Van der Waals materials offer unprecedented control of electronic properties via stacking of different types of two-dimensional materials. A fascinating frontier, largely unexplored, is the stacking of strongly correlated phases of matter. We study 4Hb-TaS₂, which naturally realizes an alternating stacking of 1T-TaS₂ and 1H-TaS₂ structures. The former is a well-known Mott insulator, which has recently been proposed to host a gapless spin-liquid ground state. The latter is a superconductor known to also host a competing charge density wave state. This raises the question of how these two components affect each other when stacked together. We find a superconductor with a T_c of 2.7 Kelvin and anomalous properties, of which the most notable one is a signature of time-reversal symmetry breaking, abruptly appearing at the superconducting transition. This observation is consistent with a chiral superconducting state.

**RESULTS**

We have grown single crystals of 4Hb-TaS₂−xSeₓ with x = 0.01, using a standard chemical vapor transport method (19). The small amount of Se stabilizes the 4Hb structure. Details about the sample preparation process and the structure characterization appear in the Supplementary Materials.

4Hb-TaS₂ was first synthesized by Di Salvo et al. (19). The transport data can be described as a mixture of 1T and 2H, with metallic conductivity in the ab plane and semiconducting conductivity along the c axis. The in-plane resistivity was shown to be three orders of magnitude smaller than the out-of-plane resistivity. This “mixture” of 1T and 2H is also visible in the x-ray photoelectron spectroscopy spectrum of the Ta 4f core levels, which displays three peaks — two from the “1T” layers and one from the “1H” layers (fig. S2) (20).

The electronic dispersion along the Γ-M direction was measured using angle-resolved photoemission spectroscopy (ARPES) and is presented in Fig. 1D. The main finding is that the band structure of the 4Hb-TaS₂ is a mixture of the metallic 2H layer and the band structure of the 1T shifted toward the Fermi level, leaving no spectral gap. This should be compared with the 1T structure where a bandgap of 0.2 eV was measured and interpreted as a Mott gap (21, 22). The parts of the band structure associated with the 1T and the 1H layers are marked in the figure.

Two electron pockets, similar to the ones in 2H-TaS₂, can be observed surrounding the points k = ±1/2Å together with the shifted band structure of 1T-TaS₂. The 1T part of the band structure is
Fig. 1. Structure of 4Hb-TaS2. (A) 3D schematic drawing of a unit cell of 4Hb-TaS2 showing the alternate stacking of octahedral (T) and trigonal prismatic (H) layers. Top views of 1H and 1T layers are shown in (B) and (C), respectively. The top view of the 1H layer displays the in-plane broken mirror symmetry. (D) An ARPES detector image obtained at T = 15 K using 72 eV of photon energy reveals the electronic band structure along the Γ-M direction. (E) A Fermi surface mapping under the same conditions. The band structure is a combination of 2H-TaS2 and CDW reconstructed 1T-TaS2, which was rigidly shifted toward the Fermi level [horizontal white dashed line in (D)]. The dashed line represents the 2H-TaS2 Fermi surface.

Fig. 2. Specific heat and transport measurements. (A) The electronic contribution to the heat capacity divided by the temperature C_e/T is plotted as function of T. The dashed line represents the total electronic specific heat in the normal state, and the dotted line is a residual linear contribution coming from the 1T layers (see the main text for details). (B) The electronic-specific heat after the removal of the 1T contribution displaying a BCS-type behavior with Δ = 0.4 meV. Inset: Resistance versus temperature shows enhanced T_c. (C) H_c2 as a function of temperature for in-plane (red circles) and out-of-plane (blue triangles) field orientations. For better visibility, H_c2 is multiplied by 10. Inset: The angular dependence of H_c2 showing strong anisotropy.

reconstructed by the well-known $\sqrt{13} \times \sqrt{13}$ charge density wave (CDW).

An ARPES intensity map at the Fermi level is shown in Fig. 1E. The intensity map reveals that within the alternate-stacking layered crystal, every layer retains its original electronic dispersion. The Fermi surface is a mixture of the Fermi surface of 2H-TaS2 with its familiar constant density of states, at least down to an energy resolution equivalent to 300 mK.

In the inset of Fig. 2C, we show the critical field, H_c2, as a function of the angle θ, between the applied field and the ab plane (θ = 0 denotes field aligned in the plane), measured at T = 30 mK. The magneto-resistance exhibits strong anisotropy, with H_c2/\perp > 17. The angular dependence of H_c2, plotted in the inset, is consistent with the predictions of a highly anisotropic Ginzburg-Landau theory (see the Supplementary Materials), reflecting the quasi-2D nature of superconductivity in 4Hb-TaS2.

We also note that a naïve calculation of the Clogston-Chandrasekhar limit using the estimated minimal gap from the exponential decay of the specific heat (see the Supplementary Materials) $\Delta_{\text{min}} = 0.36$ meV, yields a paramagnetic limit of H_p = 5 T, much smaller than the observed H_c2. Moreover, because of strong Ising spin-orbit coupling, we anticipate the critical Zeeman field to greatly exceed this value (27).
The quasi-2D picture is further supported by the temperature dependence of $H_c^2$ shown in Fig. 2C. We observe an unusual linear dependence of the in-plane critical field through the entire temperature range. Similar behavior has been reported in Bi$_2$Se$_3$ under pressure (28), where it was interpreted as a result of a polar p-wave state, and also in KO$_2$O$_6$, where it was ascribed to a multiband effect (29). We note that the Zeeman-limited $H_c^2$ typically results in a nonlinear temperature dependence, and thus, we argue that even the in-plane field is most likely orbitally limited.

To extract coherence lengths from the orbital limited fields, we use the highly anisotropic Ginzburg-Landau theory. The in-plane coherence length is found from the perpendicular critical field (see Fig. 2C) $\xi_{ab} = \frac{\phi_0}{2\pi n c} = 186$ Å, and using $H_{c2}^0 = \frac{\phi_0}{\xi_{ab}^2}$, we find the out-of-plane coherence length to be $\xi_c = 9.8$ Å. This length is comparable to the interlayer spacing of 1H layers. We can therefore conclude that 4Hb-TaS$_2$ is a stack of weakly coupled 2D superconductors with weak orbital out-of-plane tunneling currents.

We now turn to the main result of our work: evidence of TRS breaking in the superconducting state seen in a $\mu$SR measurement. In the absence of a magnetic order, the muon depolarization is a breaking in the superconducting state seen in a $\mu$SR measurement.

In the following, we discuss topological properties of such a chiral state. The weak interlayer coupling discussed above motivates us to study the superconducting state on isolated 1H layers with point group symmetry $D_{3h}$. With TRS present in the normal state, chiral superconductivity requires a multicomponent gap function. Within the relevant symmetry group, there is only one such representation (31), which allows us to pinpoint the gap function

$$\Delta_E(k) = \Delta_0 \left(1 - \alpha \sigma_0 + \alpha \sigma_0^2 \right) i \sigma^y$$

where $\alpha_k = \sum_{j=1}^3 \omega \cos(k \cdot T_j)$ and $\sigma_k = \sum_{j=1}^3 \omega \sin(k \cdot T_j)$ are the d-wave and p-wave basis functions in the $D_{3h}$ point group. Here, we have chosen only one chirality, in other words, only Cooper pairs with positive orbital angular momentum, while their negative counterparts are given by complex conjugation. The vectors $\pm T_j$ point to the six nearest neighbors on the triangular Ta lattice, $\omega = \exp(2\pi i/3)$, and $\alpha$ is a non-universal weight, which quantifies the mixing of the d-wave and p-wave components that is allowed by the lack of an inversion center in the plane. Last, $\sigma^0$ and $\sigma^y$ denote the identity and Pauli matrices. Note that because of the alternate stacking of the 1H layers, the relative phase of the order parameters in Eq. 2 changes from layer to layer (31).

Chiral superconductivity belongs to symmetry class D in the 10-fold way (32), which allows us to classify isolated 1H layers using a Chern number. Using a tight-binding model for TaS$_2$ including up to the third-nearest-neighbor hopping (27, 33), we compute the Chern number within a BdG Hamiltonian as a function of $\alpha$, allowing us to interpolate between the pure d + id- and p + ip-wave pairing channels. The phase of the superconducting order parameter in Eq. 2 is presented in Fig. 4 (A and B) for the extreme cases $\alpha = 0$ (purely d-wave) and $\alpha = 1$ (purely p-wave), respectively. We find that the Chern number vanishes in the limit of $\alpha = 0$, i.e., $\zeta = 0$, because the inner and outer Fermi surfaces cancel each other. On the other hand, the Chern density is cooperative in the limit $\alpha = 1$, where we obtain $\zeta = -6$. The interpolation between these two points is plotted in Fig. 4C. Note that the data points were computed numerically (not rounded to an integer) using the full BdG band structure with a mesh grid of $9.5 \times 10^4$ equally spaced points. Overall, we find that the Chern number of the Chiral state is highly sensitive to the mixing ratio $\alpha$ (34). A challenging experimental goal is thus to measure a quantized thermal Hall conductance in this system.
We now turn to the microscopic origin of the possible chiral superconductivity. Phonon-mediated interactions typically favor $s$-wave pairing (38). In such a case, unconventional pairing is expected only if strong local repulsion, which reduces the attraction in the $s$-wave channel, is present. On the other hand, an attractive interaction mediated by spin fluctuations naturally prefers non-$s$-wave superconductivity and, in particular, chiral symmetry when the Fermi surface encloses the $\Gamma$ point as given here (see Fig. 1E). From this perspective, it is interesting to understand whether the proximity between the superconductor in the 1H layers and the Mott insulating state in the 1T layers is an essential ingredient. Our ARPES data in Fig. 1E suggest the possibility that the Mott insulator is lightly doped due to the stacking structure, resulting in strong spin fluctuations. Electronic pairing mediated by spin fluctuations in a quantum spin ice has been studied in (39) for the case of a rotationally symmetric Fermi surface. There, the authors found that the strongest pairing channel is odd-parity with the possibility of a multicomponent order parameter, consistent with the chiral superconductor proposed here. The results presented here, thus, raise a host of theoretical questions regarding the interaction between superconductivity, charged, and neutral itinerant fermionic excitations, which invite further study.

To summarize, we have investigated 4Hb-TaS$_2$ and found signs of TRS breaking in the form of an abrupt rise in the muon relaxation rate upon cooling below the superconducting transition temperature. Given the hexagonal symmetry and the Fermi surface topology, these findings suggest that 4Hb-TaS$_2$ is a chiral superconductor. We further show that the unique structure of 4Hb-TaS$_2$ consisting of stacked, weakly coupled layers of 1H-TaS$_2$ and 1T-TaS$_2$ results in a band structure, which combines the properties of both constituents: a 2D superconductor (1H) and a doped Mott insulator proposed to be a gapless spin liquid (1T). Both constituents show clear signatures both in ARPES and in the low-temperature specific heat. Its relatively high superconducting $T_c \approx 2.7$ K, the quasi-2D structure, and the ability to grow very large and clean single crystals make this material a promising platform for future study and applications. Furthermore, it opens new directions in the study of topological superconductivity using van der Waals heterostructures.

**MATERIALS AND METHODS**

High-quality single crystals of 4Hb-TaS$_2$ were prepared using the chemical vapor transport method. The appropriate amounts of Ta and S were ground and mixed with a small amount of Se (1% of the S amount). The powder was sealed in a Quartz ampoule, and a small amount of iodine was added as a transport agent. The ampoule was placed in a three-zone furnace such that the powder is in the hot zone. After 30 days, single crystals with a typical size of 5 mm x 5 mm x 0.1 mm grew in the cold zone of the furnace.

High-resolution ARPES measurements were performed at the I05 beamline at Diamond (Didcot, UK) and at the SIS Beamline at the SLS (Villigen, Switzerland) using a photon energy of 72 eV. The samples were cleaved in vacuum better than $5 \times 10^{-11}$ torr at base temperature and measured for not more than 6 hours. The samples were measured at a temperature of 10 K. The energy resolution was 6 meV in both beamlines.

Both zero-field and transverse-field $\mu$SR measurements were performed at the DOLLY beamline at PSI (Villigen, Switzerland) over a temperature range from 7 K down to 300 mK. The transverse-field measurements were performed using a 145-G field.
Heat capacity measurements at various fields were performed using Quantum Design PPMS He3 probe. The addenda was measured in all fields and temperatures to ensure proper background subtraction.

Transport properties were measured using standard lock-in technique in a dilution refrigerator equipped with an 18-T magnet and a rotator probe at the Tallahassee National Laboratory. For the higher temperature range, a He3 probe in a PPMS was used.

SUPPLEMENTARY MATERIALS
Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/full/6/13/eaax9480/DC1

REFERENCES
9. P. K. Biswas, H. Luetkens, T. Neupert, T. Stürzer, C. Baines, G. Pascua, A. P. Schnyder, et al.
11. A. Pustogow, Y. Luo, A. Chronister, Y.-S. Su, D. A. Sokolov, F. Jerzembeck, A. P. Mackenzie, et al.
10. M. H. Fischer, T. Neupert, C. Platt, A. P. Schnyder, W. Hanke, J. Goryo, R. Thomale, et al.
7. E. R. Schemm, W. J. Gannon, C. M. Wishne, W. P. Halperin, A. Kapitulnik, Observation of broken time-reversal symmetry in the heavy-fermion superconductor UPt 3.
6. J. Xia, Y. Maeno, P. T. Beyersdorf, M. M. Fejer, A. Kapitulnik, High resolution polar kerr effect measurements of Sr2 RuO 4: Evidence for broken time-reversal symmetry in the superconducting state.
5. G. M. Luke, Y. Fudamoto, K. M. Kojima, M. I. Larkin, J. Merrin, B. Nachumi, Y. J. Uemura, Y. Maeno, Z. Q. Mao, Y. Mori, H. Nakamura, M. Sigrist, Time-reversal symmetry-breaking superconductivity in SrRuO 3.
4. J. Xua, Y. Maeno, P. T. Beyersdorf, M. M. Fejer, A. Kapitulnik, High resolution polar kerr effect measurements of SrRuO3: Evidence for broken time-reversal symmetry in the superconducting state.
3. C. Nayak, S. H. Simon, A. Stern, M. Freedman, S. Das Sarma, Non-Abelian anyons and topological quantum computation. Rev. Mod. Phys. 80, 1083–1159 (2008).
2. J. D. Sau, R. M. Lutchyn, S. Tewari, S. Das Sarma, Generic new platform for topological superconductivity.
1. N. Read, D. Green, Paired states of fermions in two dimensions with breaking of parity and time-reversal symmetries and the fractional quantum Hall effect.

RECOMMENDATIONS
Downloaded from https://www.science.org at LiB4RI on February 06, 2022
42. H. P. Hughes, R. A. Pollak, Charge density waves in layered metals observed by X-ray photoemission. *Philos. Mag. A J. Theor. Exp. Appl. Phys.* **34**, 1025–1046 (1976).

43. K. Ishizaka, T. Kiss, T. Yamamoto, Y. Ishida, T. Saitoh, M. Matsuurai, R. Eguchi, T. Ohtsuki, A. Kosuge, T. Kanai, M. Nohara, H. Takagi, S. Watanabe, S. Shin, Femtosecond core-level photoemission spectroscopy on 1T-TaS$_2$ using a 60-eV laser source. *Phys. Rev. B* **83**, 081104 (2011).

44. J. A. Scarfe, H. P. Hughes, Core-level lineshapes in photoemission from transition-metal intercalates of TaS$_2$. *J. Phys. Condens. Matter* **1**, 6865 (1999).

45. H. Padamsee, J. E. Neighbor, C. A. Shiffman, Quasiparticle phenomenology for thermodynamics of strong-coupling superconductors. *J. Low Temp. Phys.* **12**, 387–411 (1973).

46. D. C. Johnston, Elaboration of the $\alpha$ model derived from the BCS theory of superconductivity. *Supercond. Sci. Technol.* **26**, 115011 (2013).

47. M. Tinkham, *Introduction to Superconductivity* (Dover Publications Inc., Mineola, N.Y, Ed. 2, 2004).

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