Superconductivity with broken time-reversal symmetry inside a superconducting s-wave state

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In general, magnetism and superconductivity are antagonistic to each other. However, there are several families of superconductors in which superconductivity coexists with magnetism, and a few examples are known where the superconductivity itself induces spontaneous magnetism. The best known of these compounds are Sr$_2$RuO$_4$ and some non-centrosymmetric superconductors. Here, we report the finding of a narrow dome of an s + is' superconducting phase with apparent broken time-reversal symmetry (BTRS) inside the broad s-wave superconducting region of the centrosymmetric multiband superconductor Ba$_{1-x}$K$_x$Fe$_2$As$_2$ (0.7 ≤ x ≤ 0.85). We observe spontaneous magnetic fields inside this dome using the muon spin relaxation (μSR) technique. Furthermore, our detailed specific heat study reveals that the BTRS dome appears very close to a change in the topology of the Fermi surface. With this, we experimentally demonstrate the likely emergence of a novel quantum state due to topological changes of the electronic system.

The complexity of the Fermi surface may result in competition between different superconducting pairing symmetries in multiband systems. For a two-band s-wave superconductor, the interband phase difference is either 0 or π in the ground state (Fig. 1). However, for a superconductor with more than two bands, repulsive interband interactions might result in a complex order parameter with the interband phase difference being neither 0 nor π. Such a complex s + id or s + is' ground state breaks time-reversal symmetry and can be considered to be a result of the competition between s- and d-or different s-wave components. These states with a frustrated phase of the order parameter (Fig. 1e) are qualitatively different from the previously studied chiral pairing or non-unitary states.

In all known multiband superconductors, the phase difference of the superconducting order parameter between different bands was observed to be either 0 or π. For example, most iron-based superconductors are in close proximity to a spin density wave phase, in which the interaction between fermions in hole- and electron-like Fe pockets is strongly enhanced, giving rise to an s$_g$ state. Therefore, frustrated superconductivity might be expected in iron-based superconductors, which are quite far from the spin density wave phase. For the Ba$_{1-x}$K$_x$Fe$_2$As$_2$ system, it has been argued that the change of the order parameter with doping is caused by topological changes of the Fermi surface at a Lifshitz transition (schematically shown in Fig. 1). According to angle-resolved photoemission spectroscopy (ARPES) at optimal doping, the Fermi surface consists of hole- and electron-like pockets. This band structure favours an s$_g$ state with a gap function having different signs (π phase shift) on the hole and electron pockets (Fig. 1d). With further K doping, the electron pockets disappear and additional propeller-like hole pockets appear at the Brillouin zone corner (not shown in Fig. 1 for simplicity). These changes suppress the hole–electron interpacket interaction, resulting in a change of the s$_g$ gap symmetry to another s- or a d-wave state. As a consequence, the frustration of the order parameter due to competing interband interactions may lead to phase shifts different from 0 and π (Fig. 1e). It has been predicted that, close to the Lifshitz transition, incipient electron bands still contribute to the pairing until the distance from the top of these pockets to the Fermi level is comparable with the gap size. It is therefore expected that this frustrated broken time-reversal symmetry (BTRS) superconducting state appears in the Ba$_{1-x}$K$_x$Fe$_2$As$_2$ system at a doping level at which the electron bands just sink below the Fermi level.

It has been shown that, in the presence of inhomogeneities, s + is' and s + id phases can generate spontaneous currents and related magnetic fields. These spontaneous magnetic fields in the superconducting state can be observed experimentally. In our first muon spin relaxation (μSR) experiments, we detected an enhancement of the zero-field muon spin depolarization rate below the transition temperature $T_c$ in heavy-ion-irradiated Ba$_{1-x}$K$_x$Fe$_2$As$_2$ single crystals with $x ≈ 0.73$ (ref. 29). The observed behaviour indicates a BTRS in the superconducting state. However, so far, the nature of the BTRS state remains elusive. In particular, a very strong inhomogeneity might result at low temperatures in a BTRS state even in a two-band s$_g$ superconductor. Here, we have performed systematic investigations of high-quality Ba$_{1-x}$K$_x$Fe$_2$As$_2$ single crystals to elucidate the fundamental mechanism responsible for the spontaneous magnetic fields in the superconducting state. By combined μSR and specific heat studies we show that the apparent BTRS state occupies a narrow region inside a broad s-wave superconducting state with broken time-reversal symmetry.
Fig. 1 | Multiband superconductivity. Schematic of the change of the topology of the Fermi surface at the Lifshitz transition ($x_c$) in the Ba$_{1-x}$K$_x$Fe$_2$As$_2$ system with possible s-wave superconducting states. (The propeller-like pocket around the X-point and an additional hole pocket in the zone centre is not shown for the sake of simplicity.) a, b, The Brillouin zone with two-hole and one-electron Fermi pockets (optimal doping) (a) and the Brillouin zone with two-hole Fermi pockets (high doping level) (b). c–g, Possible s-wave pairing states in a clean limit. The relative phase $\phi$ of the superconducting order parameter components is shown by the direction of the arrows inside the circles and the magnitude is indicated by the length. A frustrated pairing $s + i s$ state with arbitrary phase shifts between the components of the order parameter in a clean limit is possible in the three-band case.

Fig. 2 | Thermodynamic properties. a, Temperature dependence of the molar susceptibility $\chi$ of the Ba$_{1-x}$K$_x$Fe$_2$As$_2$ single-crystal stacks used in the $\mu$SR experiments. b, Temperature dependence of the electronic specific heat ($\Delta C_{el}/T$) of Ba$_{1-x}$K$_x$Fe$_2$As$_2$ single crystals with various doping levels. c, Double logarithmic plot of the normalized specific heat jump $\Delta C_{el}/\gamma T$ at $T_c$ versus $T_c$. d, $\Delta C_{el}/\gamma T$ close to the region with the BTRS state observed in the $\mu$SR experiments.

dome of the Ba$_{1-x}$K$_x$Fe$_2$As$_2$ phase diagram. We also propose theoretical arguments in favour of an $s + i s$ superconductivity in the BTRS state, and define the relationship of this superconducting state with topological changes of the Fermi surface.

The superconducting and normal state physical properties of Ba$_{1-x}$K$_x$Fe$_2$As$_2$ single crystals were characterized by d.c. susceptibility and specific heat measurements. The magnetic susceptibility in the normal state of the samples used in the $\mu$SR experiments is shown in Fig. 2a. The systematic increase of the susceptibility with K doping is consistent with reported data. The increase in the susceptibility correlates with an enhancement of the electronic specific heat in the normal state (see below). A pronounced narrow anomaly in the specific heat at $T_c$ indicates the high quality of the crystals (Fig. 2b).

X-ray and transmission electron microscopy did not reveal any
Fig. 3 | Zero-field μSR. a–c, Examples of zero-field μSR time spectra above and below \( T_c \) for the muon spin polarization component \( P_\parallel \) for Ba\(_{1-x}\)K\(_x\)Fe\(_2\)As\(_2\) samples with different K doping: \( x = 0.68(3) \) (a), \( x = 0.78(3) \) (b) and \( x = 0.85(2) \) (c). Symbols: experimental data; solid lines: fits using equation (1). For the sample shown in b the muon spin polarization was 45° in respect to the c axis. This results in a reduced initial asymmetry \( A_i(0) \) by \( \cos(45°) \) as compared to \( A_i(0) \) for the samples shown in a and c. 

b) The temperature dependence of the muon spin depolarization rate \( \Lambda \) for the intermediate doping level \( x = 0.71(2) \) (d), \( x = 0.78(3) \) (e), \( x = 0.85(2) \) (f), \( x = 0.71(2) \) (g) and \( x = 0.81(2) \) (h). The dashed lines are linear fits at \( T \geq T_{BTRS} \). The solid curves are fits at \( T \leq T_{BTRS} \). Right axes: temperature dependence of the volume susceptibility measured in a low-magnetic-field \( B = 0.5 \) mT applied along the a-b plane after cooling in zero field, subsequent warming in the field, and cooling again in the same field, for the same doping levels. i, Summary of the temperature dependencies of \( \Lambda \) for the samples shown in a–c. The displayed error bars correspond to one standard deviation from the \( \chi^2 \) fit. 

Examples of the zero-field asymmetry time spectra for three samples with different doping levels are shown in Fig. 3a–c and Supplementary Section 2. For the samples with \( x = 0.68(3) \) and \( x = 0.71(2) \), the depolarization rate is nearly unchanged after cooling below \( T_c \). This behaviour is expected for a superconductor that preserves time-reversal symmetry. In contrast, the enhanced relaxation for the intermediate doping level \( x = 0.78(3) \) indicates the appearance of spontaneous magnetic fields in the superconducting state. To obtain the temperature-dependent muon spin depolarization rate \( \Lambda \), we analysed the spectra using the simplest possible model: 

\[
A(t) = A_i(0) \exp (-\Lambda t) \exp \left( \frac{1}{2} (\sigma t)^2 \right) + A_{bg}
\]

where \( A_i(0) \) is the initial sample asymmetry and \( A_{bg} \) is the background asymmetry obtained from transversal-field measurements for each sample. We consider \( \sigma \) as the temperature-independent Gaussian muon spin depolarization rate to account for the nuclear contribution. However, allowing for a temperature-dependent \( \sigma \) does not affect the results. Further details on the analysis are provided in the Methods and Supplementary Section 2. The temperature dependencies of the zero-field muon spin depolarization rate \( \Lambda \) together with the magnetic susceptibility are shown in Fig. 3d–h and, on a larger scale, the depolarization rates are compared in Fig. 3i. The normal state \( \Lambda \leq 0.1 \) \( \mu s^{-1} \) is temperature- and doping-dependent. The absolute values of the depolarization rate are sensitive to the value of \( A_{bg} \) fraction. However, the temperature dependence is insensitive to the value of \( A_{bg} \) (Supplementary Fig. 4h). We found that the depolarization rate \( A_e \) extrapolated to \( T = 0 \) increases with doping, qualitatively following the behaviour of the normal state bulk susceptibility (Extended Data Fig. 1). The increase of \( A_e \) with K doping is in line with the behaviour of the normal state spin-lattice relaxation rate \( 1/T_1 \) and the NMR Knight shift, anticipating the proximity of KFe\(_2\)As\(_2\) to an as-yet-unknown quantum critical point. This suggests that the depolarization rate \( \Lambda \) reflects intrinsic electronic properties of the samples.

For the samples with \( 0.71 \leq x \leq 0.81 \) we observe a systematic increase of \( \Lambda \) in the superconducting state below a characteristic temperature \( T_{BTRS} \). To determine the \( T_{BTRS} \) values we fitted the temperature dependencies of \( \Lambda \) using a power law in reduced temperature \( \Lambda = \Delta \Lambda (1 - T/T_{BTRS})^{\beta} + A_0 + b_1 T \), where \( \Delta \Lambda \) is the additional depolarization rate below \( T_{BTRS} \), \( \beta \approx 0.4-0.5 \) is an exponent, and \( A_0 \) and \( b_1 \) describe a linear dependence of the \( \Lambda \) in the normal state. We found that the quality of the fits, characterized by \( \chi^2 \), is improved after including the \( \Delta \Lambda \) term for the samples with \( 0.71 \leq x \leq 0.81 \) only. For other doping levels the linear fits result in smaller \( \chi^2 \) values. The \( T_{BTRS} \) temperatures are summarized in Fig. 5.
later. Note that, for the sample with $x = 0.71(2)$, we cannot exclude a weak enhancement of $\Lambda$ in the superconducting state. However, a transition temperature $T_{\text{BTRS}}$ could not be unambiguously assigned. For this reason we did not include a point for this doping level in the phase diagram shown in Fig. 5.

The enhancement of the depolarization rate is attributed to the appearance of spontaneous magnetic fields in the superconducting state at the BTRS transition temperature $T_{\text{BTRS}}$. The doping range in which the BTRS is observed and the magnitude of $\Delta \alpha$ are consistent with our previous observations for the heavy-ion-irradiated sample with $x \approx 0.73$ (ref. 13). However, a quantitative comparison is complicated due to the sensitivity of local fields to the strength and orientation of the defects.

In Fig. 4 the temperature dependence of $\Lambda$ is shown within a broad temperature range for two samples exhibiting a BTRS state. We present the data for two muon spin polarization components $P_c || c$ and $P_a || a$ measured along the crystallographic $c$ and $a$ axes (the data for other samples are provided in Supplementary Section 2). In the normal state, $\Lambda$ is moderately anisotropic $\Delta \alpha \approx 1.7$ and exhibits a nearly linear temperature dependence. We could clearly detect an enhancement of the muon depolarization rate for $P_c || c$, whereas for $P_a || a$ such an enhancement is not observed. Moreover, even a slight suppression of the depolarization rate cannot be excluded below $T_{\text{BTRS}}$ for $P_c || a$. The suppression might be related to a reduction of the nuclear depolarization rate due to the longitudinal component of the spontaneous fields (see Supplementary Section 2 for details). These data indicate that the internal fields in the BTRS state have a preferred orientation within the $a$-$b$ plane.

To understand this anisotropy of the internal field strength, we modelled the dependence of the spontaneous magnetic fields by adopting a local change of the superconducting coupling constants due to the sample inhomogeneities (see Methods and Supplementary Section 6) using the approach proposed in ref. 13. The sample inhomogeneities lead to variation of the effective coupling constant $\lambda$ in the superconductor and $\Delta \delta$ that parametrizes the interband pairing, where $\lambda_e$ is the coupling constant without inhomogeneities and $\Delta \delta$ describes the variation of the coupling constant due to them. We found that, in a broad range of $\Delta \delta$ for an anisotropic $s + i\delta$ state, the spontaneous magnetic fields are polarized mainly within the $a$-$b$ crystal plane (Extended Data Figs. 2 and 3 and Supplementary Section 6), while for an $s + id$ state their $a$-$b$-plane and $c$-axis components would be of the same order. Thus, the observed strong anisotropy of the spontaneous internal fields can be understood as an indication for an anisotropic $s + i\delta$ state.

The magnitude of the additional depolarization rate in the BTRS state $\Delta \alpha$ corresponds to an average internal field $(B_{\text{int}}) = \Delta \alpha / \gamma_\mu$ of $\approx 0.01 \text{ mT}$, where $\gamma_\mu = 0.85 \text{ s}^{-1} \text{ mT}^{-1}$ is the gyromagnetic ratio of the muon. Such weak fields can be explained by the same model ascribing a small variation of the coupling constants with $\pm \delta \alpha$ of a few percent (Extended Data Fig. 3 and Supplementary Section 6). We attribute these weak defects to inhomogeneities in the doping level because no extended crystalline defects or impurity phases were found in our transmission electron microscopy investigations (Supplementary Section 1). In addition, the analysis of the electrical resistivity data (Extended Data Figs. 4 and 5 and Supplementary Section 4) indicates that the amount of disorder is nearly doping independent in the range $x = 0.65$–0.85. Experimentally, the strength of these inhomogeneities $\delta \alpha$ can be estimated from the superconducting transition width measured by the specific heat. Assuming $\Delta T_C = 1$–2 K and using the Bardeen–Cooper–Schrieffer (BCS) expression for $T_C \propto \exp(-1/\alpha T_C)$ we get that $\delta \alpha$ varies within $\pm 5\%$, which is in a reasonable agreement with the expected theoretical value estimated in Supplementary Section 6.

The evidence for a change of the order parameter with doping is provided by the $T_C$ dependence of the specific heat jump $\Delta C_p / \gamma_\mu T_C$ at $T_{\text{C}}$ (Fig. 2c). For Ba$_{1-x}$K$_x$Fe$_2$As$_2$ single crystals with a doping level of $x \leq 0.7$, $\Delta C_p / \gamma_\mu T_C$ approximately follows the well-known $\text{Bud’ko–Ni–Canfield}$ scaling behaviour $\Delta C_p / \gamma_\mu T_C \propto T_C^\alpha$ with $\alpha \approx 2$ (ref. 13), which is considered to be a consequence of the nodal multiband $s_\pm$ superconductivity in iron pnictides. For a doping level of $x \geq 0.8$, $\Delta C_p / \gamma_\mu T_C \propto T_C^\alpha$ results in another scaling curve with $\alpha \approx 0.4$. This exponent value is also above the single-band BCS value $\alpha = 0$ ($\Delta C_p / \gamma_\mu T_C = \text{const}$). It can be obtained numerically within some theoretical models for an $s_\pm$ superconductor in the clean limit. The nodal gap structure for the Ba$_{1-x}$K$_x$Fe$_2$As$_2$ system at this high doping level$^{26,27}$ excludes a conventional $s_\pm$-wave gap. Therefore, we expect an unconventional superconductivity. It might be a different kind of sign change $s$-wave state. The simplest theoretical proposal (ignoring nodes) for such an $s_\pm$ state is that the order parameter changes its sign between the two inner-hole Fermi pockets (see Fig. 1g for an illustration)$^{14}$. In the intermediate doping regime $0.7 \leq x \leq 0.8$, $\Delta C_p / \gamma_\mu T_C$ behaves unusually by exhibiting a local maximum at the BTRS transition temperature $T_{\text{BTRS}}$ (Fig. 2d). The negative exponent $\alpha < 0$ for the intermediate region is striking, especially in view of the monotonously decreasing $T_C$ value. The observed crossover between two distinct scaling behaviours in a narrow doping range indicates an essential modification of the pairing interactions.

Evidence for a peculiar superconducting gap structure inside the BTRS phase can also be found in high-resolution ARPES measurements$^{35}$. In the BTRS state, the nodes exist only on the outer-hole Fermi surface centred at the $\Gamma$-point, whereas at higher doping outside the BTRS dome, additional nodes appear on the middle-hole Fermi surface. Therefore, our specific heat data, together with the available ARPES data, demonstrate that the BTRS state observed in the $\mu$SR measurements exists in an intermediate region of the phase diagram between two different types of unconventional $s$-wave states.
To understand the microscopic reasons for the change of the order parameter symmetry, we performed detailed investigations of the electronic specific heat in the normal state by evaluating the Sommerfeld coefficient \( \gamma_n \). Above optimal doping up to \( x \approx 0.65 \), \( \gamma_n \) reduces slightly with doping, in qualitative agreement with a linear suppression of \( T_c \) (Fig. 5a). The reduction of \( T_c \) and \( \gamma_n \) is attributed to a weakening of the interband interactions due to a gradual reduction of the size of the electron Fermi pockets while increasing the doping\(^{26,27}\). In this part of the phase diagram, the gap symmetry is \( s \pm i \sigma \) with different signs of the order parameter on the electron and hole Fermi pockets (Fig. 1d).

For \( x \geq 0.65 \), \( \gamma_n \) steeply increases with doping. In contrast, \( T_c \) sharply reduces with doping above \( x \approx 0.7 \), but flattens after the crossing of the BTRS dome. In the BTRS state, the experimental data are consistent with an \( s + i \sigma \) frustrated superconducting state having a ground-state interband phase difference of neither 0 nor \( \pi \) (Fig. 1e). To locate the position of the Lifshitz transition in the phase diagram, we performed density functional theory (DFT) calculation of the electronic band structure (see Methods and Supplementary Section 5). The doping dependence of the bare Sommerfeld coefficient \( \gamma_{\text{DFT}} \) is shown in Fig. 5b. The calculation cannot correctly reproduce the position of the Fermi level, so we plot the theoretical doping axis to fit the minimum value \( \gamma_{\text{DFT, min}} \) to the experimental minimum in \( \gamma_n \). The behaviour of \( \gamma_{\text{DFT}} \) with doping is qualitatively similar to the experimentally observed one. \( \gamma_{\text{DFT}} \) is weakly doping-dependent on the low-doping side and increases by a factor of two on the overdoped side of the phase diagram. However, the sharp maximum at the Lifshitz transition around \( x = 0.6 \) is not observed in the experiment.

There are several reasons that may explain the suppression of the maximum in the experimental data. First, the experimental values of the Sommerfeld coefficient at this doping are obtained in the normal state at \( T > T_c \approx 20 \text{ K} \). This temperature is comparable with the width of the maximum (Supplementary Section 3). Second, the strong maximum in \( \gamma_{\text{DFT}} \) is related to a quasi-two-dimensional (2D) Fermi surface, resulting in divergent behaviour of the density of states (DOS) at the Lifshitz transition. However, the experimental Fermi surface in the Ba\(_{1-x}\)K\(_x\)Fe\(_2\)As\(_2\) system has a stronger dispersion along the \( Z \) direction as compared to the DFT result\(^{26,27}\). Third, the disorder due to K substitution also smears out the sharp DOS anomaly at the Fermi level\(^{14}\).

Finally, in Fig. 5c we plot the predicted doping dependence of the mean field \( T_c \) which takes into account the effect of incipient bands close to the Lifshitz transition\(^{14}\). This effect is relevant when the magnitude of the superconducting gaps is larger (comparable) than the distance between the zone bottom (top) and the Fermi energy. To compare our DFT theoretical predictions with the experimental phase diagram, we scaled the doping axis in Fig. 5c to match the position of the Lifshitz transition in Fig. 5b and the position of the BTRS dome centre in Fig. 5a. We found that the overall behaviour of the calculated \( T_c \) is quite similar to the experimental one, despite the calculations assuming simple parabolic bands and neglecting any dispersion and/or correlational effects on the DOS. The observed qualitative similarity provides additional confidence that the Lifshitz transition occurs at a lower hole doping level than the observed \( s + i \sigma \) dome.

The Lifshitz transition at \( x_c \approx 0.6 \) is supported by a large set of experimental data. The ARPES data in ref.\(^ {27,31-35} \) were obtained on crystals prepared in the same way as our samples. In this case, the Lifshitz transition, related to the shift of the electron pockets at the M-point of the Brillouin zone above the Fermi level, was observed for doping levels between \( x \approx 0.5 \) (\( T_c \approx 31–35 \text{ K} \)) and \( x \approx 0.6 \) (\( T_c \approx 23–27 \text{ K} \)). According to these \( T_c \) values, in our phase diagram (Fig. 5) this corresponds to doping levels of \( 0.4–0.5 \) and \( x = 0.55–0.63 \), respectively. In ref.\(^ {26,27} \), the Lifshitz transition was observed between \( x = 0.7 \) (\( T_c \approx 22 \text{ K} \)) and \( x = 0.9 \) (\( T_c \approx 9 \text{ K} \)). In our phase diagram this corresponds to doping levels of \( x \approx 0.64 \) and \( x \approx 0.83 \), respectively.

We also found a consistency between our data and the transport measurements. For example, the minimum in the thermoelectric power at \( x \approx 0.55 \) was attributed to the Lifshitz transition of the electron Fermi surface\(^ {42} \). According to the \( c \)-axis value, there is a nearly exact correspondence between doping levels from this Article and our phase diagram (Supplementary Fig. 12). Finally, the Hall measurements strongly suggest that the electron pocket at the M-points contributes to the Hall coefficient up to a doping level of \( x \approx 0.65–0.8 \) (\( T_c \approx 24–16 \text{ K} \))\(^ {19} \). According to \( T_c \), this doping level corresponds to \( x \approx 0.6–0.7 \) in our phase diagram.

Thus, our detailed specific heat study combined with literature data\(^ {26,27,30,42} \) and theoretical calculations allows us to locate the position of the Lifshitz transition in the phase diagram at \( x_c = 0.6(1) \) (Fig. 5). At this doping, the electron Fermi pockets sink below the Fermi level; however, they are still close enough to contribute to pairing in the \( s \pm i \sigma \) channel\(^ {14} \). Therefore, the BTRS dome appears at \( x \geq x_c \), in agreement with the scenario proposed in ref.\(^ {14} \).

Our results show the apparent existence of a yet unexplored regime of coexistence of superconductivity and magnetism and
the closeness to Lifshitz transitions in multiband systems to be the guiding principle for finding such states in materials. Developing methods to control this new form of magnetism and its interplay with superconductivity with, for example, controlled introduction of impurities or creating heterostructures may further open new possibilities for superconducting device engineering.

**Online content**

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Methods

Samples. The samples used in our μSR measurements consist of c-axis-oriented stacks of plate-like Ba$_x$K$_{1-x}$Fe$_2$As$_2$ single crystals selected according to their $T_c$ values. The phase purity and crystalline quality of the crystals were examined by X-ray diffraction (XRD) and transmission electron microscopy (TEM). The c-lattice parameters were calculated from the XRD data using the Nelson–Riley function. The K doping level x of the single crystals was calculated using the relation between the c-axis lattice parameter and the K doping obtained in previous studies.

Specific heat and magnetization measurements. The $T_c$ values of the samples (consisting of a stack of single crystals) used for the μSR experiments were defined from d.c. susceptibility measurements using a commercial superconducting quantum interference device (SQUID) magnetometer from Quantum Design. The $T_c$ values of the individual crystals given in Fig. 5 were obtained using the energy derivative method from $A_i$, by applying the specific heat measured in a Quantum Design physical property measurement system. The phonon contribution in the specific heat was determined experimentally for single crystals with $T_c \lesssim 10$ K (Supplementary Fig. 10). For crystals with higher $T_c$ (that is, in the doping range 0.8 ≤ x ≤ 0.65) we used the phonon contribution of the low $T_c$ samples with an adjustment coefficient, following the procedure proposed in ref. 3.

μSR experiments. Most μSR experiments on the stacks of Ba$_x$K$_{1-x}$Fe$_2$As$_2$ single crystals were performed at the GPS instrument at the Paul Scherrer Institute (PSI) in Switzerland, while the sample with x = 0.98(2) was measured on the LTF instrument of the E3M beamline at PSI. Fully spin-polarized positive muons with an energy of 4.2 MeV were implanted in the sample (parallel to the crystallographic c axis). The sample size and sample mounting were similar to those used in our previous measurements. To optimize the amount of muons stopped in the sample, we used an Ag degrader with a thickness of $d_{Ag} \approx 50$ μm. The measurements were performed in the longitudinal and transverse polarization modes. In the longitudinal mode, the muon spin is parallel to the beam, and in the transverse polarization mode, the muon spin polarization is at 45° with respect to the muon beam (pointing towards the upward counter) and the sample c axis. Using the veto detectors of the GPS instrument we were able to measure small samples with a mass of 10–50 mg. For the measurements at the LTF instrument we used a bigger sample with a mass of ~60 mg, as this instrument is not equipped with a veto detector system. The depolarization rates of the muon polarization components $P_x$ and $P_y$ were determined from forward–backward and up–down positron detector pairs, respectively. The background contribution to the sample signal was carefully determined for each sample using transverse-field measurements above and below $T_c$, as shown in Supplementary Section 2. The obtained background contribution was fixed in the analysis of the zero-field data. For zero-field measurements, external fields were actively compensated to a value lower than 2 μT. In addition, before each measurement, the compensation was verified using a three–component probe magnetometer.

Usually, positron detectors are combined into pairs to obtain the asymmetry $A(t)$. In this case, paired detectors are characterized by a common asymmetry, whereas the geometrical differences and efficiency between detectors are accounted for by the parameter $A$. This allows us to reduce the number of fitting parameters and cancel the muon decay function. In this approach, the dark count rate in each detector is measured and subtracted from the total counts of a detector $N(t)$ using a short time interval immediately before measurements. However, when relaxation is slow, as in the present case, the resulting fitted relaxation rates are very sensitive to errors in the dark rate. We thus obtained $A(t)$ by a procedure known as a single histogram fit, in which the count numbers versus time of the individual detectors are fit using the dark rate $N_{dark}$ of each detector as the fitting parameter. As a result, the whole set of the data is used to minimize the error in the calculation of $N_{dark}$. In this procedure, the count numbers $N(i)_t$, where $i$ = {1, 2}, are fit by $N(i)_t = N_{dark} + A(i)_t(t - t_{mu})^{-\tau(t)}$ where $\tau(t)$ is the muon lifetime and $N_{dark}$ is a fitting parameter setting the overall number of triggered counts. The used functional form of $A(t)$ is the same for both detectors and is given by equation (1). The depolarization rate $A(t)$ is determined from fits to the counts from both detectors simultaneously, using the MUSRFRIT program. We generally plot $A(t) = \frac{1}{2}(A_1(t) - A_2(t))$, using the fitted form of $A_1(t)$ and the experimental $A_2(t)$ as $A_1(t) = N_{dark}(t) + N_{light}(t) - N_{dark}(0) \exp(-t/t_{mu})^{-1}$

In this analysis, $A_1(t)$ and $A_2(t)$ need to be determined separately, because for slow relaxation the analysis has a low resolving power for these parameters and $N_{dark}$, respectively. We performed the μSR experiments on Ba$_x$K$_{1-x}$Fe$_2$As$_2$ single crystals in the doping range 0.65 ≤ x ≤ 0.85. J.M. and S.A. prepared Ba$_x$K$_{1-x}$Fe$_2$As$_2$ single crystals with x = 0.98. P.C. performed and W.S. supervised TEM measurements.

DFT calculations. Fully relativistic DFT calculations of the band structure for the Ba$_x$K$_{1-x}$Fe$_2$As$_2$ system were carried out within the generalized gradient approximation using the Full Potential Local Orbital band structure package (FPLO). The K doping was taken into account within the virtual crystal approximation. A k-mesh of 36 × 36 × 36 k-points in the whole Brillouin zone was employed. The calculations were performed using the FPLO Ab-Initio Simulation Package within the Perdew, Burke and Ernzerhof functional for the exchange–correlation potential. The normalized electronic specific heat at different doping levels was obtained from the total electronic DOS at the Fermi level, $\gamma(T)/\gamma_{FPLO} = N_{elect}(0)/N_{max}(0)$, normalized by the minimal DOS value at the considered doping range.

Calculation of the spontaneous currents. The anisotropy and magnitude of the spontaneous magnetic fields in the BTRS state were estimated using the phenomenological model proposed in ref. 48. To calculate spontaneous fields in the anisotropic s + i's and s − i's states generated by sample inhomogeneities, such as the inhomogeneous doping level distribution, we adopted the Ginsburg–Landau free energy derived in ref. 49. The intrinsic sample inhomogeneity, parametrized by the interband pairing constant, is reflected in the spatially dependent coefficients of the Ginsburg–Landau functional. Further details are provided in Supplementary Section 6.

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Author contributions

V.G. designed the study, initiated and supervised the project and wrote the paper, performed the μSR, specific heat, magnetic susceptibility and X-ray diffraction measurements. K.S. performed μSR experiments. K.K. and C.H.P. prepared Ba$_x$K$_{1-x}$Fe$_2$As$_2$ single crystals in the doping range 0.65 ≤ x ≤ 0.85. J.M. and S.A. prepared Ba$_x$K$_{1-x}$Fe$_2$As$_2$ single crystals with x = 0.98. P.C. performed and W.S. supervised TEM measurements.

Data availability

The data represented in Figs. 2–5 are available as Source Data. All other data that support the plots within this paper and other findings of this study are available from the corresponding author upon reasonable request.

Code availability

The code for calculating spontaneous fields within the Ginsburg–Landau model is available with the Supplementary Information files attached to this paper. 47 Kihou, K. et al. Single-crystal growth of Ba$_x$K$_{1-x}$Fe$_2$As$_2$ by KAS self-flux method. J. Phys. Soc. Jpn 85, 034718 (2016).

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Acknowledgements

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measurements. K. Nenkov performed specific heat and magnetization measurements. B.B, R.H. and K. Nielsch supervised the research at IFW. S.-L.D. provided interpretation of the experimental data. VL.V. and M.A.S. performed calculation of the spontaneous magnetic fields in the BTRS state. P.A.V. and I.E. analysed specific heat in the BTRS state. H.L. performed μSR experiments and supervised the research at PSI. H.-H.K. initiated the project and supervised the research. All authors discussed the results and implications and commented on the manuscript.

Competing interests
The authors declare no competing interests.

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Extended Data Fig. 1 | Normal state depolarization rate. (Left axis) Doping dependence of the normal state depolarization rate $\Lambda_0$ extrapolated to zero temperature as shown in Fig. 3 of the main text obtained assuming temperature independent $\sigma$. The error-bars in the absolute value of the depolarization rate is caused by uncertainty in the background contribution. (Right axis) Doping dependence of the static susceptibility measured at $T = 20$ K given in Fig. 2a of the main text. Dashed lines are guides to the eyes. Inset: Doping dependence of the temperature independent depolarization rate $\sigma$. 
Extended Data Fig. 2 | The structure of the spontaneous fields and currents in an s+ is superconductor. The structure of the spontaneous magnetic field (left panels) and spontaneous currents (right panels) produced by the spherically-symmetric inhomogeneity in anisotropic s+ is and s− is states. In the left panels the red/blue arrows show clockwise/counter-clockwise parts of the magnetic field distribution. The clockwise and counter-clockwise field is generated by the supercurrents with jz > 0 (red arrows) and jz < 0 (blue arrows) shown in the right panels. Notice that the magnetic field and current directions are opposite in s+ is and s− is states. The length-scale in the axes is given in units of the zero-temperature coherence length ħν/F. The x, y and z axes are chosen along the a, b and c crystallographic directions, respectively.
Extended Data Fig. 3 | Anisotropy of the internal fields in an $s + i s$ superconductor. Two orthogonal components of the normalized internal spontaneous fields $B_{int}/B_{c2}$ depending on a strength of the variation of the SC coupling constant $\Delta \eta_2$ due to an inhomogeneity. Inset: $\Delta \eta_2$ dependence of the anisotropy ratio of the internal fields $\gamma_{int}$. In the main text $\Delta \lambda \equiv a \Delta \eta_2$ with $a = 1$ (see section 6 in the Supplementary information for details).
Extended Data Fig. 4 | Electrical resistivity. (a) Temperature dependence of the resistivity of the Ba$_{1-x}$K$_x$Fe$_2$As$_2$ single crystals with different doping levels. Inset: Zoom into the temperature range close to $T_c$. (b) The resistivity versus squared temperature. Dashed curves are the fits using $\rho(T) = \rho_0 + A_T T^2$. Inset: Doping dependence of the $A_T$ coefficient. The data for $x=1$ are taken from Ref. 46.

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Extended Data Fig. 5 | Impurity effect on the phase diagram. Doping dependence of the residual resistivity $\rho_0$ of the $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$ single crystals (green triangles, right axis) on top of the phase diagram with the region close to the BTRS dome.