

Supplementary Information

I. CRYSTAL CHARACTERIZATION

The Te composition x of each $\text{FeSe}_{1-x}\text{Te}_x$ single crystal was determined by the following method. The $x \sim 0.35$ crystals, which were synthesized by the chemical vapor transport (CVT) method (see Method), were determined from the value of c -axis length obtained from single-crystal x-ray diffraction (RIGAKU XtaLAB P200 diffractometer with $\text{Mo-K}\alpha$ radiation) at room temperature [S1]. From our evaluation, the variation in Te composition from 0.35 was about $\pm \sim 0.05$. The homogeneity and compositions of high-Te doped samples synthesized by the Bridgman method (see Method) were evaluated using energy-dispersive x-ray (EDX) spectroscopy (RIGAKU MicroMax-007 HF). As shown in Fig.S1, we have no evidence of significant distributions of each element in our single crystals. TableS1 summarizes the composition ratios of each element in each Bridgman-grown $\text{FeSe}_{1-x}\text{Te}_x$ obtained from EDX. We used 4 samples for nominal compositions of 0.6, 0.7, 0.8 and 3 samples for 0.9, and we took the data at 4 different positions for each sample. For the nominal Te compositions of 0.6, 0.7, 0.8, and 0.9 crystals, the averaged actual Te composition ratios x obtained are 0.64(2), 0.75(1), 0.83(1), and 0.94(1), respectively. Furthermore, the EDX results confirmed that the iron (Fe) element compositions were very close to (or slightly less than) 1 in all cases, which indicates that there were no excess Fe elements. Recent reports have shown that excess Fe elements have a significant effect on the properties of this system, but that slight Fe deficiencies have no effect [S2].

II. RESISTIVITY, MAGNETIZATION, AND HEAT CAPACITY MEASUREMENTS

The temperature dependence of resistivity for $\text{FeSe}_{1-x}\text{Te}_x$ is shown in Fig.S2a. We observe the clear superconducting transition at all compositions and the nematic transition at $T_s \sim 45$ K for the $x \sim 0.35$ sample, consistent with the previous report [S1]. As shown in Figs.S2b, c, the superconducting transitions are also observed in the specific heat and magnetization data. The $x = 0.64$ sample has almost 100% superconducting volume fraction and no residual density of states, while for $x \geq 0.75$ samples, smaller volume fractions and

finite residual density of states were observed. Our results on the temperature dependence of resistivity and magnetization show that $x \sim 0.35$, $x = 0.64$, and 0.75 samples show a monotonic decrease with decreasing temperature, indicating no noticeable effects from excess iron impurities. However, the $x = 0.83$ sample has an increase in resistivity and magnetization at low temperatures, and thus we cannot exclude the possibility that a small amount of Fe impurities remain for this composition [S3, S4]. For the $x = 0.94$ sample, a pronounced antiferromagnetic transition was observed at $T_N \sim 45$ K from the magnetization result (Fig. S2d).

III. μ SR MEASUREMENTS AND ANALYSIS

A. Measurement set up

Our μ SR measurements were performed at the M20D beamline using the LAMPF spectrometer and a He gas flow cryostat. The lowest temperature is about 2 K. This setup offers the advantage of minimal background contribution, which is essential for observing the tiny magnetic fields in the samples for the detection of time-reversal symmetry breaking (TRSB) state in the superconductor. A schematic overview of our measurement arrangement is shown in Fig. S3. Our samples were mounted in wrapped mylar tape, which does not stop muons and has no contribution to the relaxation and background signals, with the c -axis parallel to the beam incident direction. The incident muon energy is 4.1 MeV, and the average stopping depth for FeSe-based materials is estimated as $\sim 320 \mu\text{m}$, ensuring that we can get information on the bulk states. In our experiments, we utilized two configurations: the non-spin-rotated (NSR) mode (Fig. S3a), where the muon spin is perpendicular to the ab -plane of the sample ($P_\mu \perp ab (\parallel c)$), and the spin-rotated (SR) mode (Fig. S3b), where it aligns parallel to the ab -plane ($P_\mu \parallel ab (\perp c)$). Muons stop inside the sample and cause precession due to magnetic field components not parallel to the muon spin and decay. Thus, the NSR mode is sensitive to the in-plane fields of the sample ($B_{\text{int}} \parallel ab$), while the SR mode is sensitive to the out-of-plane fields ($B_{\text{int}} \parallel c$). Utilizing both configurations allows us to obtain information on the magnetic anisotropy of samples. The detectors for the positrons, which are emitted upon muon decay, are arranged around samples as shown in Fig. S3, with detectors positioned backward (B), forward (F), upward (U), and downward (D). In this

setup, the NSR mode is detected by the detectors B and F. In contrast, the SR mode is detected by the detectors U and D. In our measurements, zero-field (ZF)- μ SR measurements were performed with NSR and SR mode, longitudinal-field (LF)- μ SR measurements were performed with only NSR mode, and transverse-field (TF) μ SR measurements were performed with only SR mode.

B. Analysis of zero field (ZF) and longitudinal field (LF)- μ SR

The μ SR data analysis was conducted using the open-source software package *musrfit* [S5]. In the ZF- μ SR measurements, we took measurements with both NSR and SR mode (Figs. S3a, b) for $x \sim 0.35$ and $x = 0.64$ samples. For $x = 0.75, 0.83$, and 0.94 samples, we measured with only NSR mode. In the LF- μ SR measurements, we employ the NSR mode configuration (Fig. S3a). In our measurements for $x \sim 0.35$ samples, we fitted the asymmetry time spectra $A(t)$ using the following stretched exponential function,

$$A(t) = A_s \exp(-\Lambda t)^\beta + A_{\text{BG}}, \quad (\text{S1})$$

where A_s is the initial asymmetry due to samples, Λ is the relaxation rate, and β is the stretching exponent in the range $0 < \beta \leq 1$. A_{BG} is the background contribution determined from our TF- μ SR measurement at the lowest temperature, and the background fraction $A_{\text{BG}}/(A_s + A_{\text{BG}})$ is 0.31. The stretched exponential model has been employed for the spatially inhomogeneous distribution of the relaxation [S6]. β represents the inhomogeneity of the internal field. We determined β by global fittings and obtained $\beta = 0.37$ (1.0) in the NSR (SR) mode.

For the results of $x = 0.64$ samples, we fitted the data using the simple exponential function,

$$A(t) = A_s \exp(-\Lambda t) + A_{\text{BG}}, \quad (\text{S2})$$

where the background fraction $A_{\text{BG}}/(A_s + A_{\text{BG}})$ is 0.23, determined from the TF- μ SR measurement at the lowest temperature.

For $x = 0.75, 0.83$, and 0.94 samples, we fitted the data using the following two-component exponential function with fast and slow relaxations,

$$A(t) = A_{\text{fast}} \exp(-\Lambda_{\text{fast}} t) + A_{\text{slow}} \exp(-\Lambda_{\text{slow}} t) + A_{\text{BG}}, \quad (\text{S3})$$

where the first and second terms represent the fast and slow relaxation components due to the sample, respectively. $A_{\text{fast (slow)}}$ is the fast (slow) relaxation rate. In $x = 0.75$ and 0.83 , $f_{\text{BG}} = A_{\text{BG}}/A_{\text{total}} = 0.13$ and 0.074 (where $A_{\text{total}} = A_{\text{fast}} + A_{\text{slow}} + A_{\text{BG}}$) obtained from the TF- μ SR measurements at the lowest temperature. On the other hand, in $x = 0.94$, f_{BG} could not be accurately estimated from the TF- μ SR measurements due to the large amplitude damping caused by the magnetic phase, so it was determined from the ZF NSR mode measurements in the normal state at about 14 K, resulting in $f_{\text{BG}} = 0.14$.

C. Analysis of transverse field (TF) and weak TF (wTF) - μ SR

Our TF- μ SR was performed in the normal and superconducting states with the applied field of about 500 G along the c -axis and the SR mode configuration (Fig. S3b). In our TF- μ SR measurements for $x \sim 0.35$ and $x = 0.64$ samples, the asymmetry spectra in the normal and superconducting states (Figs. S4a, b) were fitted using the following functions.

$$A(t) = A_s \exp\left(-\frac{\sigma_s^2 t}{2}\right) \cos(\gamma_\mu B_s t + \phi) + A_{\text{BG}} \cos(\gamma_\mu B_{\text{BG}} t + \phi), \quad (\text{S4})$$

where the first and second terms represent the sample and background contribution, respectively. σ_s is the relaxation rate due to the samples, and ϕ is the initial phase shift. γ_μ is the muon gyromagnetic ratio, $\gamma_\mu/2\pi = 135.5 \text{ MHz/T}$, and $\gamma_\mu B_{s(\text{BG})}$ is the frequency of the muon precession due to the sample (background) contribution under the external field. The fraction of the sample component $f_{\text{BG}} = A_{\text{BG}}/A_{\text{total}}$ (where $A_{\text{total}} = A_s + A_{\text{BG}}$), determined by the fitting the data at the lowest temperature about 2 K, is 0.31 in $x \sim 0.35$ and 0.23 in $x = 0.64$. As shown in Figs. S4a, b, we find the significant enhancement of relaxation in the superconducting state, reflecting the formation of the vortex lattice. It is also confirmed by the linewidth broadening and shift of the magnetic field peaks in the amplitude of the fast Fourier transform (Figs. S4e, f). The obtained relaxation rate σ for each temperature are shown in Figs. S4i, j. The relaxation in the superconducting state includes a contribution from the superconducting component σ_{SC} reflecting the superfluid density and the nuclear dipole moment σ_n . σ_{SC} can be extracted by quadratically subtracting; $\sigma_{\text{SC}}^2 = \sigma_s^2 - \sigma_n^2$. σ_{SC} is associated with the London penetration depth in the vortex state by

$$\sigma_{\text{SC}} = 0.06091 \frac{\gamma_\mu \phi_0}{\lambda^2}, \quad (\text{S5})$$

where λ is the London penetration depth and ϕ_0 is the flux quantum. The obtained temperature dependence of σ_{SC} and $\lambda^{-2}(T)$ are shown in inset of Figs. S4i, j. Our current data on the magnetic penetration depth were not sufficient to fit the temperature dependence, resulting in significant ambiguity and thus preventing us from obtaining useful information regarding the superconducting gap symmetry.

For $x = 0.75$ and 0.83 samples, Figs. S4c, d show the asymmetry spectra in the normal and superconducting states. We fitted the data using the following functions.

$$A(t) = A_{\text{fast}} \exp\left(-\frac{\sigma_{\text{fast}}^2 t}{2}\right) \cos(\gamma_{\mu} B_{\text{fast}} t + \phi) + A_{\text{slow}} \exp\left(-\frac{\sigma_{\text{slow}}^2 t}{2}\right) \cos(\gamma_{\mu} B_{\text{slow}} t + \phi) + A_{\text{BG}} \cos(\gamma_{\mu} B_{\text{BG}} t + \phi), \quad (\text{S6})$$

where the first and second terms represent the fast and slow relaxation components due to the sample contribution, and the third term is the background contribution. The fast and slow relaxation rates σ_{fast} and σ_{slow} for each temperature are shown in Figs. S4k, l.

For wTF- μ SR measurements, we fitted the data using following function,

$$A(t) = A_0 \exp(-\sigma t) \cos(\gamma_{\mu} B_{\text{wTF}} t + \phi), \quad (\text{S7})$$

where A_0 is the oscillation amplitude and B_{wTF} is the internal field of the sample in wTF measurements. For $x = 0.94$ samples, we estimated the magnetic volume fraction V_{M} from $V_{\text{M}} = 1 - \frac{A_0(t)}{A_0(T_{\text{max}})}$, where $A_0(T_{\text{max}})$ is the amplitude in the paramagnetic state at the highest temperature of about 70 K.

IV. THE TEMPERATURE DEPENDENCE OF RELAXATION RATES

To clarify whether the enhanced relaxation rates Λ_{ZF} observed in ZF- μ SR for the $x \sim 0.35$ and $x = 0.64$ samples arise from time-reversal symmetry breaking in the superconducting states, we compare them with the TF- μ SR relaxation rates σ_{TF} as shown in Fig. S5. The TF data represents the temperature dependence of the superfluid density (an order parameter of superconductivity), which is found to be scaled roughly to that of the ZF relaxation rate. When TRS is broken in the superconducting state, the TRSB field is expected to appear near the defects or domain boundaries and the field profile is essentially determined by the supercurrent around them. Thus, the rough scaling between the superfluid density and ZF

relaxation rate strongly supports that the observed temperature dependence of ZF data comes from the spontaneous TRSB field.

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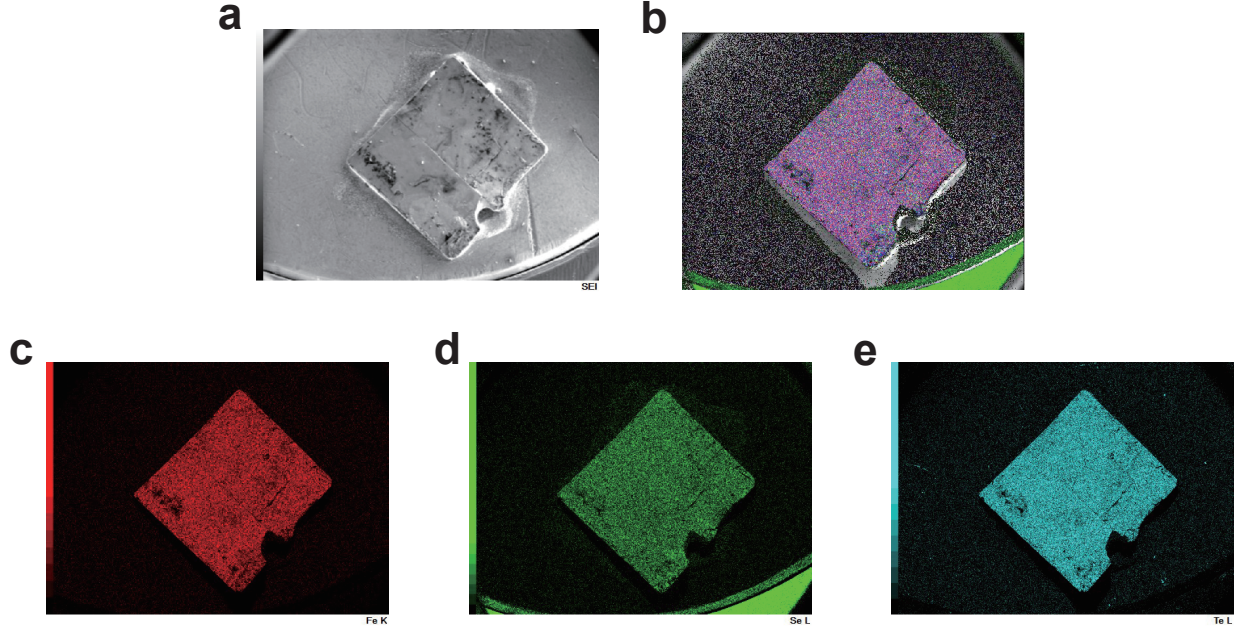


Fig. S1. Distribution mapping of Fe, Se, and Te elements. **a**, The scanning electron microscopy (SEM) image of the $\text{FeSe}_{1-x}\text{Te}_x$ ($x = 0.64$) sample. **b**, Overlay of the Fe (red), Se (green), and Te (blue) distribution mapping on the SEM image obtained from Energy Dispersive X-ray Spectroscopy (EDX) analysis. **c-e** Distribution mappings of each Fe (c), Se (d), and Te (e) element.

TABLE S1. Compositional ratios of each element in the $\text{FeSe}_{1-x}\text{Te}_x$ obtained from EDX. The numbers in parentheses are standard deviations.

nominal Te	Fe	Se	Te
0.6	0.991 (0.00633)	0.373 (0.0244)	0.636 (0.0228)
0.7	0.985 (0.00663)	0.263 (0.0121)	0.0752 (0.00907)
0.8	0.983 (0.00634)	0.158 (0.0189)	0.831 (0.0143)
0.9	0.987 (0.00487)	0.0753 (0.00635)	0.937 (0.00779)

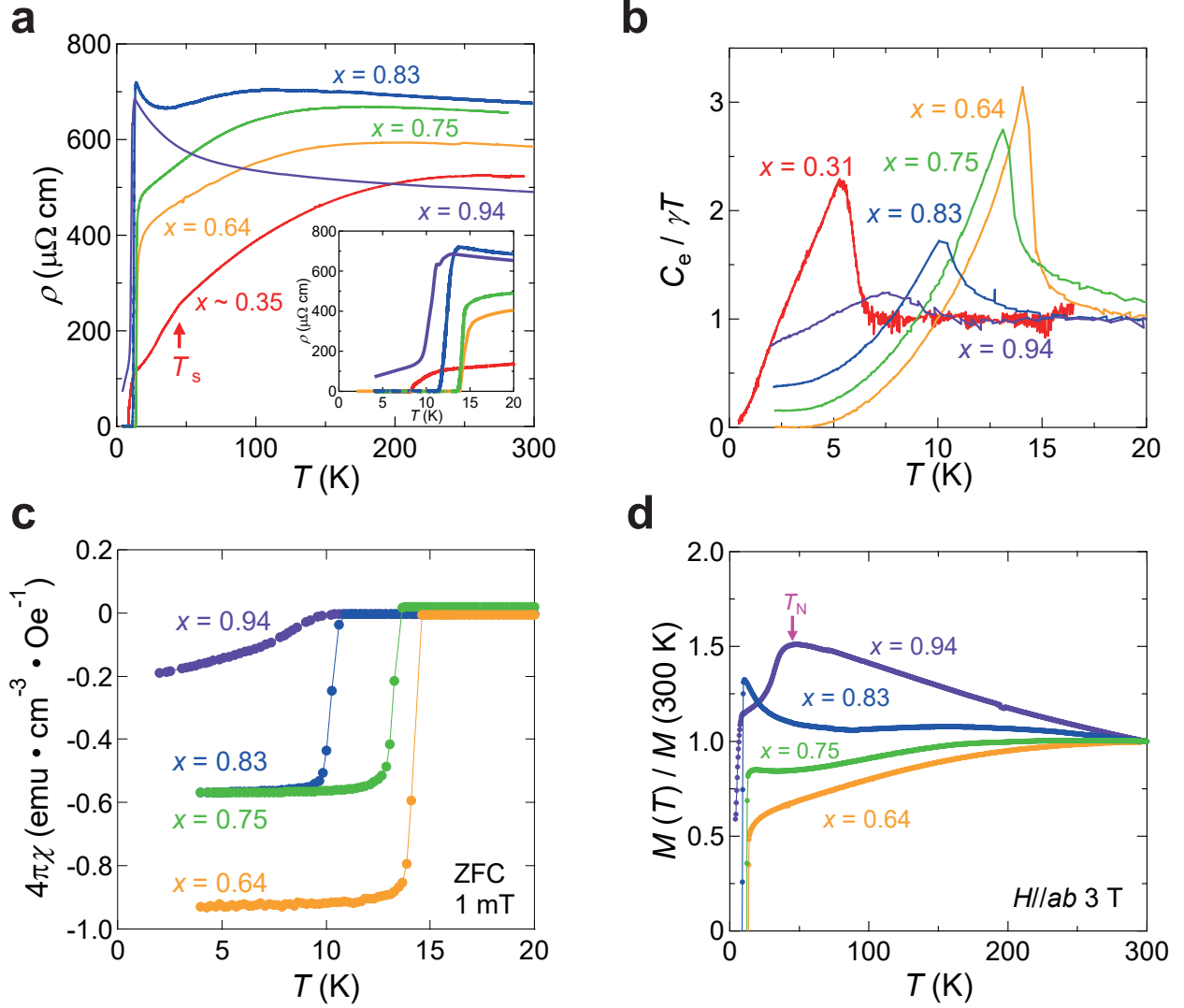


Fig. S2. Temperature dependence of resistivity, specific heat, magnetic susceptibility and magnetization. **a**, The temperature dependence of resistivity for the samples we used in the present study. The inset is the low-temperature part below 20 K. **b**, The temperature dependence of the electronic specific heat below 20 K. The phonon contribution has been subtracted and the data are normalized by the normal-state temperature dependence γT . Here, we show $x = 0.31$ data as a representative of the nematic phase in FeSe_{1-x}Te_x. **c**, The results of the magnetic susceptibility after zero-field cooling and under small magnetic field (1 mT). **d**, The temperature dependence of magnetization under 3 T normalized by each 300-K value. T_N represents the magnetic phase transition for the $x = 0.94$ sample.

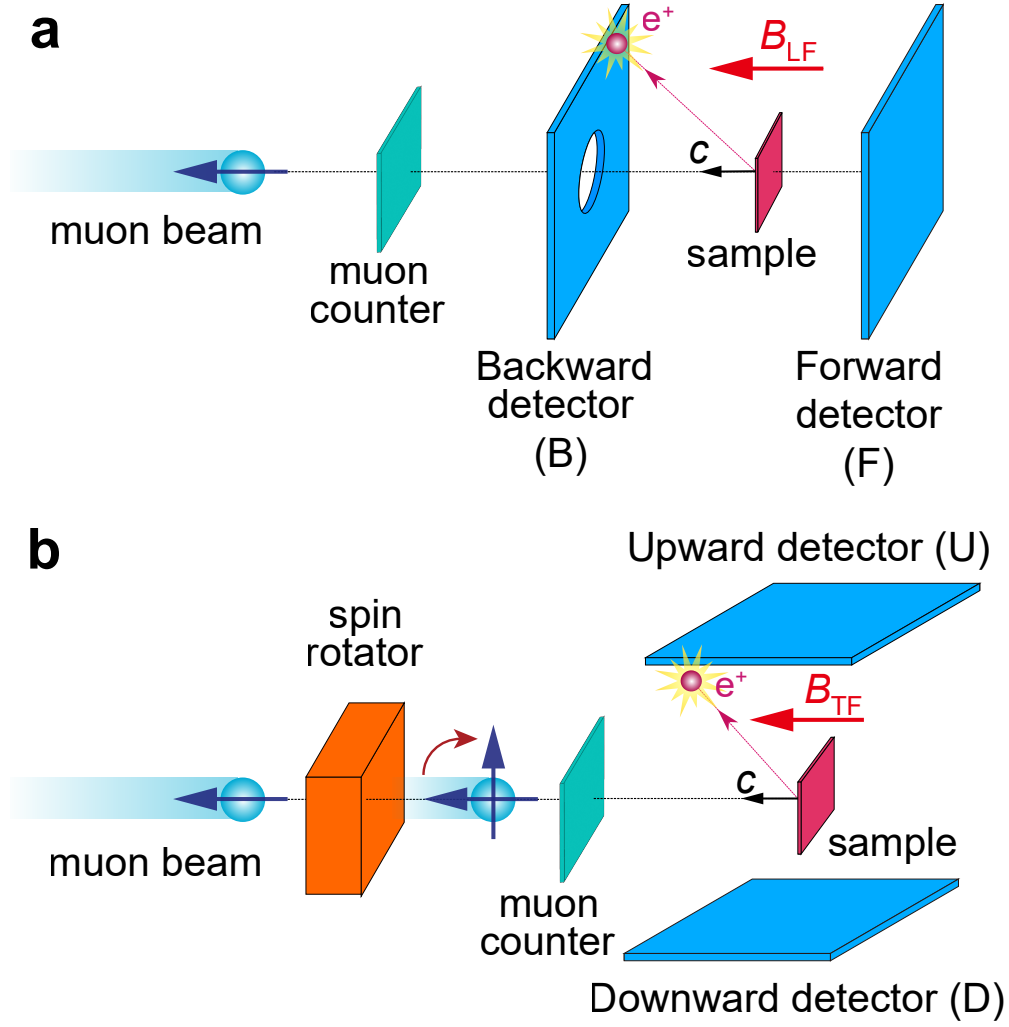


Fig. S3. Schematic diagrams of experimental setup in the μ SR measurements. **a**, Our experimental setup of zero field (ZF) and longitudinal field (LF)- μ SR with non-spin-rotated (NSR) mode measurements. **b**, Our setup of ZF and transverse field (TF)- μ SR with spin-rotated (SR) mode measurements. Initially, the muon beam direction and spin are aligned parallel to the c -axis of the samples. In the NSR mode, the muon beam is injected into the sample with the muon spins remaining aligned along the c -axis, and the positrons emitted with muon decay are detected by the backward (B) and forward (F) detectors (**a**). In the SR mode, the muon spins are rotated to be perpendicular to the c -axis by a spin rotator before being injected into the sample, and the emitted positrons are detected by the upward (U) and downward (D) detectors (**b**).

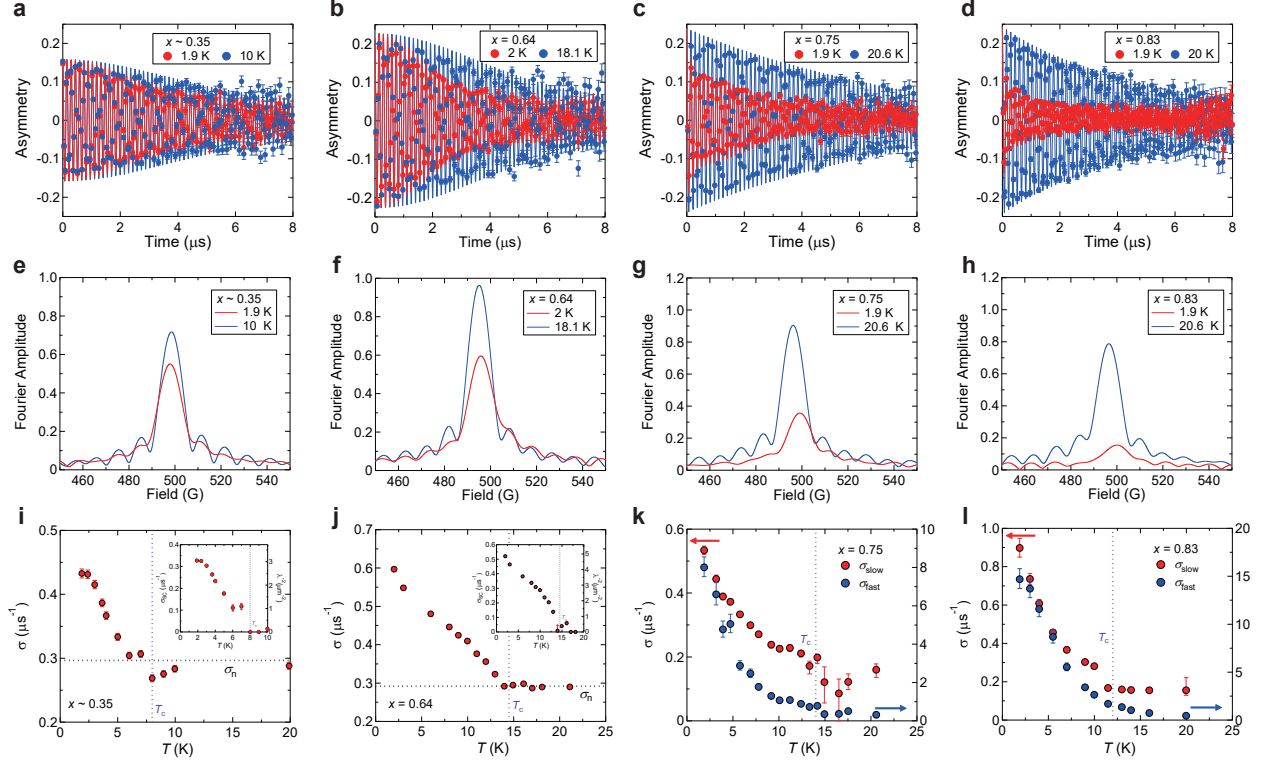


Fig. S4. Transverse field μ SR spectra. **a - d**, Time spectra of the asymmetry in transverse field (TF) 500 G μ SR for $x \sim 0.35$ (**a**), $= 0.64$ (**b**), 0.75 (**c**) and 0.83 (**d**) samples. These spectra are representative of the lowest temperature below T_c (red), and above T_c (blue). The solid lines represent fitting curves. **e - h**, The Fourier transform of the time spectra above (blue) and below T_c (red) for the $x \sim 0.35$ (**e**), $= 0.64$ (**f**), 0.75 (**g**) and 0.83 (**h**) samples. **i - l**, Temperature dependence of the relaxation ratio σ (μs^{-1}) obtained from our fittings. For $x \sim 0.35$ (**i**) and $= 0.64$ (**j**), σ obtained by the fitting with the function Eq.S4. The black dashed lines represent the averaged σ in the normal state. The inset shows the relaxation rate in the superconducting state σ_{SC} and the superfluid density obtained from Eq.S5. For $x = 0.75$ (**k**) and 0.83 (**l**), the fitting function is Eq.S6 with two-component Gaussian relaxation. The slow (red) and fast (blue) components correspond to the left and right axis, respectively. The vertical dashed lines in **i-l** show the superconducting transition temperatures.

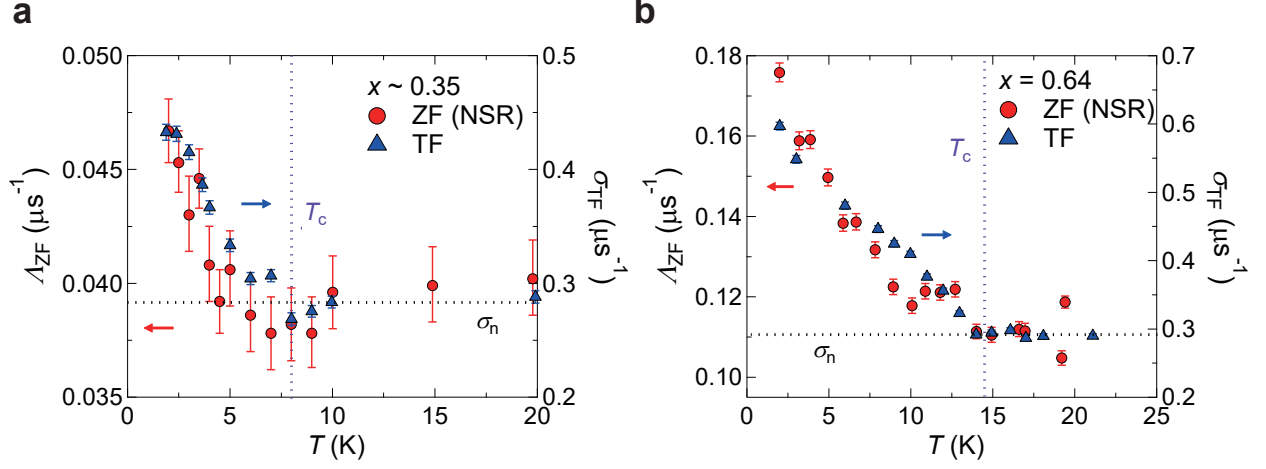


Fig. S5. Comparison of the temperature dependence of the relaxation rates in ZF and TF- μ SR in the $x \sim 0.35$ and $x = 0.64$ samples. **a, b** The temperature dependence of the relaxation rates in ZF- μ SR (NSR mode) measurements λ_{ZF} (red circle, correspond to left axis) and in TF- μ SR σ_{TF} (blue triangle, correspond to right axis) for $x \sim 0.35$ (a) and $x = 0.64$ (b) samples.