# Observation of a robust zero-energy bound state in iron-based superconductor Fe(Te,Se)

Materials and Methods:

All the crystals, with nominal composition $FeTe_{0.5}Se_{0.5}$, used in this study were grown using a self-flux method. A mixture of appropriate amount of iron (99.998 wt. %), tellurium (99.999 wt. %), and selenium (99.999 wt. %) powders was ground, pressed, and sealed in an evacuated double wall quartz ampoule after purging repeatedly with high purity Ar gas to ensure an oxygen free environment. The ampoule was then heated in a vertical tube furnace with the following procedure: Slowly heating over the temperature range of 400^oC to 600^oC, holding at 1100^oC for 36 h, cooling in a rate of $1^oC/h$ to 500^oC, then quenching it into ice water. The phase purity of the crystals was characterized using a Rigaku Geigerflex x-ray powder diffractometer on the powder of grounded crystals. Inductively coupled plasma mass spectrometry (ICP) measurement of these samples gave Te:Se ratio = 0.57:0.43, which might be due to the reaction of Se with quartz tube during sample growth. The content of interstitial Fe was tuned by post annealing process in evacuated quartz tubes. For the longest annealed sample, the DC magnetic susceptibility $4\pi\chi(T)$, measured using a Quantum Design Magnetic Properties Measurement System, shows a sharp transition at onset of 14.5 K with transition width of 0.3 K and 1 K under zero-field cooled and field cooled conditions, respectively (Fig. S1a). The screening volume fraction is about 100% and Meissner fraction is as high as 53% after demagnetization factor correction, indicating that high quality crystals with bulk superconductivity were used in our STM studies.

The samples used in the experiments were cleaved in cryogenic ultra-high vacuum at 4.2 K and immediately inserted into the STM head before imaging with atomic resolution. STS spectra were recorded using a standard lock-in technique, with set point of V = -10mV, I = 0.3nA. The modulation energy V_{mod} = 0.1mV, except for that in Fig. 4b where V_{mod} = 0.06meV was used. The energy step was V_{step} = 0.1mV, except that in for Fig. 4b where V_{step} = 0.02mV.
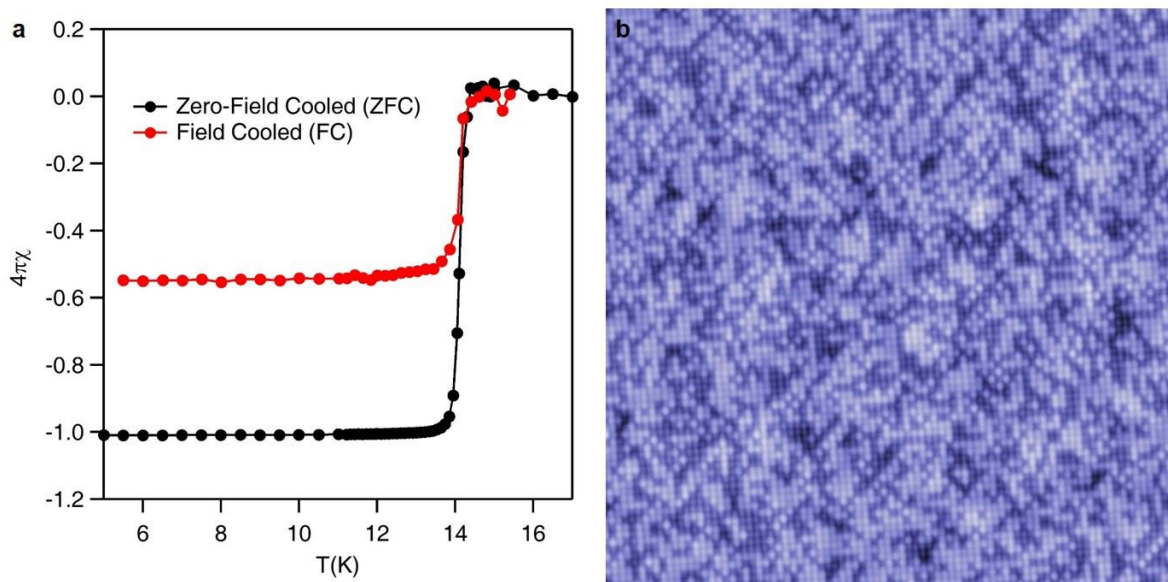
Figure. S1. Superconductivity property of the pristine Fe(Te,Se) sample. **a**, DC volume susceptibility of Fe(Te, Se) measured in 1 Oe magnetic field. Black and red solid circle represent zero-field cooled and field cooled susceptibility, respectively. **b**, STM topography of the Fe(Te, Se) sample showing no interstitial Fe in a large area of 300×300Å. The brighter spots represent Te atoms and the less bright spots represent Se atoms[26]. This assignment also agrees with the ratio of Te:Se given by the ICP measurement of this sample mentioned above.

Further data analysis:

Figure. S2a presents the full data of the line-cut spectra in Fig. 3. The integrated low energy (-3meV to 3meV) spectra weight is almost invariant for all the spectra along the line-cut as shown in Fig. S2b.
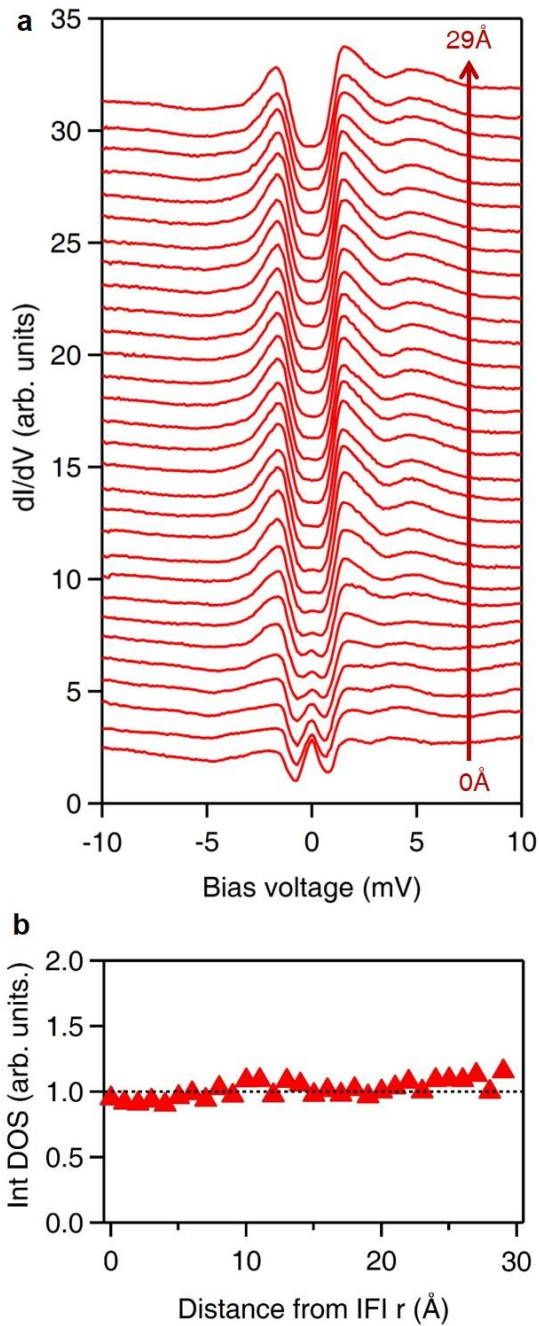
**Figure. S2.** Further analysis of the line-cut spectra. **a**, Line-cut spectra along the line in Fig. 3a (V = -10mV, I = 0.3nA). The spectrums are offset for clarity. **b**, Integrated density of states (Int DOS) from -3meV to 3meV for the line-cut spectra.

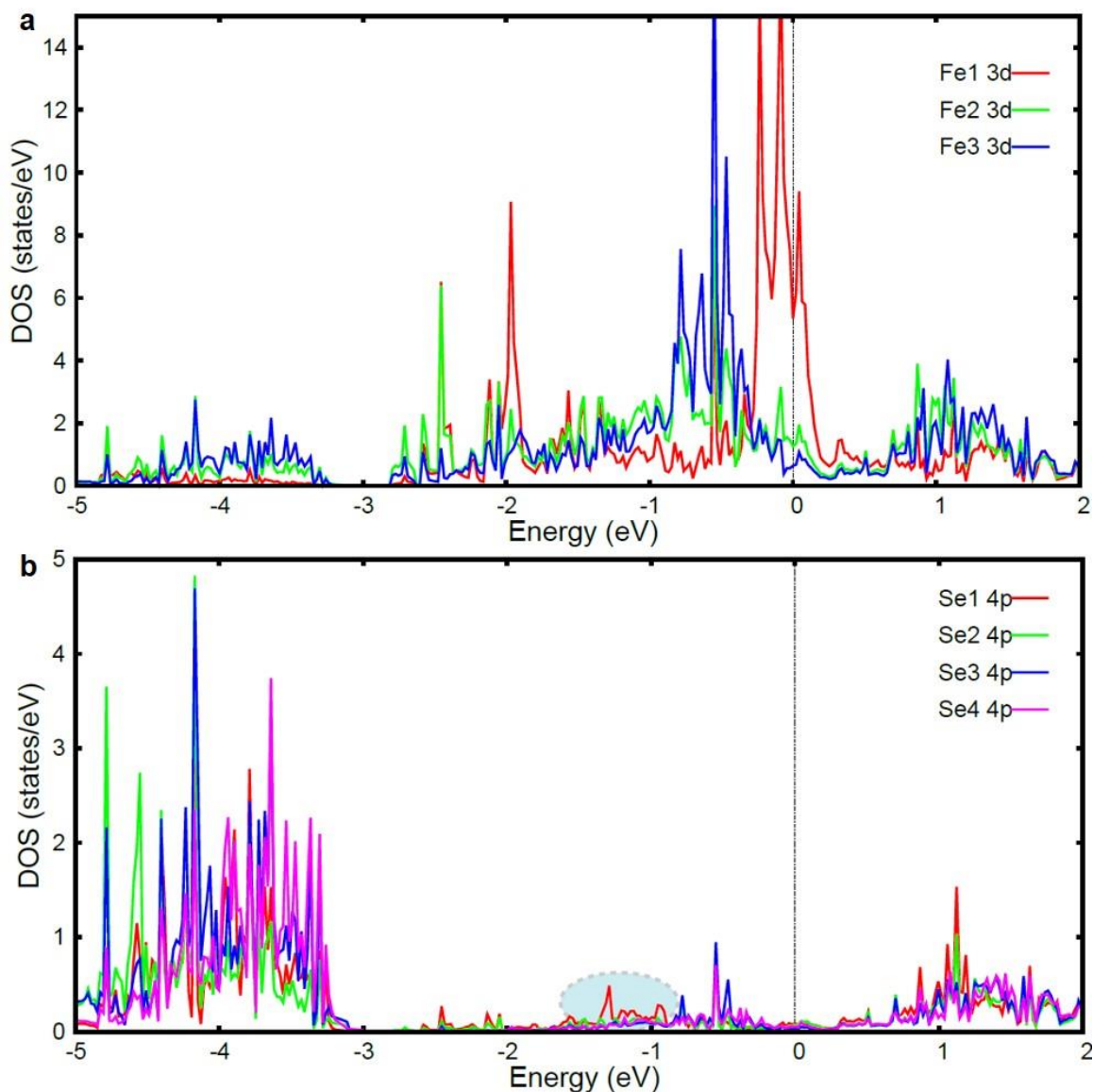## DFT calculation for interstitial Fe atom and discussion

Our DFT calculations employ the projector augmented wave (PAW) method encoded in Vienna ab initio simulation package (VASP), and the local density approximation (LDA) for the exchange correlation functional is used. Throughout this work, the cut-off energy of 400 eV is taken for expanding the wave functions into plane-wave basis. In the calculation, the Brillouin-zone is sampled in the k space within Monkhorst-Pack scheme. The number of these k points are (5 × 5 × 1) in the surface calculation. We model a surface using 3 × 3 × 1 supercell containing two FeSe layers plus a vacuum layer of 15 Å. The bottom FeSe layer is frozen in the relaxation. The experimental lattice constants are adopted through the calculation. Forces are minimized to less than 0.02 eV/Å for slab calculation. The model in our calculation is shown in Fig. S3a and S3b. The bond lengths of Fe1-Se1 and Fe1-Se2 are 2.79 and 2.60 Å, respectively. The tiny difference means that Fe1 can couple with both Se1 and Se2. To illustrate this point, we plot the projected density of states of these atoms in Fig. S4a and S4b. The p orbital of Se2 couples strongly with the d orbital of Fe1 in the range from -5.0 eV to -3.0 eV. In contrast with Se2, there is an enhanced peak at -1.2 eV in the DOS of Se1, which is contributed by the hybridization of d_z^2 of Fe1 and p_z of Se1. The simulated STM images are shown in Fig. S3c, which are in agreement with that in experiment as shown

in Fig. 2. We also calculate the charge density difference and the result is shown in Fig. S5. There is some electron depletion near both up and down Se atoms, which clearly indicates that interstitial Fe forms covalent bonds with both of them. Especially, the depleted states are redistributed and mixed in the red area. This strong coupling between the IFI and both up and down Se layers is very unique. According to a recent theoretical proposal of odd parity spin singlet pairing symmetry[22], which predicts a spatial sign reversal of the up and down Se layers, this unique coupling of IFI will contribute to the robustness of the ZBS.
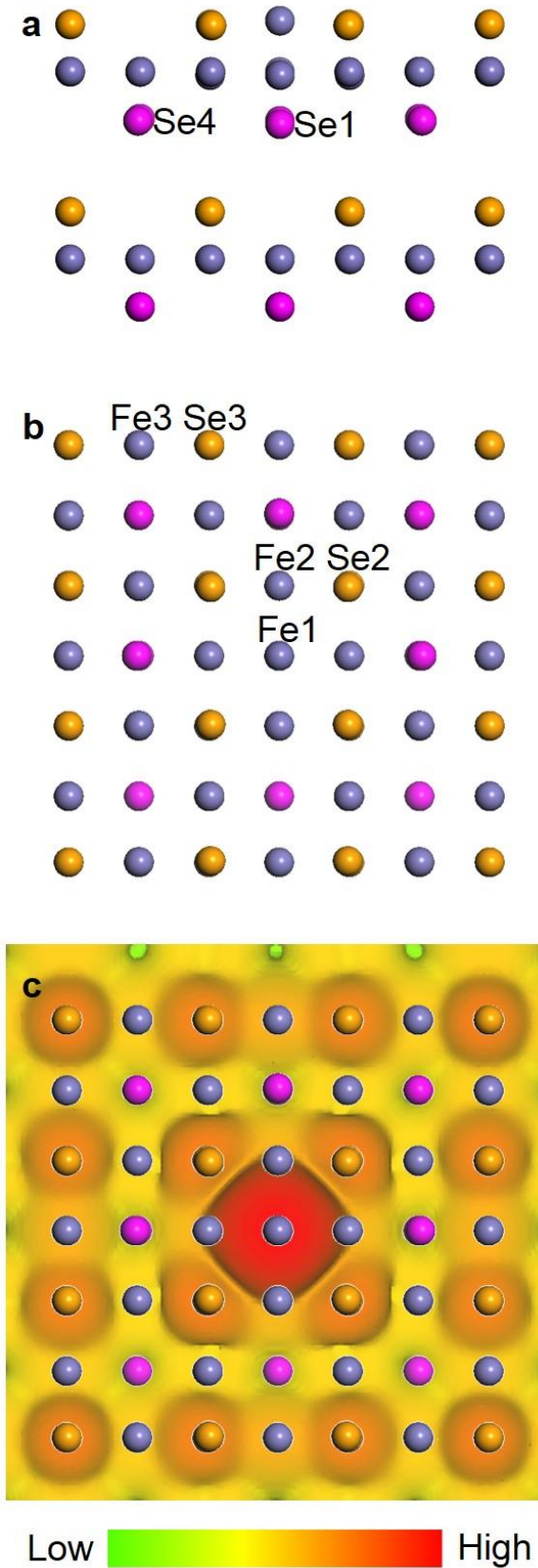
Figure. S3. DFT calculation on interstitial Fe in FeSe, Geometric structure of $Fe_{1+x}Se$, side

view **a** and top view **b**, where interstitial Fe is at surface Se layer. **c**, Simulated STM image.

Figure. S4. DFT calculation of projected density of states (DOS) of special Fe and Se atoms in $Fe_{1+x}Se$. **a**, **b** DOS calculation for special Fe and Se atoms as marked in Fig. S3a and S3b. The shaded area marks the strong coupling between the interstitial Fe atom the Se atom in the sub layer.
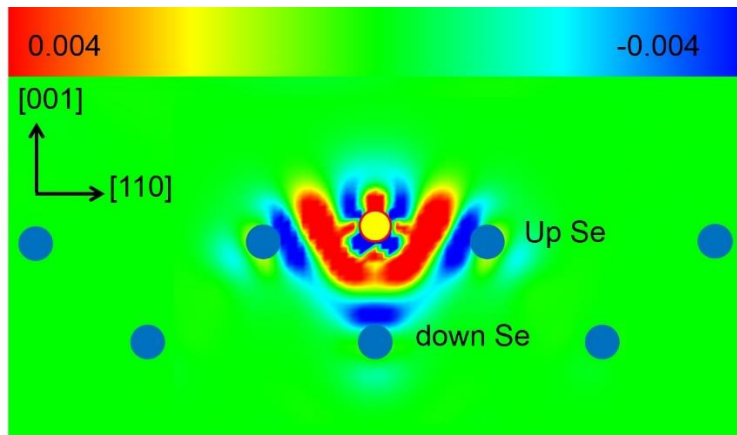
Figure. S5. DFT calculated charge density difference plot in units of e/(a.u.^{3}).

Reference:

1. Hoffman, Jennifer E. Spectroscopic STM insights into Fe-based superconductors. *Rep. Prog. Phys.* **74**, 124513 (2011).