Reversible transition between Yu-Shiba-Rusinov state and Majorana zero mode by magnetic adatom manipulation in an iron-based superconductor

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Defects in a superconductor can generate in-gap bound states, including Yu-Shiba-Rusinov (YSR) states at magnetic impurities and Majorana zero modes (MZMs) inside magnetic vortices. Here we reveal by scanning tunneling microscope that both types of bound states can be generated by magnetic Fe adatoms deposited on the surface of Fe(Te,Se). We observe two types of Fe adatoms: Type-I induces integer quantized in-gap states anchored by a robust zero-bias peak in the tunneling spectrum that shows no Zeeman splitting under an applied magnetic field, consistent with a MZM in the quantum anomalous vortex (QAV); Type-II generates YSR states at nonzero energies that show magnetic field induced Zeeman splitting. More remarkably, we discover a reversible transition between YSR states and MZM by manipulating the coupling between Fe adatoms and surface, and annihilation of two MZMs hosted in a QAV and a field-induced vortex. Our findings pave a new path to manipulate and braid MZMs.

In superconductor, there are two known kinds of localized excitations that appear as bound states inside the pairing energy gap: the Yu-Shiba-Rusinov (YSR) gap (1-9) induced by a magnetic impurity and the Caroli-de-Gennes-Matricon (CdGM) vortex core states (10, 11) generated by a magnetic field in type-II superconductors states. The energy of the YSR states changes with the exchange coupling strength between the magnetic moment and the superconductor. This phenomenon has been observed by continuous tuning of the exchange coupling using scanning tunneling microscope/spectroscopy (STM/S) (12, 13). Furthermore, in the presence of strong Rashba spin-orbit coupling (SOC), 1D and 2D magnetic-impurity lattices on a superconductor can induce topological nontrivial states, which have been reported theoretically and experimentally (14-18).

The superconducting topological surface state (TSS) in the iron-based superconductor (FeSC) FeTe$_{0.55}$Se$_{0.45}$ was proposed (19, 20) and confirmed recently by spin-resolved angle-resolved photoemission spectroscopy (SR-ARPES) (21). Strong evidence of MZMs inside magnetic vortices was observed by STM/S on the same material (22-27). In this new Majorana platform, localized excitations created by magnetic impurities have also been found to be highly unconventional. Robust zero-bias peaks
(ZBPs), sharing spectroscopic features of MZMs, were observed at the interstitial Fe impurities (IFIs) of FeTe$_{0.55}$Se$_{0.45}$ (28) but without applying a magnetic field, which demand new basic understanding of defect excitations in superconductors with strong SOC and superconducting TSS. A recent theoretical proposal (29) attributes the observed ZBP as a MZM bound to a quantum anomalous vortex (QAV) nucleated spontaneously at the magnetic Fe atom in the absence of external magnetic field.

Here we report STM/S experiments performed on Fe adatoms deposited on the surface of FeTe$_{0.55}$Se$_{0.45}$ and reveal the remarkable nature of the localized excitations in the superconducting TSS, including spontaneous vortex excitations with CdGM states and MZM, the vortex-free YSR states, and the reversible transition between them induced by modulating the exchange coupling strength with the STM tip. Moreover, our findings provide strong evidence that iron-based superconductors with a nontrivial topological $\mathbb{Z}_2$ invariant band structure such as FeTe$_{0.55}$Se$_{0.45}$ provide a zero-external-field, manipulatable, quantum materials platform for studying the physics of MZMs and fault-tolerant topological quantum computing.

We deposit Fe atoms on the cleaved (001) surface of a single crystal of FeTe$_{0.55}$Se$_{0.45}$ with the substrate temperature lower than 20 K. The STM images of the surface before and after depositing Fe are shown in Figs. 1A and 1B with the corresponding atomic-resolution STM images displayed in the insets. Before deposition, this region on the surface is clean and free of growth-induced IFI (Fig. 1A). After deposition, scattered Fe adatoms manifest as bright spots (Fig. 1B) with a coverage of ~0.04 %. The STS intensity map, taken at zero energy in the same area of Fig. 1B, shows relatively high density of states at the locations of Fe adatoms (Fig. 1C), consistent with the physical picture that magnetic Fe impurities generate in-gap states.
From the statistics of hundreds of measurements, we identify two main types of in-gap states localized around the Fe adatoms, as shown in Fig. 1D. For type-I Fe adatoms, a sharp ZBP is observed to coexist with other in-gap states, as shown in the typical example (the green curve) in Fig. 1D. In the case of type-II, the YSR states are observed, featuring a pair of in-gap states with particle-hole symmetric peak positions but asymmetric peak weights, as shown in the typical example (the red curve) in Fig. 1D. For comparison, we also show a typical dI/dV spectrum on the clean surface, where a hard superconducting gap has been resolved (the black line in Fig. 1D).

Before presenting more measurements and analysis, we first characterize the deposited Fe adatom impurities. A single Fe adatom is usually located at the high-symmetry sites of the FeTe$_{0.55}$Se$_{0.45}$ lattice, which can be seen in the STM topographic contour images (Supplementary Information (SI) Fig. S2A)\(^{(30)}\). However, unlike the growth-induced IFIs that couple strongly to the lattice atoms and have a distance ~1 Å to the Te/Se plane \((28)\), the height of Fe adatoms varies significantly from 1.1 Å to 2.0 Å (Supplementary Information Fig. S2C)\(^{(30)}\). When an external magnetic field is applied, we also observed MZMs inside the vortices away from the Fe adatoms, confirming the presence of superconducting TSS (Supplementary Information Fig. S1) \(^{(30)}\).

We now turn to the detailed analysis of the type-I Fe adatoms. The Fe adatom in Fig. 2A locates at the C4 symmetric center of four Te/Se atoms (a verification is shown in section I of SI) \(^{(30)}\). The zero-energy dI/dV map in the vicinity of the Fe site (the red circle) in Fig. 2B shows a circular pattern. The center of the zero-energy intensity pattern (highlighted by the white circle) deviates slightly from the Fe site. The waterfall-like plot and the intensity map along the green dashed line in Fig. 2A are displayed in Figs. 2C
and 2D. The ZBP and other in-gap states can be clearly resolved. The region of the ZBP extends about 2.5 nm, indicating the existence of a localized zero-energy state bound to the Fe adatom whose spatial extent is comparable to that of MZM in the vortex core of FeTe\(_{0.55}\)Se\(_{0.45}\) (22). However, this is about one order of magnitude larger than the characteristic length of the ZBP unaccompanied by other in-gap states reported on the IFIs in FeTe\(_{0.55}\)Se\(_{0.45}\) (28). To explore the nature of the discretized in-gap states, we extract several dI/dV spectra from Fig. 2C and show them as a stacking-plot in Fig. 2E. Doing so accounts for the spatial distributions of the in-gap states and the sample inhomogeneity, which has proven to be useful for studying the core states of magnetic field-induced vortices in FeTe\(_{0.55}\)Se\(_{0.45}\) (24). The sequence of discretized bound states localized at the Fe adatom, including the zero-energy state, is clearly visible as the pronounced peaks as labelled L\(_0\), L\(_{±1}\), L\(_{±2}\). The energy values of the conductance peaks at different spatial positions are plotted in Fig. 2F. Surprisingly, the average energies (solid lines) of the discrete quantum states bound to the Fe adatom follow closely a sequence of integer quantization \(E_n = \hbar \omega \mathbf{k} \approx n\epsilon\), \(n = 0, ±1, ±2, \ldots\), where the minigap \(\epsilon \sim 1.0\) meV (more cases in section II of SI) (30). It is remarkable that integer quantized vortex core states have been observed recently (24) in the magnetic field-induced vortices that host the MZM (22, 23). Such an integer sequence is the hallmark of the CdGM vortex states of the superconducting TSS (24), i.e. a topological vortex (24). Our observations thus provide strong evidence that topological defect, vortex-like excitations such as the QAVs nucleate spontaneously at type-I Fe adatoms and the ZBP corresponds to a MZM.

We observe that the emergence of ZBP is sensitive to the atomic surrounding of the Fe adatom. To explore this effect, we manipulate an Fe adatom to different locations (section III of SI) (30). We first use the STM tip to move the Fe adatom away from the C4 symmetric center of four Te/Se atoms (Supplementary Information Fig. S4A)(30), and observe that the ZBP disappears and a pair of in-gap states at nonzero
energy emerge. We then anneal the sample to 15 K and perform the measurement again at 0.4 K. The Fe adatom diffuses back to its original high-symmetry site and the ZBP reappears (Supplementary Information Fig. S4B)(30). The zero-energy dI/dV map recovers the spatial distribution of the zero-mode from the one before manipulation as shown in Fig. 2B. Our controllable manipulation of the Fe adatom indicates that the high-symmetry site is an important prerequisite for the induced ZBP, which agrees well with the proposed theory of QAV(29).

The temperature-dependence of the ZBP on the Fe adatom is very similar to that of the MZM in a topological vortex (22). As shown in Fig. 2E, the ZBP intensity decreases with increasing temperature, and becomes almost invisible at 4.2 K. The magnetic field dependence of the ZBP is also very similar to that of the MZM. As shown in Fig. 2F, there is no splitting of the ZBP even at 8 T. We note that here there is no field-induced vortices pinned at the Fe adatoms in the region when applying the magnetic field.

We then investigate the in-gap states of type-II Fe adatoms where the tunneling conductance exhibits a pair of YSR states without the ZBP, as displayed in Figs. 3B and 3C. With increasing magnetic field, the YSR states shift to higher energies gradually (Fig. 3D). The energy positions of the YSR states under different magnetic fields can be fitted well by a linear function with the g-factor of about 0.88 (Fig. 3E). We also observe YSR states located very close to the zero energy also split under the magnetic field (section IV of SI) (30), which is distinct from the robust ZBP on the type-I Fe adatoms. We note that the g-factor obtained here for Fe adatoms on FeTe0.55Se0.45 is smaller by about a factor of two than the one associated with Fe-vacancy-induced bound states on the surface of KFe2Se2 (31).
It is known that the exchange coupling between a magnetic impurity and a substrate can be tuned by varying the tip-sample distance (12, 13). In STM/S, the tunnel coupling characterized by the tunnel-barrier conductance, \( G_N \equiv I_t/V_s \), changes with the tip-sample distance, where \( I_t \) is the tunneling current and \( V_s \) is the bias voltage. We first perform the STM measurement as a function of \( G_N \) on type-II Fe adatoms. For the example shown in section V of SI(30), the YSR states showing electron-hole weight asymmetry are located close to the zero energy when the tip is relatively far away. When the STM tip approaches closer to the Fe adatom, the stronger YSR peak at the negative energy shifts to the positive energy and finally merges into the continuum above the superconducting gap (Supplementary Information Fig. S6)(30). This phenomenon is attributed to the fact that the approaching tip at the Fe adatom site can increase the exchange coupling between the magnetic impurity and the substrate (12, 13).

We next carry out the same measurements on type-I Fe adatoms. The normalized STM intensity plots as a function of the tunneling conductance are shown in Figs. 4A and 4B, as the tip approaches the Fe adatom under 0 T and 6 T, respectively. The ZBP at type-I Fe adatoms is remarkably robust and does not shift or split with increasing \( G_N \) up to a field as high as 6 T.

What is surprising is that quite frequently, when the STM tip approaches some type-II Fe adatoms, the YSR states shift with increasing \( G_N \), and then coalesce into a robust ZBP (Figs. 4C and 4D). This behavior is reversible for withdrawing the tip (section VI of SI) (30). The same reversible YSR-ZBP transition tends to occur for the Fe adatoms located over patched regions. As we move such an Fe adatom to another high-symmetry site 1 nm away from the original place (Figs. 4G and 4H), the coalescence of the YSR states into a ZBP is reproduced (Fig. 4I). These observations suggest that type-II Fe adatoms exhibiting a transition from YSR states to ZBP are located in the topological region, whereas the other type-II Fe
adatoms shown in Supplementary Information Fig. S6 (30) may be located in a non-topological region (24).

The emergence of the ZBP out of the YSR states with approaching the STM tip is different from the quantum phase transition between the screened- and free-spin ground states (12, 32). In Fig. 4C and Supplementary Information Fig. S6 (30), the peak highlighted by the red arrow crosses the zero energy in zero external magnetic field quickly and splits into a pair of peaks. Note that the YSR peaks in a magnetic field of 6 T do not cross the zero energy, likely due to the Zeeman splitting of the YSR states. The emergent robust ZBP does not split or shift in 0 T and 6 T when the exchange coupling changes, indicating a phase transition from YSR states to MZM, fully consistent with the theoretical prediction that a large exchange coupling between a magnetic Fe impurity atom located at the high-symmetry site can induce a QAV which hosts a MZM in the topological region (29).

One of the hallmarks of the MZM is the coupling between two MZMs leads to annihilation of the zero modes and creation of a pair of fermionic states at nonzero energies. This fusion process, critical for topological quantum computing, usually requires two overlapping magnetic field induced vortices. Our system allows a new possibility: i.e. the fusion between a QAV and a field-induced vortex with MZMs, as demonstrated in Fig. 5. The zero-energy dI/dV map (Fig. 5A) and intensity plot (Fig. 5B) measured at -0.2 T show sharp ZBPs across a type-I adatom. At this weak field, a field-induced vortex is observed to creep into view and locate very close to the Fe site and the zero-energy pattern is significantly enlarged (Fig. 5C). Remarkably, the ZBP splits into two peaks separated by an energy spacing of 0.25 meV (Fig. 5D). When the field-induced vortex creeps away, the zero-energy map recovers (Fig. 5E) and the ZBP reemerges (Fig. 5F). For better comparison, we extract three dI/dV spectra respectively from the three
conditions and displayed in Fig. 5G. We repeat the measurements on the same adatom at the higher magnetic field of -3 T. The splitting of the ZBP is again observed, with a larger energy spacing of 0.35 meV (Fig. 5I), possible due to the shorter distance between the two MZMs, as indicated by the smaller ring feature in the zero-energy map (Figs. 5C and 5H).

Our results suggest that the robust ZBP is likely attributed to the MZM in the QAV nucleated at the magnetic Fe adatom by the exchange coupling between the local moment and the spin-momentum-locked superconducting TSS. Indeed, an in-plane component of the Fe adatom moment can cause the center of the zero-mode associated with the ZBP to shift away from the Fe adatom site, i.e. the center of the QAV(33). This is consistent with our observation (Fig. 2B). The theoretical proposal of the QAV also predicts a transition from the YSR state to the MZM state depending on the coupling strength of the magnetic moment and the TSS, which is also observed here by pushing the STM tip closer to an Fe adatom. We note that the MZM and QAV are not affected by the applying a magnetic field as long as there is no field-induced vortex nearby. More significantly, the MZM will split once a field-induced vortex appears in its close vicinity. Our findings suggest that magnetic adatoms coupled to the superconducting TSS offer a platform with more flexibility for braiding and fusion of MZMs which are critical to topological quantum computation.
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Fig. 1. Identification of deposited Fe adatoms on FeTe$_{0.55}$Se$_{0.45}$ surface. A, STM image before depositing Fe atoms, showing a clean surface. Inset is the corresponding atomic resolution image (4 nm x 4 nm). B, STM image after depositing Fe atoms. The bright dots are Fe adatoms scattered on the surface of FeTe$_{0.55}$Se$_{0.45}$ with a coverage of 0.04 %. Inset is the atomic resolution image of a single Fe adatom (4 nm x 4 nm) locating at the high-symmetry site. C, dI/dV map of (B) at the zero energy. The high conductance areas and the Fe adatoms are in good spatial correspondence, as highlighted by red dashed circles. D, dI/dV spectra showing zero bias peak (the green curve), YSR states (the red curve), and superconducting gap (the black curve). Settings: A, B and C, $V_s = -10$ mV, $I_t = 100$ pA. D, $V_s = -10$ mV, $I_t = 200$ pA.
Fig. 2. Spatial, temperature and magnetic field dependence of ZBP on a type-I Fe adatom. A, Atomic-resolution image of a single type-I Fe adatom. B, dI/dV map of the same area of (A) at 0 V, showing a round-shaped pattern. The red circle outlines the Fe site in (A). The white circle indicates the center of the pattern. C and D, A line-cut STS and corresponding intensity plot acquired along the green dashed arrow in (A). The decay length of ZBP is about 2.5 nm. E, Stacking plot of several dI/dV spectra from (C) (pointed by black arrows in (C)). The energies of impurity stats are labelled L₀, L₋₁, L₋₂. F, The energy values of the impurity states at different spatial positions. Error bars are the FWHM fitted with a Gaussian function. The energy values of the solid lines are calculated as the average energy of each level. F, Dependence of ZBP on temperature at the white circle in (B). The intensity of ZBP decreases with increasing temperature and becomes indistinguishable at 4.2 K. G, Dependence of ZBP on magnetic field at 0.4 K at the white circle in (B). The ZBP is robust without splitting. Settings: A and B, Vₛ = -10 mV, Iᵣ = 100 pA. C, D, E, and F, Vₛ = -10 mV, Iᵣ = 200 pA.
**Fig. 3. Zeeman splitting of a pair of YSR states.** A, Atomic resolution of a single type-II Fe atom locating at the high-symmetry site. B and C, A line-cut STS and corresponding intensity plot acquired along the green dashed arrow in (A). The YSR states are highlighted by dashed lines. D, The dependence of YSR states (red dashed lines) on external magnetic field, showing Zeeman splitting. E, A linear fit of the energy positions of YSR states. The fitted $g$-factor is about 0.87. Settings: A, $V_s = -10$ mV, $I_t = 100$ pA. C, D, and E, $V_s = -10$ mV, $I_t = 200$ pA.
Fig. 4. Transition between robust ZBP and vortex-free YSR state induced by modulating the exchange coupling strength with the STM tip. A and B, Intensity plots of $dI/dV$ spectra showing tunneling barrier evolution of a robust ZBP at 0 T (A) and 6 T (B). There is no obvious change of the spectra with approaching the tip. C and D, Intensity plots of $dI/dV$ spectra showing tunneling barrier evolution of a vortex-free YSR state at 0 T (C) and 6 T (D). Vortex-free YSR states evolve into a robust ZBP with approaching the tip. E and F, Schematic showing two cases in the phase diagram of Fe adatom induced impurity states of FeTe$_{0.55}$Se$_{0.45}$ where the initial exchange coupling is different: robust ZBP with the increasing $J_{ex}$ (E) and evolvement from YSR states into a ZBP with the increasing $J_{ex}$ (F). G and H, STM images showing the initial position (red dotted circle) and final position (green dotted circle) of Fe adatom during the STM manipulation. The intensity plots of $dI/dV$ spectra in (C) correspond to the adatom in (G). I, Intensity plots of $dI/dV$ spectra at the Fe adatom corresponding to (H). Settings: A, B, C, D and I, $V_s = -10$ mV. G and H, $V_s = -10$ mV, $I_t = 100$ pA.
Fig. 5 Interaction between an Fe adatom and a magnetic field-induced vortex. A and B, dI/dV map (A) and line-cut along the red dashed arrow (B) of a type-I Fe adatom without a vortex nearby at -0.2 T, showing a robust ZBP. C and D, dI/dV map (C) and line-cut along the red dashed arrow of the same Fe adatom with a magnetic field-induced vortex nearby at Fe site (D). The local maximum intensity is highlighted by the dashed black circle in (C). The ZBP disappears and two in-gap states with the energy level spacing of 0.25 meV emerge. E and F, dI/dV map (E) and line-cut along the red dashed arrow (F) of the same Fe adatom after the vortex creeping away. The ZBP appears again. G. Three typical dI/dV spectra obtained on the Fe adatom corresponding to the case of (A), (C) and (E), respectively. H, dI/dV map of the same Fe adatom with another field-induced vortex nearby at -3 T. The local maximum intensity is highlighted by dashed black circle. I, dI/dV spectra obtained on the Fe adatom after the field-induced vortex resides nearby at – 3 T corresponding to (H), showing that ZBP disappears and two in-gap states with the energy level spacing of 0.35 meV emerge. Settings: A, C, E and H: V_s = -10 mV, I_t = 100 pA. B, D, F, G and I: dI/dV spectra, V_s = -10 mV, I_t = 200 pA.
Supplementary Materials for

Reversible transition between Yu-Shiba-Rusinov state and Majorana zero mode by magnetic adatom manipulation in an iron-based superconductor

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This PDF file includes:

Supplementary Text

Figs. S1 to S7

References

Materials and methods

High-quality single crystals of FeTe$_{0.55}$Se$_{0.45}$ with Tc of 14.5 K are grown using the self-flux method (22). The samples are cleaved in situ and immediately transferred into a STM head. The Fe adatoms are deposited from a high-purity (99.95%) single crystal Fe rod acquired from ESPI METALS to the surface of FeTe$_{0.55}$Se$_{0.45}$ at a temperature below 20 K. Before Fe deposition, we scan the surface of FeTe$_{0.55}$Se$_{0.45}$ to ensure that there were no visible interstitial Fe impurities (IFI). The STM experiments are performed in an ultrahigh vacuum (1 $\times$ 10$^{-11}$ mbar) LT-STM systems (USM-1300s-$^3$He), which can apply a perpendicular magnetic field up to 11 T. STM images are acquired in the constant-current mode with a tungsten tip. The energy resolution calibrated on a clean Pb (111) surface is about 0.27 meV. The voltage offset calibration is followed by a standard method of overlapping points of I-V curves. Differential conductance (dI/dV) spectra are acquired by a standard lock-in amplifier at a frequency of 973.1 Hz, under modulation voltage $V_{mod}$ = 0.1 mV. Low temperature of 0.4 K is achieved by a single-shot $^3$He cryostat.

I. Characterizations of the sample and Fe adatom

Previous measurements on vortices under an external magnetic field in FeTe$_{0.55}$Se$_{0.45}$ have indicated that there are two types of regions, topological trivial and topological nontrivial regions, on the surface (24). We also detect a MZM in a vortex with an external magnetic field displayed in Fig. S1, which demonstrates the sample has topological nontrivial regions. Then we focus on a single Fe adatom, as shown in Fig. S2. In the atomic-resolution STM image, we highlight the crystal lattice by dashed white
lines, and it can be seen clearly that the Fe adatom is located at the high-symmetry site. Away from the Fe adatom, the higher sites are Te atoms sites and the lower ones are Se atoms. The line-profile of the Fe adatom yields the height of 1.61 Å and the peak width at half maximum of 1.5 nm (Fig. S2B). From the statistics of hundreds of measurements, we find that the height of deposited Fe adatoms varies from 1.1 Å to 2 Å with an average value of 1.56 Å which are higher than the typical height (~1 Å) of interstitial Fe impurities in FeTe$_{0.55}$Se$_{0.45}$ (Fig. S2C).

II. Integer quantized energy level spacing of in-gap states

We analyze three cases with sharp ZBPs and find that there are several pairs of in-gap states, which do not shift at different spatial positions (Fig. S3). By examining the spectra carefully, we find that the level spacing of these in-gap states usually has a near-integer quantized energy spacing. The energy positions and ratios are displayed in Figs. S3D-F. The similar phenomenon has been observed in the magnetic vortex of FeTe$_{0.55}$Se$_{0.45}$ (24), where the integer-spaced level is attributed to the additional $\pi$ phase from the topological surface states. Compared with the previous result (24), the ZBP coexisted with integer energy level spacing in-gap states at the Fe adatom may likely emerge from the topological surface states.

III. Manipulation of single Fe adatom

To study the role of the high-symmetry site in our system, we manipulate the single Fe adatom characterized in Fig. 2 of the main text. We first move the Fe adatom away from the center of four Te/Se atoms (Fig. S4A). Then we measure the dI/dV map of the zero energy and the dI/dV spectra cross the Fe site, as shown in Fig. S4A. The pattern in the dI/dV map changes significantly: the ZBP disappears and a pair of non-zero in-gap states emerge. After that, we heat the sample to 15 K and the Fe atom diffuses back to the original high-symmetry site (Fig. S4B). We then cool the sample back to 0.4 K and perform the measurement again (Fig. S4B). The dI/dV map at the zero energy recovers back to the density of states of the one before the manipulation (Fig. 2B in the main text). We finally remove the Fe adatom by using the STM tip (Fig. S4C). The measured spectra show a hard superconducting gap in the same area, which
demonstrates that the impurity states originate from the Fe adatom. The results indicate that the high-symmetry site is necessary for the induced ZBP.

IV. Near-zero YSR states with Zeeman splitting

We show an example of the YSR states located very close to the zero energy (the near-zero YSR states) with Zeeman splitting in Fig. S5. The spectra along the red line in Fig. S5A show the near-zero YSR states without the magnetic field. When the magnetic field is applied, the near-zero YSR states split linearly into two symmetric YSR states with g-factor about 0.5, which indicates that one can distinguish the near-zero YSR states from the robust ZBP by applying the magnetic field. This near-zero YSR states with Zeeman splitting is about 6.4% in hundreds of measured cases.

V. Approaching the STM tip at an Fe adatom with YSR states

The method of varying tip-sample distance has been used to change the coupling between the adatoms and the surface. In recent papers (12, 13), the exchange coupling between a magnetic impurity and a BCS superconductor (Pb) is tuned and the quantum phase transition of YSR states by approaching the STM tip at the impurity sites is realized. We first check the effectiveness of this method in our system by approaching the tip at the Fe adatom site shown in Fig. S6. Before we approach the tip, the particle-hole symmetric YSR states have a larger weight on the negative energy side. Then with the tunnel-barrier conductance $G_N$ increasing the YSR states cross the zero energy and shift to the gap edge with a larger weight on the positive energy side, which means that the exchange coupling between the Fe adatom and the superconducting surface can increase with the increasing of $G_N$. We note that the z-offset decreases smoothly with $G_N$ in an exponential way, indicating that there is no change of the tip and the Fe atoms during the whole approaching process.

We note that there are two types of behavior with the increase of $G_N$. One behaves in such way that the larger weight YSR state shift from negative energy to positive energy as shown in Fig. S6D. Another behaves inversely, which means that the coupling strength may increase or decrease when approaching the tip.
VI. Reversibility of changing exchange coupling

A set of reversibility data of tuning the exchange coupling between an Fe adatom and surface of FeTe\textsubscript{0.55}Se\textsubscript{0.45} are shown in Fig. S7, which is measured at the same Fe adatom as the one in Figs. 4C and 4D of the main text. We find that behaviors of energy shift of the in-gap states are reversible during approaching (Fig. S7C) and withdrawing (Fig. S7D) the tip.
Fig. S1 MZM in a vortex detected on FeTe$_{0.55}$Se$_{0.45}$. A, Atomic-resolution STM image of the area in A. No adatom can be seen. B, $\text{dI/dV}$ map of a vortex with an MZM at 0 meV. The vortex is isotropic. The vortex center is highlighted by the red circle in (A) and (B). C, Line-cut of along the red dashed arrow in (A), showing a sharp ZBP that does not split or shift with the changes of spatial position which consistent with previous observation of MZM. Settings: A and B, $V_s = -10$ mV, $I_t = 100$ pA. C, $V_s = -10$ mV, $I_t = 200$ pA.
Fig. S2 Site identification of deposited single Fe adatoms on FeTe$_{0.58}$Se$_{0.45}$ surface. A, High-resolution STM image of a single Fe adatom, showing the Fe adatom located at the high symmetric site. The white lines highlight the crystal lattice. B, Line-profile along the light blue line in (A), showing that the single Fe adatom is 1.61 Å in height and 1.5 nm in width (defined as the peak width at half maximum). C, Statistic of the height of hundreds of Fe adatom. The height varies from 1.1 Å to 2.0 Å. Settings: A and B, $V_s = -10$ mV, $I_t = 100$ pA.
**Fig. S3** Integer quantized in-gap states on type-I Fe adatoms. A-C Waterfall plot and color map measured at three Fe adatoms, showing a sharp ZBP coexisting with several pair of discrete in-gap states. D-F, Lists of the energy positions of in-gap states corresponding to (A)-(C), respectively, showing a near-integer quantized energy level spacing. Settings: **A, B** and **C**, $V_s= -10$ mV, $I= 200$ pA. Fig. S3A is reproduced from Figs. 2C and 2D in the main text.
**Fig. S4 Manipulation of the Fe adatom shown in Fig. 2 of main text.**

A, Upper panel: STM image showing that the Fe adatom has been moved from the high symmetric site to a corner. Middle panel: dI/dV map in the same region. Bottom panel: dI/dV line-cut along the red dashed arrow showing that the ZBP disappears and other in-gap states emerge. B, Upper panel: STM image showing that the Fe adatom moves 2 nm...
back to the center of four Te adatoms by *in situ* annealing the sample to 15 K and cooling back to 0.4 K. Middle panel: dI/dV map in the same region. Bottom panel: dI/dV line-cut along the red dashed arrow showing that the ZBP appears again. C, Upper panel: STM image showing that the Fe adatom is moved away by the tip. Both dI/dV map (middle) and line-cut (bottom) show that there is no impurity state. Settings: The first row and the second row in A-C: $V_s = -10$ mV, $I_t = 100$ pA. The third row in A-C: $V_s = -10$ mV, $I_t = 200$ pA.
Fig. S5 Near-zero YSR states with Zeeman effect. A, Atomic-resolution STM image of a type-II Fe adatom. B, dI/dV map at zero energy of the same area in (A). C, Spectra along the red dashed arrow in (A). D, Color map of (C). E, Spectra at Fe adatom site under different magnetic field showing Zeeman splitting of the YSR states. The green dashed lines highlight the Zeeman splitting of YSR peaks. Settings: A and B, V_s = -10 mV, I_t = 100 pA. C, D and E, V_s = -10 mV, I_t = 200 pA.
Fig. S6 Approaching the tip at Fe adatom with YSR states. A, Atomic-resolution STM image of the Fe adatom. B, Tip-sample distance offset v.s tunnel-barrier conductance during the tip approaching. C, Normalized dI/dV spectra under different tunnel-barrier conductance without magnetic field, showing the shift of YSR states. D, Color map of normalized dI/dV spectra in (C) showing the shift of YSR states.

Settings: A, V̄ = -10 mV, Ī = 100 pA. C and D, V̄ = -10 mV.
Fig. S7 Reversibility of changing exchange coupling at the same Fe adatom shown in Figs. 4C and 4D of the main text. A, Atomic-resolution STM image of the type-II Fe adatom. B, Tip-sample distance offset v.s tunnel-barrier conductance during the tip approaching. C, Color map of normalized spectra when
approaching the tip. D. Color map of normalized spectra when withdrawing the tip, showing the similar transition with the one in (C). Settings: A, $V_s = -10$ mV, $I_t = 100$ pA. C and D, $V_s = -10$ mV.
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