Titanium-based kagome superconductor CsTi$_3$Bi$_5$ and topological states

Haitao Yang$^{1,2,3}$, Zhen Zhao$^{1,2}$, Xin-Wei Yi$^{2,3}$, Jiali Liu$^{1,2}$, Jing-Yang You$^{2,3}$, Yuhang Zhang$^{1,2}$, Hui Guo$^{1,2,3}$, Xiao Lin$^{2,3}$, Chengmin Shen$^{1,2}$, Hui Chen$^{1,2,3}$, Xiaoli Dong$^{1,2,3}$, Gang Su$^{2,3}$*, and Hong-Jun Gao$^{1,2,3}$*

1 Beijing National Center for Condensed Matter Physics and Institute of Physics, Chinese Academy of Sciences, Beijing 100190, PR China

2 School of Physical Sciences, University of Chinese Academy of Sciences, Beijing 100190, PR China

3 CAS Center for Excellence in Topological Quantum Computation, University of Chinese Academy of Sciences, Beijing 100190, PR China

#These authors contributed equally to this work

*Correspondence to: hjgao@iphy.ac.cn, gsu@ucas.ac.cn, dong@iphy.ac.cn
Since the discovery of a new family of vanadium-based kagome superconductor $\text{AV}_3\text{Sb}_5$ (A=K, Rb, and Cs) with topological band structures, extensive effort has been devoted to exploring the origin of superconducting states and the intertwined orders $^{1-13}$. Meanwhile, searching for new types of superconductors with novel physical properties and higher superconducting transition temperatures has always been a major thread in the history of superconductor research. Here we report a successful fabrication and the topological states of a Titanium-based kagome metal CsTi$_3$Bi$_5$ (CT$_3$B$_5$) crystal. The as-grown CT$_3$B$_5$ crystal is of high quality and possesses a perfect two-dimensional kagome net of Titanium. The superconductivity of the CT$_3$B$_5$ crystal shows that the critical temperature $T_c$ is of $\sim$4.8 K. First-principle calculations predict that the CT$_3$B$_5$ has robust topological surface states, implying that CT$_3$B$_5$ is a $\mathbb{Z}_2$ topological kagome superconductor. This finding provides a new type of superconductors and the base for exploring the origin of superconductivity and topological states in kagome superconductors.
We first present the crystal structural geometry of CsTi$_3$Bi$_5$ (CT$_3$B$_5$). The crystalline structure of the CT$_3$B$_5$ is of hexagonal with the space group of P6/mmm (Fig. 1a) $^1$. The compound forms a layered structure. The perfect kagome net of Ti atoms mixed with a simple triangular net of Bi$\text{I}$ atoms is located in the middle layer, which is sandwiched by two additional honeycomb layers of Bi$\text{II}$ atoms (Fig. 1b). The upper and lower triangular layers of Bi metal atoms have large bond distances with respect to the middle Ti layer and are loosely bonded to them.

We synthesize the CT$_3$B$_5$ crystal through a self-flux method. A typical CT$_3$B$_5$ crystal with a lateral size of over 3 mm and regular hexagonal morphology is shown in the inset of Fig. 1c. The representative x-ray diffraction (XRD) pattern of the CT$_3$B$_5$ crystal confirms the pure phase of the as-grown single crystal with a preferred [001] orientation (Fig. 1c). The rocking curve obtained from the (004) reflection shows a full-width-at-half-maxima (FWHM) of $\sim$0.078°, demonstrating the single crystal nature of the as-grown CT$_3$B$_5$ (Fig. 1d). The peaks in the XRD curve agree with the theoretical prediction (Fig. S1), indicating that the atomic structure of the as-grown CT$_3$B$_5$ is consist with the one shown in Fig. 1a. The lattice parameters $a$, $b$, and $c$ are measured to be 5.839, 5.839 and 9.295 Å, respectively, by single crystal diffraction (Fig. S2) $^7$. The layered structures are confirmed by the scanning electron microscopy (SEM) measurements (Fig. S3). The characterizations above, therefore, demonstrate the high-quality of the as-synthesized CT$_3$B$_5$.

We then verify the superconductivity by collecting the zero-field cooled (ZFC, hollow symbols) and field cooled (FC, solid symbols) magnetic susceptibility (Fig. 2a). The onset superconducting transition temperature is 4.8 K. The existence of superconducting phase was unambiguously confirmed by the Meissner effect. A superconducting volume fraction above 50% under a magnetic field of 0.05 mT was obtained at 1.8 K, indicating that the superconductivity is bulk in nature. The heavily field-dependent diamagnetism shown in Fig. 2a implies an unusual superconducting feature of this new type superconductor. The measurements of lower critical fields $H_{c1}(T)$ can also provide important information on superconductivity in the as-grown kagome metal CT$_3$B$_5$, which are subtracted from isothermal magnetization $M(H)$ with magnetic field along the $c$ axis (Fig. 2b) and $ab$ plane (Fig. 2c), respectively. The $H_{c1}$ data follow a single-band s-wave relation with the fitted values $\Delta (0) = 1.76$ k$_B$T$_c$, and $\mu_0H_{c1}(0)$ = 13.3$\pm$0.3 mT, $\mu_0H_{c1}^{\text{ab}}(0)$ = 19.0 $\pm$0.3 mT , respectively (Fig. 2d), indicating a conventional BCS
character. Moreover, the abnormal $H_{C1}$ anisotropy of CT$_3$B$_5$ ($H_{C1}^{ab} > H_{C1}^{c}$), resembling the CsV$_3$Sb$_5$ case \cite{14}, implies a similarity in Fermi surface topology between these two types of kagome superconductors.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{Atomic structure of the Ti-based kagome superconductor CsTi$_3$Bi$_5$. \textbf{a}. Crystal structure for CT$_3$B$_5$ with Cs atoms in black, Bi atoms in light orange, Ti atoms in azure. \textbf{b}, Atomic arrangements of the Cs, TiBi and Bi atomic layers. The dashed lines represent a unit cell. Cs layer forms a hexagonal lattice, while the Bi2 layer consists of a honeycomb lattice. The perfect kagome net of Ti atoms is mixed with a simple triangular net of Bi1 atoms. \textbf{c}, XRD pattern of the CT$_3$B$_5$ single crystal, revealing that the crystal surface is parallel to the (001) plane. Inset: a photo of a typical CT$_3$B$_5$ single crystal. \textbf{d}, The x-ray rocking curve of the (004) reflection shows a small FWHM of 0.078°.}
\end{figure}
Fig. 2 | Magnetization measurements of the CsTi$_3$Bi$_5$ single crystal. a, The magnetic susceptibilities, corrected for the demagnetization factor, at different field for $H \parallel c$ with ZFC and FC progress between 1.8 K and 10 K. b, c, The isothermal magnetization at various temperatures with magnetic fields along the $c$ axis (b) and $ab$ plane (c). d, Temperature dependence of lower critical fields $\mu_0H_c$ for $H \parallel c$ and $H \parallel ab$, respectively.

Superconductivity in CT$_3$B$_5$ is also confirmed by electrical transport measurements. The CT$_3$B$_5$ sample shows a metallic behavior (Fig. 3a) with a superconducting transition at onset $T_c \sim 4.8$ K and zero-resistivity at ~3.6 K (Fig. 3b). It is noticeable that this new kagome superconductor CT$_3$B$_5$ exhibits $T$-linear resistivity over a wide temperature range (~70 – 300 K), which might be caused by electron-phonon scatterings. The residual resistance ratio (RRR) subtracted from the temperature dependence of the resistivity is about 26, further supporting the relatively high quality of the as-grown CT$_3$B$_5$ crystals.
Finally, we predict the physical property of the CT$_3$B$_5$ crystal with first-principles DFT calculations. The electronic band structure and corresponding density of states (DOS) with spin–orbit coupling (SOC) for CT$_3$B$_5$ (Fig. 4a) show that the band structures in $k_z=0$ and $k_z=\pi$ planes are very similar, indicating a strong 2D characteristic similar to AV$_3$Sb$_5$. Ti and Bi atoms mainly contribute to the DOS near the Fermi level, forming a small peak, and at slightly above and below the Fermi level there are dips of the DOS owing to the energy gap opened by the strong SOC. We note that the energy bands colored by red, blue and green in Fig. 4a give rise to a strong topological Z$_2$ index, resulting in topologically nontrivial surface states near the Fermi level (Figs. 4b and c), which indicates that CT$_3$B$_5$ is a Z$_2$ topological superconductor. Combining the time-reversal and inversion symmetries in CT$_3$B$_5$, we obtain Z$_2$ topological invariant (Fig. 4d) of several bands near Fermi level by calculating the parity of the wave functions at all time-reversal invariant momenta (TRIM)$^{15}$. Thus, the CT$_3$B$_5$ reveals the coexistence of superconductivity and nontrivial topological surface states.

*Fig. 3* | Temperature dependence of resistivity of the CsTi$_3$Bi$_5$ single crystal. a, Temperature-dependent resistance between 2 K and 300 K under zero magnetic field, showing the RRR is about 26. b, Temperature-dependent resistivity between 2 K and 9 K under zero magnetic field, showing the $T_{C\text{onset}}=4.8$ K and $T_{C\text{zero}} \sim 3.6$ K.
**Fig. 4** Calculated band structures and $Z_2$ band indices of CsTi$_3$Bi$_5$ single crystal. 

- **a**, The electronic energy bands and density of states calculated with spin-orbit coupling for CT$_3$B$_5$. Energy bands near Fermi level are drawn in different colors.
- **b, c**, The surface states along (b) M-$\Gamma$-M and (c) K-$\Gamma$-K paths projected on (001) plane for CT$_3$B$_5$.
- **d**, Product of parity of four time reversal invariant momenta and $Z_2$ indices of the bands near Fermi level. The colors of band indices are consistent with (a).
- **e**, The Brillouin zone with high symmetry paths.

### Table

| Band Index | Product of Parity | $Z_2$ |
|------------|-------------------|-------|
| 59         | + + + +           | 1     |
| 61         | - - + +           | 1     |
| 63         | - - - +           | 1     |
| 65         | + + - -           | 0     |
| 67         | - + - +           | 0     |
In summary, we have successfully fabricated the Ti-based kagome superconductor CsTi$_3$Bi$_5$ crystal of high quality and discovered the bulk superconductivity for the first time. The transition superconducting temperature is of 4.8 K. The DFT calculations show that the CT$_3$B$_5$ superconductor has robust topological surface states, implying that CT$_3$B$_5$ is a $Z_2$ topological kagome superconductor and Majorana zero modes are expected to be observed at the CT$_3$B$_5$ surface. These findings provide a new platform for future studies on topological superconductivity, correlated electronic states, and topological quantum computations.
References

1. Ortiz, B. R. et al. New kagome prototype materials: discovery of KV₃Sb₅, RbV₃Sb₅, and CsV₃Sb₅. *Phys. Rev. Mater.* **3**, 094407 (2019).
2. Ortiz, B. R. et al. CsV₃Sb₅: A Z₂ topological kagome metal with a superconducting ground state. *Phys. Rev. Lett.* **125**, 247002 (2020).
3. Ortiz, B. R. et al. Superconductivity in the Z₂ kagome metal KV₃Sb₅. *Phys. Rev. Mater.* **5**, 034801 (2021).
4. Yang, S.-Y. et al. Giant, unconventional anomalous Hall effect in the metallic frustrated magnet candidate, KV₃Sb₅. *Sci. Adv.* **6**, eabb6003 (2020).
5. Jiang, Y.-X. et al. Unconventional chiral charge order in kagome superconductor KV₃Sb₅. *Nat. Mater.* **20**, 1353 (2021).
6. Zhao, H. et al. Cascade of correlated electron states in the kagome superconductor CsV₃Sb₅. *Nature* **599**, 216-221 (2022).
7. Chen, H. et al. Roton pair density wave in a strong-coupling kagome superconductor. *Nature* **599**, 222-228 (2022).
8. Tan, H., Liu, Y., Wang, Z. & Yan, B. Charge density waves and electronic properties of superconducting kagome metals. *Phys. Rev. Lett.* **127**, 046401 (2021).
9. Chen, K. Y. et al. Double superconducting dome and triple enhancement of Tc in the kagome superconductor CsV₃Sb₅ under high pressure. *Phys. Rev. Lett.* **126**, 247001 (2021).
10. Nie, L. et al. Charge-density-wave-driven electronic nematicity in a kagome superconductor. *Nature* **604**, 59-64 (2022).
11. Mielke, C. et al. Time-reversal symmetry-breaking charge order in a kagome superconductor. *Nature* **602**, 245-250 (2022).
12. Luo, H. et al. Electronic nature of charge density wave and electron-phonon coupling in kagome superconductor KV₃Sb₅. *Nat. Commun.* **13**, 273 (2022).
13. Kang, M. et al. Twofold van Hove singularity and origin of charge order in topological kagome superconductor CsV₃Sb₅. *Nat. Phys.* **18**, 301-308 (2022).
14. Ni, S. et al. Anisotropic Superconducting Properties of Kagome Metal CsV₃Sb₅. *Chin. Phys. Lett.* **38**, 057403 (2021).
15. Fu, L. & Kane, C. L. Topological insulators with inversion symmetry. *Phys. Rev. B* **76**, 045302 (2007).
16. Blöchl, P. E. Projector augmented-wave method. *Phys. Rev. B* **50**, 17953-17979 (1994).
17. Kresse, G. & Furthmüller, J. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Phys. Rev. B* **54**, 11169-11186 (1996).
18. Perdew, J. P., Burke, K. & Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* 77, 3865-3868 (1996).
19. Mostofi, A. A. et al. An updated version of wannier90: A tool for obtaining maximally-localised Wannier functions. *Comput. Phys. Commun.* **185**, 2309-2310 (2014).
20. Sancho, M. P. L., Sancho, J. M. L., Sancho, J. M. L. & Rubio, J. Highly convergent schemes for the calculation of bulk and surface Green functions. *Journal of Physics F: Metal Physics* **15**, 851-858 (1985).
21. Vergniory, M. G. et al. A complete catalogue of high-quality topological materials. *Nature* **566**, 480-485 (2019).