Zero-Field $\mu$SR Search for a Time-Reversal-Symmetry-Breaking Mixed Pairing State in Superconducting $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$

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We report the results of a zero-field muon spin relaxation (ZF-$\mu$SR) study of superconducting $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$ $(0.5 \leq x \leq 0.9)$ in search of weak spontaneous internal magnetic fields associated with proposed time-reversal-symmetry breaking mixed pairing states. The measurements were performed on polycrystalline samples, which do not exhibit the mesoscopic phase separation previously observed in single crystals of $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$. No evidence of spontaneous internal magnetic fields is found in any of the samples at temperatures down to $T \sim 0.02$ K.

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The microscopic mechanism responsible for superconductivity in iron-based superconductors manifests itself in the Cooper-pair wave function symmetry, and consequently the symmetry of the superconducting ground state has been a central issue of investigation. In the 122 iron-based superconductor $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$ there is evidence for a transformation of the pairing symmetry with hole doping. Near optimal hole-doping ($x \sim 0.4$) the pairing state is widely believed to be of $s_\pm$ symmetry, with a full superconducting (SC) gap occurring on hole Fermi surface (FS) pockets at the Brillouin zone (BZ) center ($\Gamma$ point), and a full SC gap of opposite sign present on electron FS pockets centered about the $M(\pi,0)/(0,\pi)$ point. Such an $s_\pm$-wave pairing state may be mediated by spin fluctuations.

Currently being debated is the situation at strong doping, where the electron FS pockets essentially vanish. Laser angle-resolved photoemission spectroscopy (ARPES) measurements indicate that $\text{KFe}_2\text{As}_2$ ($x = 1$) has a complicated SC gap structure, with full and nodal gaps on the inner and middle BZ-centered hole FS pockets, respectively. Meanwhile, magnetic penetration depth, thermal transport, and specific heat measurements on $\text{KFe}_2\text{As}_2$ favor a state of $d$-wave pairing symmetry. The latter results support calculations predicting the evolution of $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$ into a nodal $d$-wave superconductor concomitant with the disappearance of the electron FS pockets. Yet recent ARPES measurements of $\text{Ba}_1\text{K}_9\text{Fe}_2\text{As}_2$ show that despite such a drastic change in the FS topology, isotropic SC gaps consistent with $s$-wave symmetry persist on unaltered hole FS pockets at the $\Gamma$ point.

While it remains unclear whether or how $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$ transforms from a nodeless $s$-wave to nodal $d$-wave superconductor at full doping, a change from one pure pairing symmetry state to another may occur via an intermediate phase of mixed symmetry, where the pure states are nearly degenerate. In particular, a time-reversal-symmetry breaking (TRSB) $s+id$ state has been predicted to occur over some unspecified range of $x$ between optimal and full hole doping. The possibility of a mixed $s+id$ symmetry state in $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$ and other iron-based superconductors has been considered in several subsequent theoretical works. Recently it has been proposed that pure $\text{KFe}_2\text{As}_2$ actually has $s_\pm$ pairing symmetry, but differs from $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$ at optimal doping in that the $s$-wave gaps of opposite sign occur on the hole FS pockets at the $\Gamma$ point. In this case there is the possibility of an intermediate $s+is$ state between optimal and full doping where the $s$-wave gaps on the hole FS pockets transform from having the same to opposite signs. Like the proposed $s+id$ state, the $s+is$ state breaks time-reversal symmetry.

In a bulk superconductor with a TRSB order parameter, weak spontaneous currents are generated around impurities and lattice defects. This should occur even for the above mentioned TRSB multiband $s+is$ state. In such systems ZF-$\mu$SR has been demonstrated to be an ideal local probe of the weak internal magnetic fields ($\sim 0.05$ to 1 G) produced by the spontaneous currents. To date, weak internal fields compatible with a TRSB pairing state have been detected by ZF-$\mu$SR in the superconducting phases of $\text{U}_{1-x}\text{Th}_x\text{Be}_{13}$, $\text{Sr}_2\text{RuO}_4$, $\text{PrOs}_4\text{Sb}_{12}$, $\text{LaNiC}_2$, $\text{PrPt}_4\text{Ge}_2$, $\text{Pr}(\text{Os}_{1-x}\text{Ru}_x)_4\text{Sb}_{12}$, and $\text{Pr}_{1-x}\text{La}_x\text{Os}_4\text{Sb}_{12}$ and most recently in $\text{SrPtAs}_2$. The TRSB states that have been proposed for $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$ do not necessarily occur immediately below the superconducting transition temperature ($T_c$), but may emerge at lower $T$. These two possibilities are depicted in Fig. Here we report a ZF-$\mu$SR search for a TRSB pairing state in $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$ ($0.5 \leq x \leq 0.9$) at temperatures extending down to $T \sim 0.02$ K.
was sealed in a Ta tube, and the Ta tube subsequently
sealed in a quartz tube under 1/3 atmosphere of ultra-
high purity argon. The ampoule was gradually heated
to 750 °C in a programmable furnace at a ramp rate of
15 °C per hour. After staying at 750 °C for 48 hours,
the furnace was shut off. The mixture was taken out of
the alumina crucible and thoroughly ground to ensure
homogeneity, and then pelletized inside of a glove box.
The pellets have a diameter of 1.8 cm and weigh ~4.5 g.
Each pellet was then loaded into an alumina crucible and
sealed in a Ta tube. The final sintering was performed
at 900 °C for 48 hours. Room temperature x-ray pow-
der diffraction was performed on a PANalytical X’Pert
Pro MPD powder x-ray diffractometer using Cu Kα radia-
tion. The x-ray powder diffraction pattern confirmed
that all of the samples are essentially single phase. The
$T_c$ value of each sample was determined from the temper-
ature dependence of the bulk magnetization, measured at
an applied magnetic field of 20 Oe with a Quantum De-

FIG. 1: (Color online) Schematic phase diagram of
$\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$ as a function of temperature $T$ and $x$, show-
ing a predicted mixed TRSB pairing state ($s+id$ or $s+is$)
occurring somewhere between $x=0.4$ and $x=1$. The $s_\pm$
(he) state corresponds to $s$-wave gaps of opposite sign on the
hole (h) and electron (e) FS pockets. The $s_\pm$ (hh) state corre-
sponds to $s$-wave gaps of opposite sign on the hole FS pockets
at the Γ point in the BZ (in the absence of electron FS pockets)
as proposed in Ref. [18]. In (a) the TRSB mixed symmetry
state onsets at $T_c$ for a certain value of $x$, whereas in (b) it
occurs significantly below $T_c$, irrespective of $x$. In (b) the pure
$s_\pm$ (he) state evolves continuously into the pure $s_\pm$ (hh) state
at temperatures above the $s+is$ state. On the other hand,
a first-order transition (represented by a nearly vertical line)
occurs between the pure $s_\pm$ (he) and d-wave states at tem-
peratures between $T_c$ and the onset of the $s+id$ state.

Single crystal growth of $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$, especially for
overdoped compositions, is rather challenging due to the
vaporization and reaction of K with the alumina cru-
cibles. Our own growth efforts failed to obtain uniform
crystals with controlled K-contents, and consequently
polycrystalline samples were used in the present study.
The $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$ ($x=0.5$, 0.6, 0.7, 0.8, and 0.9) samples were synthesized starting with the individual el-
ments. First, purified Fe and As powders, and small
pieces of Ba and K were mixed and loaded into an alu-
mina crucible inside of a glove box. The alumina crucible
was sealed in a Ta tube, and the Ta tube subsequently

FIG. 2: (Color online) Representative ZF-$\mu$SR asymmetry
spectra of $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$ for (a) $x=0.5$, (b) $x=0.8$, and
(c) $x=0.9$, measured with the sample contained in a He$^4$
continuous-flow cryostat. The solid curves superimposed on
the data points are fits to Eq. (1), which are described in the
main text.
sign Magnetic Properties Measurement System — yielding $T_c = 47, 30, 20, 11,$ and 8 K for the $x = 0.5, 0.6, 0.7, 0.8,$ and 0.9 samples, respectively. The transition width for all samples is $\pm 1$ K. These values of $T_c$ agree with previous literature reports.

The ZF-$\mu$SR measurements were performed at TRIUMF in Vancouver, Canada, on the M15 surface positive muon ($\mu^+$) beam line, using a Quantum Technology Corp. side-loading, He$^4$ continuous-flow cryostat for measurements down to $T \sim 2$ K, and an Oxford Instruments dilution refrigerator for measurements down to $T \sim 0.02$ K. In the cryostat the samples were suspended with thin aluminized Mylar tape, and in the dilution refrigerator mounted on a pure Ag sample holder — in both cases to avoid a temperature-dependent background contribution to the ZF-$\mu$SR signal from materials with electron magnetic dipole moments. A “veto” detector placed downstream of the sample was used to reject muons that did not stop in either the sample or the sample holder.

An implanted $\mu^+$ precesses about the local magnetic field $B$ with a Larmor frequency $\omega = \gamma_\mu B$, where $\gamma_\mu$ is the muon gyromagnetic ratio. In the SC phase, diamagnetic screening of any external magnetic field along the muon spin direction can result in the onset of an enhanced temperature-dependent relaxation of the ZF-$\mu$SR signal at $T_c$, mimicking the effect of induced weak spontaneous internal fields associated with a TRSB pairing state. Even if the mixed TRSB states predicted for Ba$_{1-x}$K$_x$Fe$_2$As$_2$ occur only at temperatures well below $T_c$, the additional temperature-dependent relaxation caused by diamagnetism can mask the contribution of the weak spontaneous fields. Hence it is crucial to minimize the external field in this type of experiment. This was achieved by using 3 orthogonal pairs of Helmholtz coils to compensate for the magnetic field penetrating quartz or pure Si placed at the sample position. In quartz or Si the positive muon binds to an electron to form the hydrogen-like state muonium (Mu $\equiv \mu^+e^-$), where the muon senses its local environment through the coupled electron. The much larger magnetic moment of the electron provides an enhanced sensitivity to internal magnetic fields, such that the gyromagnetic ratio of Mu is $\gamma_{\text{Mu}} \sim 103\gamma_\mu$. By this method the external magnetic field contribution at the sample position was reduced to less than 0.1 Oe.

Earlier $\mu$SR experiments on single crystals detected a coexistence of mesoscopic phase-separated static magnetic order and nonmagnetic/SC regions near $x = 0.5, 0.6, 0.7$ whereas a ZF-$\mu$SR study of polycrystalline samples of Ba$_{1-x}$K$_x$Fe$_2$As$_2$ reported microscopic coexistence of magnetism and superconductivity in the underdoped region $x \leq 0.23$. Figure 2 shows a comparison of the ZF-$\mu$SR asymmetry spectra of our $x = 0.5, 0.8$ and 0.9 polycrystalline samples at a temperature far above $T_c$, and in the superconducting phase at $T \sim 2$ K. The absence of a coherent oscillation in these ZF-$\mu$SR time spectra is compatible with investigations of the magnetic phase diagram of polycrystalline Ba$_{1-x}$K$_x$Fe$_2$As$_2$ by other techniques, which indicate that antiferromagnetic ordering vanishes by $x = 0.3$. Furthermore, the lack of an appreciable temperature dependence to the ZF-$\mu$SR signal indicates that randomly oriented or isolated quasi-static electronic magnetic moments are also absent.

The solid curves through the data points of the asymmetry spectra in Fig. 2 are fits to

$$A(t) = A(0)G_{\text{KT}}(t) \exp[-\lambda(T)t],$$

where $G_{\text{KT}}(t) = \left[1 + \frac{2}{3}(1 - \Delta^2t^2)e^{-\Delta^2t^2/2}\right]$ is a “static Gaussian Kubo-Toyabe function”. It is used here to account for the time evolution of the muon-spin polarization caused by the randomly oriented nuclear moments in the sample, which generally contribute a temperature-independent Gaussian distribution in field of width $\Delta/\gamma_\mu$. For the low-$T$ measurements in the dilution refrigerator there is a small additional temperature-independent contribution to the ZF-$\mu$SR signal from muons stopping in the sample holder. While this component necessarily adds to the sample signal, we find good fits are still achieved using Eq. (1). The fitted value of $\Delta$ is essentially independent of K concentration [see Fig. 3(f)], indicating a minor change in the nuclear dipole contribution. The exponential relaxation function in Eq. (1) is intended to account for any additional sources of internal magnetic field, and unlike $\Delta$ was free to vary with temperature in the fits to the ZF-$\mu$SR signals. As shown in Figs. 3(a) to 3(e), the exponential relaxation rate $\lambda$ does not systematically vary with $x$ nor
The larger value of $\lambda$ at $T = 2$ K for the $x = 0.8$ sample measured in the He$^4$ cryostat [see Fig. 3(d)] is caused by muons stopping upstream of the sample in dense helium gas, where the external magnetic field is larger. This is obvious from the low-temperature measurements carried out using the dilution refrigerator. As shown in Fig. 4(a), the ZF-$\mu$SR signal at $T = 0.02$ K does not vary with $x$. Moreover, there is no onset of an increased relaxation rate of the ZF-$\mu$SR signal at any temperature below $T_c$.

Despite the theoretical predictions, the absence of spontaneous internal magnetic fields in our measurements suggests that a TRSB mixed symmetry pairing state does not occur at or below $x = 0.9$. With this said there are a few possibilities to consider: (i) The region where the $s+id$ (or $s+is$) state is present may be very narrow and fall between two of the dopings studied here. (ii) There may simply be a first-order phase transition between the pure symmetry states at all temperatures below $T_c$. (iii) In the coexistence region, the predominant tendency may be states with the same phase, such as $s+id$, which do not break time-reversal symmetry. Possibilities (ii) and (iii) have been discussed in Ref. 17 as a consequence of the presence of nematic fluctuations. Finally, there is the possibility that formation of the $s+id$ state is thwarted by impurity scattering in the real material. In pure KFe$_2$As$_2$, substitution of Fe by small concentrations of Co rapidly suppresses $T_c$, reminiscent of the high sensitivity of a $d$-wave superconductor to impurity scattering. Likewise, it is possible that the $s+id$ state is equally sensitive to Ba substitution of K between the FeAs layers.

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