = e^{-\frac{1}{2}k_0^2 r^2}$. While our results here are presented for certain filling, zero modes continue to exist for finite doping. Second, we consider the (010) surface with the magnetic field parallel to B plane, e.g. y-direction, the vortex becomes $\Delta_\pi(x, z)$ and the $k_0$ is no longer a good quantum number. With the trial solution $\Psi_+ = (\chi_1(x, z)e^{-i y \gamma v})$ and neglecting $k_0^2$ and higher order terms, the BdG equation is reduced to a 1D model. The zero energy solutions are $\chi_1(x, z) = [g(x), 0, 0, i g(x)]^T$, $\chi_2(x, z) = [0, i g(x), g(x), 0]^T$, where the localized function $g(x)$ is given by $g(x) = e^{i \gamma v e^{-\frac{1}{2}k_0^2 x^2}}$. Therefore the zero mode solutions can be achieved on both the (001) and (010) surface if the vortex profile is sufficiently smooth so that it does not cause single-particle scattering between K and K'. In the presence of valley and spin, the zero modes are fourfold degenerate, then fermionic modes will be formed in pairs on the vortex. The doubled zero modes do not follow the non-Abelian quantum statistics, but it is possible to realize odd number of Majorana fermions with a proper hierarchy of mass scales [46] or effectively bind a single mode in the vortex core by strain [47].

In conclusion, based on first-principles calculations and model analysis, an intriguing inversion and time-reversal
symmetry protected Dirac-nodal-line state and the topological zero mode bound to vortices is revealed in high-temperature superconductor MgB$_2$. Among the known TSCs, MgB$_2$ is distinguished with outstanding features, an unprecedented high $T_c$ of 40K and a wide range of variable chemical potential of $\sim$2eV. Therefore it offers a promising material platform to building novel quantum and spintronics devices, and attracts a broader range of interest.

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