Tuning interactions between spins in a superconductor

Hao Ding (丁浩) a,b,1, Yuwen Hu a,b,1, Mallika T. Randeria a,b,2, Silas Hoffman d, Oindrila Deb c, Jelena Klinovaja c, Daniel Loss c, and Ali Yazdani a,b,3

aJoseph Henry Laboratories, Princeton University, Princeton, NJ 08544; bDepartment of Physics, Princeton University, Princeton, NJ 08544; cDepartment of Physics, University of Basel, CH-4056 Basel, Switzerland; and dDepartment of Physics, University of Florida, Gainesville, FL 32611.

Contributed by Ali Yazdani, March 2, 2021 (sent for review December 1, 2020; reviewed by M. F. Crommie and Leonid I. Glazman)

Novel many-body and topological electronic phases can be created in assemblies of interacting spins coupled to a superconductor, such as one-dimensional topological superconductors with Majorana zero modes (MZMs) at their ends. Understanding and controlling interactions between spins and the emergent band structure of the in-gap Yu–Shiba–Rusinov (YSR) states they induce in a superconductor are fundamental for engineering such phases. Here, by precisely positioning magnetic adatoms with a scanning tunneling microscope (STM), we demonstrate both the tunability of exchange interaction between spins and precise control of the hybridization of YSR states they induce on the surface of a bismuth (Bi) thin film that is made superconducting with the proximity effect. In this platform, depending on the separation of spins, the interplay among Ruderman–Kittel–Kasuya–Yosida (RKKY) interaction, spin–orbit coupling, and surface magnetic anisotropy stabilizes different types of spin alignments. Using high-resolution STM spectroscopy at millikelvin temperatures, we probe these spin alignments by precisely tuning the separation of spins and their energy splitting. Such measurements also reveal a quantum phase transition between the ground states with different electron number parity for a pair of spins in a superconductor tuned by their separation. Experiments on larger assemblies show that spin–spin interactions can be mediated in a superconductor over long distances. Our results show that controlling hybridization of the YSR states in this platform provides the possibility of engineering the band structure of such states for creating topological phases.

Significance

Majorana zero modes (MZMs) have been proposed as the building blocks for fault-tolerant topological quantum computation. Recent experiments have found both spin and charge signatures of MZMs at the ends of spin chains on superconducting surfaces. However, the properties of such chains have not been reliably controlled experimentally. Here, we present a platform in which long-range spin–spin interactions and hybridization of spin-induced in-gap states on the surface of a superconductor can be tuned with unprecedented precision by changing the distance between the spins using an atomic manipulation technique. This capability is required for tailoring magnetic textures and engineering in-gap states in spin assemblies and opens up the possibility of exploring new topological superconducting phases with tunable properties.

Here, we show that magnetic atoms on the surface of bismuth (Bi) thin films made superconducting by the proximity effect provides such a platform. The relatively large Fermi wavelength of this surface as compared to its atomic lattice spacing, and its strong spin–orbit interaction make it possible to use atomic manipulation with STM to create spin assemblies with different spin alignments. By fine-tuning the distance between pairs of interacting spins, we have precisely measured the splitting of their YSR states and observed a quantum phase transition (QPT) between phases with different electron number parity tuned by their separation. In larger spin assemblies, we find evidence that noncolinear alignment of spins controls the splitting of YSR states, thereby illustrating the potential for YSR band structure engineering with topological properties in this platform.

Results and Discussion

Experimental Platform. To realize our platform, we grow epitaxial Bi ultrathin films (six monolayers) on the surface of superconducting Nb(110) substrate in situ (see Materials and Methods and SI Appendix, Fig. S1) in a home-built millikelvin ultrahigh-vacuum STM system (18). The proximity-induced superconducting gap on the surface of the Bi thin film (Δ) is 1.52 meV, as large as that measured on the bare Nb surface (SI Appendix, Fig. S1C). The Bi films have a Bi(110)-like zig-zag atomic structure (SI Appendix, Fig. S1B) but are more likely in a metastable pseudocubic (PC) phase, as previous studies find to be most stable at such a thickness (19, 20).

The goal of realizing topological electronic phases using combinations of superconductivity, magnetism, and spin–orbit interaction has motivated efforts in creating spin chains and other magnetic assemblies on the surfaces of superconductors (1–10). There is now considerable evidence that a topological superconducting phase forms in closely packed one-dimensional ferromagnetic chains made of magnetic atoms on the surface of a superconductor with strong spin–orbit coupling, where at the ends of the chains Majorana zero modes (MZMs) have been detected in various scanning tunneling microscope (STM) experiments (11–15). The next step in advancing the study of MZMs in atomic chains is to build chains using STM atomic manipulation techniques starting from single magnetic atoms to be able to systematically probe the topological phase diagram (1, 3, 5–8). These experiments could also make it possible to test the MZMs’ non-Abelian properties, such as their fusion rules, and perhaps ultimately to braid them (16). The key parameters of the topological phase diagram of atomic chains are their spin texture and the bandwidth of their overlapping in-gap Yu–Shiba–Rusinov (YSR) states. Demonstration of atomic manipulation experiments that can control these parameters would open up a wide range of future experiments. While there have been efforts to successfully create closely packed iron chains with nearest neighbor exchange interaction on the surface of superconducting rhenium using STM atomic manipulation (17), a platform that meets the above tunability requirements has not been realized.

topological states | superconductivity | Majorana fermions | scanning tunneling microscopy | condensed matter physics

PNAS 2021 Vol. 118 No. 14 e2024837118

https://doi.org/10.1073/pnas.2024837118
For either PC phase (19, 20) or Bi(110) surface (21), the largest Fermi pocket is near \( \Gamma \) point at the Brillouin zone center with Fermi wavelength (\( \lambda_F \)) \( \sim 15 \) Å, which is much shorter than the proximitized Bi in-plane coherence length (\( \xi \) \( \sim 600 \) Å), making Ruderman–Kittel–Kasuya–Yosida (RKKY) interaction one of the dominant interactions between spins when their separation is at the scale of \( \lambda_F \) on the surface (22, 23). More importantly, the \( \lambda_F \) of Bi surface is almost three times as long as that of Nb (5.4 Å) and more than four times that of the smallest atomic spacing (3.30 Å) on the Bi surface with zig-zag lattice (SI Appendix, Fig. S1B).

---

### Fig. 1.
YSR states and magnetic ground states of Gd pairs on proximitized superconducting Bi surface. (A–D) Four examples of Gd pairs with different interatomic distances and orientations with respect to Bi lattice. \( a \) and \( b \) are the crystallographic directions of the Bi surface with lattice constants \( a = 4.75 \) Å and \( b = 4.55 \) Å (SI Appendix, Fig. S1B). (E–H) \( dI/dV \) spectra taken on the Gd pairs in A–D, respectively. The gray curves in the background are spectra taken on Bi surface away from Gd atoms, showing the superconducting gap (\( \Delta = 1.52 \) meV) for reference. The YSR states energies \( \Omega \) (or \( \Omega_1, \Omega_2 \)) are measured from the electron-like in-gap states with higher spectral intensity. The spectral weights of bonding and anti-bonding YSR states are color coded by cyan and magenta; whereas that of the degenerate YSR states are color coded by blue. After subtracting all YSR states from the whole spectra, the rest of spectral weights are color coded by gray, showing the suppressed coherence peaks (see SI Appendix, section I for detailed analysis).

---

(|) A phase diagram of the magnetic ground states of Gd pairs revealed by the YSR states analysis (see SI Appendix, sections II–IX for complete analysis). (J) A linecut of \( dI/dV \) spectra taken across a Gd pair with \( r = 2.21a \) showing the spatial distribution of bonding and anti-bonding YSR states.
which allows for significant tunability of the RKKY interaction by placing spins with separation smaller than $A_F$ on the Bi lattice. Therefore, this surface provides an ideal platform to tune interactions between spins in the presence of superconductivity. Typically, spin-polarized STM measurements are used to detect components of the spin polarization of magnetic atoms on surfaces; such measurements are most reliable when used in combination with the application of a magnetic field (24). However, an applied magnetic field can not only modify the magnetic configuration of atoms on a surface but also suppress superconductivity. Here, we probe magnetic interactions between spins in a superconductor by detecting the YSR states that magnetic impurities induce within the host superconductor energy gap. In the simplest case of a single magnetic impurity, a single YSR state appears as a pair of electron- and hole-like partner peaks in the local density of states (LDOS) at energies $E = \pm \Omega$ ($|\Omega| \leq \Delta$) with respect to the chemical potential (25–29). For weak exchange coupling between the impurity and the superconductor, YSR states lie near the gap edge at $E = \pm \Delta$ and move closer to the middle of the gap with increasing exchange interaction. Two spins induce two YSR states that can spatially overlap and hybridize, giving rise to the formation of bonding and anti-bonding YSR states and the observation of four (two pairs) peaks in LDOS with their energy splitting proportional to the overlap between the YSR wavefunctions (23, 29–37). For distances much smaller than the coherence length ($r \ll \xi$), the magnetic configuration of the spins has a rich dependence on the RKKY interaction, direct exchange interaction, and overlap of YSR states themselves (22, 23, 34). Nonetheless, the shift and splitting of YSR states can be used to probe the magnetic ground state as well as the interactions between spins in a superconductor (23, 29–37).

We probe the interactions between spins in the superconducting state by constructing precisely positioned pairs of magnetic atoms on the proximitized Bi thin film surface and probe their properties with STM spectroscopy at millikelvin temperatures (with energy resolution of 100 µeV; see Materials and Methods and SI Appendix, sections II–IX for complete analysis). The orange curve is a fit to $\Omega_1 + \Omega_2/2$ indicating the exchange coupling strength between one of the Gd atoms and the superconducting Bi electrons, and the energy splitting between the two states $|\Omega_2 - \Omega_1|$ is induced by the wavefunction overlap between the YSR states localized at two nearby Gd atoms (30–33).

### QPT Controlled by Tuning Separation of Spins.

Before analyzing the different possible regimes of spin alignments in our platform, we examine one sequence of experiments in which a pair of Gd atoms are brought close together systematically along the diagonal direction on the Bi lattice (black arrow in Fig. 1I). As shown in Fig. 2A and B, the YSR states of such a pair start at $E \sim \pm \Delta$ when the separation between spins is large. As the separation between the spins decreases, a single pair of YSR states with

![Fig. 2](image)

**Fig. 2.** Quantum phase transition (QPT) and magnetic transition controlled by tuning the distance between two Gd atoms. (A) $dI/dV$ spectra of Gd pairs with configurations along the black arrow indicated in Fig. 1I. (B) A color plot of the YSR states intensity extracted from A. The orange (purple) line indicates evolution of electron (hole)-like YSR states. The crossing of orange and purple lines implies a QPT. The QPT occurs at $r \sim 1.55a$ (for example, SI Appendix, Figs. S6C, 5TD, and S22 A and D), closer separations comparing to the pair in Fig. 1A. (C) The energy splitting between bonding and anti-bonding YSR states $|\Omega_2 - \Omega_1|$ (blue open circles) as a function of distance variable $r$. The splitting is zero if there is only one pair of YSR states. See SI Appendix, sections II–VIII for complete analysis. The orange curve is a fit to $E = \pm \sin(k_F \sqrt{r^2 + r^2})/c$, which is the theoretically predicted YSR states splitting for a pair of collinearly aligned spins as a function of their separation. Here, $c = k_F (1 - \alpha^2) / 4\Delta\sqrt{a}$, where $\Delta = \pm \Delta_0$ characterizes the single magnetic atom induced YSR state; $J$ is the exchange coupling between the spin and the superconducting electrons; $\nu_F$ is the density of states at Fermi level in the normal state of the superconductor. (D) A schematic showing the magnetic ground state of Gd pairs can be tuned from out-of-plane FM/AFM to in-plane AFM and then to in-plane FM phase as moving two Gd atoms closer.
energies $E = \pm \Omega r$ move to energies deeper inside the gap and then split into two pairs with energies $E = \pm \Omega r, \pm \Omega a$ at even smaller separations ($r \leq 2.77a$) with the energy splitting between the two states ($\Omega a - \Omega r$) increasing dramatically. For $r \leq 1.38a$, the interactions between YSR states induced by the two Gd atoms are so strong that can generate a splitting larger than $\Delta$, and therefore drive one pair of the YSR states across the chemical potential at zero bias. The zero-energy-crossing behavior is identified by a switch of the asymmetry in the intensity of the pair of YSR states, i.e., a switch of higher intensity state from positive to negative biases, as the two atoms move closer to each other from $r \geq 2.08a$ to $r \leq 1.38a$ (Fig. 2A and B). The electron- and hole-like YSR states are asymmetric in intensity because they experience different local Coulomb potential from each other from $r \geq 2.08a$ and crosses zero to negative energies when $r \leq 1.38a$ (indicated by an orange line in Fig. 2B); whereas its hole-like partner does the exact opposite (indicated by a purple line in Fig. 2B).

Theoretical works (23, 32, 33) exploring the formation of superconducting ground states when two impurity spins are interacting through a superconductor predicted that such zero-energy crossing and intensity-asymmetry switching of one pair of YSR states in LDOS measurements mark a QPT driven by spin–spin interactions. The superconducting condensates before and after QPT are predicted to differ in parity. The transition occurs when it becomes energetically favorable to breaking a Cooper pair in the ground states so that an unpaired electron can form a spin singlet with the total spin of both magnetic impurities. After QPT, the ground state parity changes from even to odd and it is accompanied by a change of the system’s total spin quantum number by 1/2. A related transition occurs when the YSR states cross zero energy in a single impurity case as a function of exchange coupling strength to the superconducting host (40–42). However, the phase transition we report here is driven by the interactions between a pair of spins and controlled by their separation (23, 32, 33). In a longer chain of spins, the ability to tune the hybridization between YSR states would allow control of the YSR bands crossing the chemical potential—i.e., a key parameter for changing the band topology of the YSR states for such chains (1, 3, 6–8).

**Magnetic Transition Controlled by Tuning Separation of Spins.** To investigate the nature of the spin–spin interactions in our platform, we measure the interaction-induced energy splitting ($\Omega a - \Omega r$) of YSR states for all Gd pairs as function of their displacement vector relative to the Bi surface and plot them as blue open circles in Fig. 2C (see SI Appendix, sections II–VIII for complete analysis), except for the spacing of 4.75 Å where they make a spin zero pair (likely in an antiferromagnetic state) with rather weak interactions with the superconductor (SI Appendix, section IX and Fig. S22). Although previous studies have shown examples of split YSR peaks indicating ferromagnetic arrangement (35–37), here we provide a detailed study of controlling spin–spin interactions as function of spacing between spins in a superconductor.

As shown in Fig. 2C, the splitting can be observed up to $r = 2.82a$. The dependence of the splitting as a function of the separation between two Gd atoms for $r \leq 2.82a$ matches that of the theoretically expected behavior (orange curve) for overlapping YSR states induced by a pair of collinearly aligned spins interacting through the superconducting host (30), from which we extract the Fermi wavelength of Bi surface states $\lambda_F = 2.53a = 12.0$ Å. More specifically, for separations $r < \lambda_F$ and $\lambda_F < r \leq 2.82a$, the splitting behavior is expected for two Gd spins in ferromagnetic (FM) ground state; whereas for $r = \lambda_F$, the splitting always vanishes, which is consistent with two Gd spins in antiferromagnetic (AFM) ground state and their YSR states wavefunctions are orthogonal to each other. The oscillatory behavior indicates the spin-spin interactions for $r \leq 2.82a$ are dominated by RKKY interaction (23).

For $r > 2.82a$, the significant deviation from RKKY behavior shown in Fig. 2C implies other interactions need to be taken into account in this range. For two Gd atoms with separation $r > 2.82a$, or more specifically for an isolated Gd atom, we only observe YSR states at energies very close to the gap edge despite of Gd’s large spin (for example, Fig. 2A, $r = 4.84a$ and SI Appendix, Fig. S2E). We distinguish the weakly bound YSR states induced by an isolated Gd atom from the BCS coherence peaks using a superconducting tip that allows higher-resolution measurements (SI Appendix, section X and Fig. S23) or by the asymmetric intensity of electron- and hole-like partner states measured with a normal tip (SI Appendix, section I and Fig. S3E). The low binding energy of this YSR state is a clear indication of small exchange interaction ($\mathbf{J} \cdot \mathbf{\sigma} \ll \Delta$, where $J$ is the exchange coupling constant) between Gd spin ($\mathbf{S}$) and Bi surface electrons ($\mathbf{e}$) that are in-plane spin polarized due to the large Rashba type spin-orbit coupling (21). The small exchange interaction ($\mathbf{J} \cdot \mathbf{\sigma} = 0$) is consistent with the out-of-plane spin polarization of the isolated Gd atom due to strong surface magnetic anisotropy, which is common for large spin magnetic atoms on an atomically ordered surface, where the full rotational symmetry is broken (43, 44).

The overall behavior of YSR states hybridization as a function of the separation between two spins can be understood, if we consider the interplay between RKKY interaction, the surface magnetic anisotropy, and the spin–orbit coupling in the substrate. For a pair of Gd spins within separation range $2.82a < r \ll \xi$, they may align in FM or AFM arrangement pointing perpendicular to the surface; therefore, only weak YSR states near gap edge are observed, due to weak exchange interaction between Gd spin and in-plane spin-polarized Bi electrons. At closer separations $r \leq 2.82a$, we expect the distance-dependent RKKY interaction overcomes the surface magnetic anisotropy and makes the Gd pair spins lie in-plane to lower the total energy, leading to strong exchange interaction with the Bi surface electrons that drives the YSR states deep inside the gap. Depending on the sign of the RKKY interaction, both in-plane FM alignment and in-plane AFM alignment of the spins can be the ground state of the system. Here, we find in-plane FM states with four YSR states at $r < \lambda_F$ (Fig. 1E and F). In addition, close to the alignment transition at $r \sim \lambda_F$, we also find evidence for in-plane AFM states with two degenerate (zero-splitting) YSR states (for example, at $E = \pm \Omega r$ in Fig. 1H), with intensities equal to the sum of split YSR states intensities of FM aligned spins at slightly closer spacing (at $E = \pm \Omega a, \pm \Omega r$ in Fig. 1F).

In the crossover region with separation $r \sim \lambda_F$, four particular pair configurations ($r = 2.16a, 2.21a, 2.77a$, and $2.82a$) show variability in their spin arrangements from location to location on the surface, sometimes displaying splitting of YSR states consistent with FM alignment, or no splitting at all as expected for AFM alignment (SI Appendix, section VI and Figs. S13 and S14). More importantly, for distances larger than $\lambda_F$, the interplay between RKKY interaction, spin–orbit coupling, and surface magnetic anisotropy makes the spin alignment of the pairs more complex.

**Theoretical Model.** A theoretical model that captures the interplay between the surface anisotropy and the RKKY interaction in the presence of strong spin–orbit coupling can be used to qualitatively describe the changing spin alignment in our system. Since we are considering interactions between spins on length scale far below the superconducting coherence length ($r \ll \xi$), the
influence of superconductivity on spin–spin interactions will not be significant. Furthermore, recent work (22, 34) considering the contribution of the overlap of the YSR state to spin–spin interactions also shows that RKKY interaction is dominant on length scale below $r < \frac{\sqrt{2}a}{3}$ which is 53 Å for our system. Therefore, for simplicity we consider a pair of spins interacting via RKKY interaction through a two-dimensional electron gas with strong spin–orbit interaction in the presence of magnetic surface anisotropy (see SI Appendix, section XI for details). For large separations of the spins, with sufficiently large surface anisotropy term $H_A = \frac{\pi \lambda}{2} A^2$, where $A > 0$ and $S_\perp$ is the spin component perpendicular to the surface, the ground state of this system is clearly either noninteracting or weakly FM or AFM with spins pointing perpendicular to the surface. As the separation between the spins becomes of the order of $\lambda_F$, the RKKY interaction begins to dominate the properties of this system, resulting in a small region of in-plane AFM aligned pairs and finally at $r < \lambda_F$, in-plane FM aligned pairs with their spins pointing along the direction perpendicular to the line connecting them (Fig. 2D). Transition between out-of-plane to in-plane spin alignments in pairs underlies our observation that YSR states of such pairs are far lower in energy than a single Gd atom. The transition is also consistent with the presence of degenerate YSR states with no splitting for Gd pairs with $r \sim 2.5a$, because in-plane Rashba type spin–orbit coupling can lift the degeneracy and lead to YSR states splitting for a pair of spins with out-of-plane AFM alignment, as shown in a recent experiment (45). However, if the pair

Fig. 3. YSR states and noncollinear magnetic ground states of three-Gd-atom chains. (A–C) Topograph and $dI/dV$ spectra of a Gd pair with $r = 2a$, showing it is in plane FM state with two pairs of YSR states. (D) Extracting YSR states coupling parameters ($\Omega_0$, $t_1$, and $t_2$) from Gd pair in A and three-atom chain in E. $\Omega_0$ is the average energy of all electron-like YSR states; $t_1$ is the nearest-neighbor coupling matrix element; $t_2$ is the next-nearest-neighbor coupling matrix element between atom 1 and atom 3 in E. $t_1' = (\frac{1}{4} (t_1^2 + t_2^2 + t_3^2))/2$, $t_2' = (\frac{1}{4} (t_1^2 + t_2^2 + t_3^2))/2$, for clarity. The small value of $t_2$ implies that the coupling between atom 1 and atom 3 in E is reduced by the noncollinear alignment of spins. (E–H) Topograph and $dI/dV$ spectra of a three-atom chain evenly spaced with $r = 2a$, built by moving atom 3 to the right side of atom 2 in A. The magenta, blue, and cyan-coded peaks are bonding (0 node), nonbonding (one node), and anti-bonding (two nodes) YSR states from further splitting after adding atom 3. (I–L) Topograph and $dI/dV$ spectra of another example of three-atom chain with $r = 2a$, built at a different location showing slightly different YSR states energies but similar behavior as the one in E.
of spins are in the in-plane AFM ground state and aligned perpendicularly to the connection between them (Fig. 2D, r ≈ 2.5 a), the degeneracy can still be preserved (see SI Appendix, section XII for details).

**Experiments on Larger Spin Assemblies.** To demonstrate that changing of spin alignment in larger assemblies opens up the possibility of engineering the band structure of YSR states in our platform, we constructed structures made of three and four Gd atoms. Fig. 3 shows that adding a third atom to a pair of in-plane FM aligned spins with separation $r < \lambda_F$ (Fig. 3 A–C) splits their overlapping YSR states further to create a six-peak structure with varying intensity on the three different atoms (Fig. 3 E–H). A minimal model (33) of the overlap between the YSR states ($\Omega_0$) with nearest ($t_1$) and next-nearest neighbors’ matrix elements ($t_2$), as shown in Fig. 3D, can be used to understand the six-peak structure for such three-atom spin chains (Fig. 3 E–L). The comparison of the energy splitting of the YSR peaks to the model calculation, however, reveals that for a three-atom spin chain with 2a spacing, the ratio $t_2/t_1$ is surprisingly smaller than what expected for three atoms in FM alignment. Fig. 2C (orange curve) shows that YSR overlap for 2a and 4a distances should yield $t_2 \sim -0.8 t_1$ for FM alignment, while to capture the data in Fig. 3 we have to use 5 to 10 times smaller $t_2/t_1$ ratio (SI Appendix, section XIII). This indicates that the three spins are not collinear, which would reduce the overlap interactions by a factor of $\cos(0/2)$, where 0 is the angle between the nearest-neighbor spins. From this simple model, we suggest that spins in a three-atom chain prefer to make an in-plane noncollinear alignment (SI Appendix, section XIII). Theories predict helical spin order to be a natural consequence of RKKY interaction for an infinite chain in one dimension (2), and could be stabilized in the presence of large spin–orbit coupling in two dimensions (46). Our experimental data show that the magnetic frustration can lead to noncollinear spin ground states in a three-atom chain, and potentially helical order when longer chains are constructed. Theoretical studies have established that when the wavelength of helical order is larger than $\lambda_F$, then such chains will be in a topological phase hosting MZMs at their ends (1–6, 8).

Examining the properties of a three-atom spin chain when a fourth atom is brought into its close proximity shows that spin–spin interactions can be mediated and controlled in the superconducting state on length scales much larger than the lattice spacing or $\lambda_F$ in our system. As shown in Fig. 4, the six-peak structure of the three-atom chain responds to the presence of the fourth atom as it couples to the chain starting from $-16$ Å away from the chain. In effect, a spin (labeled as atom 1 in Fig. 4B) is getting influenced by another spin (atom 4 in Fig. 4B) via the chain even if they are more than 26 Å apart. Compared to previous experiments where spins in a chain are coupled in a collinear manner through exchange interaction (47, 48), here the combination of long-range spin–spin exchange coupling through chains and the possibility to modulate the YSR band structure through tuning the YSR states hybridization make it possible to quantitatively control the topological phase transition of complex spin structures on a superconducting surface. With the tunability of our platform, it is possible to create well-developed helical spin states in a topological phase in longer chains which host MZMs at their ends. Detailed studies of MZMs coupling to each other as a function of chain length, as well as coupling MZMs to nearby spins can be performed in this system. Finally, it would be possible to create complex coupled chains in which $Z_2$ symmetry or fusion of MZMs can be directly tested in our platform.

---

**Fig. 4.** Long-range spin–spin interactions between a three-Gd-atom chain and a Gd atom. (A–D) A sequence of atomic manipulation moving atom 4 from the lower right corner toward atom 3 step by step. Atoms 1, 2, and 3 are evenly spaced with $r = 2a$, $r_{34}$ is the distance between atom 3 and atom 4. (E–G) Color plots of $dI/dV$ spectra taken on the atoms 1–3 in A–D, from Bottom to Top, showing YSR states evolution through the manipulation sequence. The density of states outside of the gap ($|E| \geq \Delta$) are subtracted for clarity (see SI Appendix, Figs. S26 and S27 for raw data). (H) The YSR coupling parameters ($\Omega_0$, $t_1$, and $t_2$) extracted from E–G (see SI Appendix, section XIV). Their evolution implies the spin alignment of the three-atom chain (atoms 1–3) is changing through the manipulation sequence, due to the perturbation of atom 4 via long-range spin–spin interactions.
Materials and Methods

Both sample preparation and in situ STM measurements were performed in a home-built dilution refrigerator STM (base temperature, 250 mK) equipped with ultrahigh-vacuum (UHV) preparation chambers (base pressure, 2.0 × 10⁻¹⁰ Torr) (18).

The Nb(110) single crystal was prepared by argon ion sputtering and subsequent flash annealing (10 cycles, 30 s each) at 1,600 °C to form clean and flat surface. Namely 5-monolayer (ML) Bi (99.999%) films were evaporated from standard Knudsen cells onto Nb(110) surface, which was held at –150 °C by liquid nitrogen cooling. Fully covered 4-ML Bi films and partially covered 6-ML Bi films (SI Appendix, Fig. S1 A and B) were formed uniformly after being annealed at 100 °C for 30 min and exhibit a hard superconducting gap (Δ = 1.52 meV) (SI Appendix, Fig. S1C), which is nearly identical to that of Nb due to the proximity effect (proximity effect becomes weaker once Bi films are thicker than 6 ML). Submonolayer Gd (99.9%) single atoms were then deposited on Bi surface at cryogenic temperature (–40 K) (SI Appendix, Fig. S1D).

All STM measurements were performed on 6-ML Bi films at effective electron temperature of 250 mK (calibrated by measurements of the superconducting gap; SI Appendix, Fig. S1C) using a sharp W tip. The tip was treated by field emission and controlled indentation on Cu(100) surface until it was atomically sharp. Topographic images were taken using constant current mode with closed-feedback loop at sample bias voltage V s = 1 V and tunneling current I t = 10 pA. Differential conductance (dI/dV) spectra were acquired at either V s = –4 mV, I t = 40 pA or V s = –20 mV, I t = 200 pA under open-feedback condition, using a lock-in amplifier at a frequency of 712.9 Hz with AC rms excitation V r.m.s. = 20 μV.

Gd atoms were manipulated by the tip laterally with closed feedback loop at V s = ±1.5 mV, I t = 200 pA. An example of building Gd pairs using atomic manipulation is shown in SI Appendix, Fig. S2.

Data Availability. The data that support the findings of this study are available in the paper and the SI Appendix.

ACKNOWLEDGMENTS. We acknowledge discussions with Y. Meir. This work has been primarily supported by the Gordon and Betty Moore Foundation as part of the Emergent Phenomena in Quantum Systems initiative (Grants GBMF5310 and GMBF4640). Office of Naval Research Grants N00014-17-1-2784 and N00014-14-1-0330, NSF Materials Research Science and Engineering Centers programs through Princeton Center for Complex Materials Grants DMR-142054 and NSF-DMR-2011750, as well as NSF-DMR-1608848 and NSF-DMR-1904442. This work was also supported by the Swiss National Science Foundation and the National Centre of Competence in Research Quantum Science and Technology (J.K., O.D., S.H., and D.L.) and the European Union’s Horizon 2020 Research and Innovation Program (European Research Council Starting Grant; Grant Agreement 757725 to J.K.). A.Y. acknowledges the hospitality of the Trinity College and Cavendish Laboratory in Cambridge, UK, during the preparation of this manuscript, which was also funded in part by a Quantum Emergence Exchange grant from the Institute for Complex Adaptive Matter and the Gordon and Betty Moore Foundation (Grant GBMF5305).

1. S. Nadji-Perge, I. K. Drozdov, B. A. Bernevig, A. Yazdani. Proposal for realizing Majorana fermions in chains of magnetic atoms on a superconductor. Phys. Rev. B Condens. Matter Mater. Phys. 88, 020407 (2013).
2. J. Klinovaja, P. Stano, A. Yazdani, D. Loss, Topological superconductivity and Majorana fermions in RKKY systems. Phys. Rev. Lett. 111, 186805 (2013).
3. F. Pientka, L. I. Glazman, F. von Oppen, Topological superconducting phase in helical Shiba chains. Phys. Rev. B Condens. Matter Mater. Phys. 88, 155420 (2013).
4. B. Braunecker, P. Simon, Interplay between classical magnetic moments and superconductivity in quantum one-dimensional conductors: Towards a self-sustained topological Majorana phase. Phys. Rev. Lett. 111, 147202 (2013).
5. M. M. Vazifeh, M. Franz, Self-organized topological state with Majorana fermions. Phys. Rev. Lett. 111, 206802 (2013).
6. F. Pientka, L. I. Glazman, F. von Oppen, Unconventional topological phase transitions in helical Shiba chains. Phys. Rev. B Condens. Matter Mater. Phys. 89, 180505 (2014).
7. J. Li et al., Topological superconductivity induced by ferrometallic metal chains. Phys. Rev. B Condens. Matter Mater. Phys. 90, 235433 (2014).
8. M. H. Christensen, M. Schelter, K. Flensberg, M. B. Andersen, J. Paaske, Spiral magnetic order and topological superconductivity in a chain of magnetic adatoms on a two-dimensional superconductor. Phys. Rev. B 94, 144509 (2016).
9. J. Röntynen, T. Ojanen, Topological superconductivity and high Chern numbers in 2D ferromagnetic Shiba lattices. Phys. Rev. Lett. 114, 236803 (2015).
10. J. Li et al., Two-dimensional chiral topological superconductivity in Shiba lattices. Nat. Commun. 7, 12297 (2016).
11. S. Nadji-Perge et al., Topological material. Observation of Majorana fermions in ferromagnetic atomic chains on a superconductor. Science 346, 602-607 (2014).
12. B. E. Feldman et al., High-resolution studies of the Majorana atomic chain platform. Nat. Phys. 13, 286–291 (2016).
13. S. Jean et al., Distinguishing a Majorana zero mode using spin-resolved measurements. Science 358, 772–776 (2017).
14. M. Ruby et al., End states and subgap structure in proximity-coupled chains of magnetic adatoms. Phys. Rev. Lett. 115, 197204 (2015).
15. R. Pawlik et al., Probing atomic structure and Majorana wavefunctions in mononuclear Fe chains on superconducting Pb surface. npj Quantum Inf. 2, 16035 (2016).
16. J. Li, T. Neupert, B. A. Bernevig, A. Yazdani, Manipulating Majorana zero modes on atomic rings with an external magnetic field. Nat. Commun. 7, 10395 (2016).
17. H. Kim et al., Toward tailoring Majorana bound states in artificially constructed magnetic atom chains on elemental superconductors. Sci. Adv. 4, eaar5251 (2018).
18. S. Misra et al., Design and performance of an ultra-high vacuum scanning tunneling microscope operating at dilution refrigerator temperatures and high magnetic fields. Rev. Sci. Instrum. 84, 103903 (2013).
19. Y. M. Korotov, G. Bihlmayer, E. V. Chulkov, S. Blügel, First-principles investigation of structural and electronic properties of ultrathin Bi films. Phys. Rev. B Condens. Matter Mater. Phys. 77, 045428 (2008).
39. M. I. Salkola, A. V. Balatsky, J. R. Schrieffer, Spectral properties of quasiparticle ex-
citations induced by magnetic moments in superconductors. Phys. Rev. B Condens.
Matter 55, 12648-12661 (1997).
40. K. J. Franke, G. Schulze, J. I. Pascual, Competition of superconducting phenomena and
Kondo screening at the nanoscale. Science 332, 940-944 (2011).
41. N. Hatter, B. W. Heinrich, M. Ruby, J. I. Pascual, K. J. Franke, Magnetic anisotropy in
Shiba bound states across a quantum phase transition. Nat. Commun. 6, 8988 (2015).
42. L. Farinacci et al., Tuning the coupling of an individual magnetic impurity to a su-
perconductor: Quantum phase transition and transport. Phys. Rev. Lett. 121, 196803
(2018).
43. P. Gambardella et al., Giant magnetic anisotropy of single cobalt atoms and nano-
particles. Science 300, 1130–1133 (2003).
44. T. Schuh et al., Magnetic excitations of rare earth atoms and clusters on metallic
surfaces. Nano Lett. 12, 4805-4809 (2012).
45. P. Beck et al., Spin-orbit coupling induced splitting of Yu-Shiba-Rusinov states in
antiferromagnetic dimers. arXiv [Preprint]. https://arxiv.org/abs/2010.04031 (Accessed
8 October 2020).
46. H. Imamura, P. Bruno, Y. Utsumi, Twisted exchange interaction between localized
spins embedded in a one- or two-dimensional electron gas with Rashba spin-orbit
coupling. Phys. Rev. B Condens. Matter Mater. Phys. 69, 121303 (2004).
47. C. F. Hirjibehedin, C. P. Lutz, A. J. Heinrich, Spin coupling in engineered atomic
structures. Science 312, 1021–1024 (2006).
48. A. A. Khajetoorians et al., Atom-by-atom engineering and magnetometry of tailored
nanomagnets. Nat. Phys. 8, 497–503 (2012).