The discovery of iron pnictide superconductors \[1\]–\[4\] has attracted intense research interest. The two most prominent features of high-temperature superconductivity in these systems are the following. First, the iron pnictide superconductors originate from antiferromagnetic semimetals \[3\], with multiple electron and hole Fermi surfaces which are gapped in the superconducting state \[3\]–\[6\]. Second, there are pronounced spin fluctuations \[7–9\], which are gapped and condense into a spin resonance mode \[10–13\]. These observations suggest that both magnetic correlations and interband transitions between the Fermi surfaces are essential intrinsic properties, and support an \(s^\pm\) gap symmetry in the superconducting state \[14–16\].

High-temperature superconductivity has also been observed very recently in the ternary iron selenides \(A_xFe_{2−x}Se_2\) (\(A = K, \text{Rb, Cs}, \ldots\)) \[10, 20\]. The transition temperature, \(T_c \sim 32\) K, is very much higher than that in the binary system FeSe at the ambient pressure \[21\], and is surprising because the system is thought to be heavily electron-doped. Initial angle-resolved photoemission (ARPES) studies \[22, 23\] revealed only one or more large electron bands on the Fermi surface, while a hole band is yet to be confirmed. Theoretically, a band insulator \[24\], possibly with magnetic correlation effects \[23\], has been suggested for the stoichiometric compound \(AFe_2Se_2\). However, iron-vacancy order affects both the normal-state metallic behavior and the superconductivity in \(A_xFe_{2−x}Se_2\) very strongly \[19, 20\]. These facts immediately raise the question of whether the superconducting gap symmetry and magnetic correlations in this newest family of iron selenide superconductors are in fact quite different from the pnictides and the Fe(Se,Te) systems.

Nuclear Magnetic Resonance (NMR) is a bulk probe, which is extremely sensitive to the low-energy excitations associated with electronic correlation effects, and thus to the pairing symmetry of superconducting states. The Knight shift, \(K\), probes the static electron susceptibility \(\chi(q)\) at \(q = 0\), while the spin-lattice relaxation rate \(1/T_1\) measures a weighted sum of \(\chi'(q)\) over all momenta. We have performed \(^{77}\)Se Knight-shift and \(1/T_1\) measurements on single crystals of \(K_yFe_{2−x}Se_2\). The Knight shift we observe provides direct evidence for singlet pairing symmetry in \(K_yFe_{2−x}Se_2\). However, the Hebel-Slichter coherence peak in \(1/T_1\) is not present at the field (11.764 T) of our measurements. We find Korringa-type behavior in \(^{77}\)K and \(1/T_1\) above \(T_c\), suggesting that the superconducting state forms from a Fermi-liquid state.

Single crystals \(K_yFe_{2−x}Se_2\), with \(T_c \approx 30\) K, were synthesized by the Bridgeman method \[20\]. For our NMR study, two single crystals with approximate dimensions \(~3\times2\times0.5\text{mm}^3\) were chosen. The determination of exact stoichiometries in the \(A_yFe_{2−x}Se_2\) series has been found, after several measurements by different techniques to be complex and subtle issue. For an accurate characterization of our samples, we have used inductively coupled plasma (ICP) measurements, which determined sample S1 to have composition \(K_{0.82Fe_{1.63}Se_2}\) and to show a monotonic increase of resistivity with temperature up to 300 K. Sample S2 was determined to have stoichiometry \(K_{0.68Fe_{1.62}Se_2}\) and to show a resistivity peak around 150 K \[20\]. Bulk superconductivity was confirmed by measurements of DC magnetic susceptibility \([\text{Fig. 1(a)}]\) and heat capacity \[20\]. Transmission Electron Microscopy (TEM) and X-ray diffraction measurements \[27, 28\] have suggested a bulk ordering of Fe vacancies in crystals grown under the same conditions. Enlargement of the crystalline unit cell, consistent with such ordering, is supported by the observation of many additional phonon modes observed in Raman-scattering \[20\] and infrared studies \[30\].

Sample S1 was placed on a rotator, which allows the orientation of the NMR field (11.764 T) to be changed from the crystalline \(ab\)-plane to the \(c\)-axis. The superconducting transition was monitored \textit{in situ} by the high-frequency response of the NMR coil, and \(T_c\) determined from the sharp increase in frequency upon cooling [inset \text{Fig. 1(a)}]. For S1, \(T_c\) is higher for fields in the \(ab\)-plane than for field along the \(c\)-axis. This anisotropic suppression of \(T_c\) in the NMR field is consistent with the results of Ref. \[20\]. S2 was ground into a coarse powder to gain better RF penetration below \(T_c\). The Knight shift \(^{77}\)K(\(T\)) is obtained from \(K(T) = (f − \gamma_n B)/\gamma_n B\), where \(^{77}\gamma_n = 8.118\ T/\text{MHz}\) is the gyromagnetic ratio of \(^{77}\)Se and \(f\) is the measured resonance frequency in the mag-
We suggest that the behavior below low temperatures, where it falls abruptly from $T_c$ to $T_\text{c}/2$, however, $\gamma^2 K(T)$ changes little. We suggest that the behavior below $T_c/2$ is governed by vortex-core contributions, because the RF screening effect is strong in the superconducting regions. Here we neglect the superconducting diamagnetic shift, which has been found \[31\] to be very small in another superconductor from the same structural family of iron selenides.

To gain further insight into the gap symmetry, we have measured the spin-lattice relaxation rate of $^{77}\text{Se}$, shown in Fig. 3. For S1, data was taken from 30 K to 100 K with field along the $c$-axis. For S2, measurements were performed from 2 K to 35 K. Above $T_c$, $^{77}\text{K}$ increases with temperature, and in the overlapping temperature range we find no appreciable difference between the two field orientations. This indicates an isotropic Knight shift above $T_c$. Figure 2(c) shows the detailed features of $^{77}\text{K}(T)$ at low temperatures, where it falls abruptly from $T_c$ down to $T_c/2$. Below $T_c/2$, however, $^{77}\text{K}(T)$ changes little. We suggest that the behavior below $T_c/2$ is governed by...
1/\(T_1 \sim T^6\). If 1/\(T_1\) were determined by a single, constant energy gap, one would expect 1/\(T_1 \sim e^{-\Delta/k_B T}\). Taking the value \(\Delta \approx 10.3\) meV from the ARPES measurements of Ref. 23, the activation curve offers a reasonable fit to our data only in the region from \(T_c\) down to approximately \(T_c/2\).

The absence of a coherence peak in cuprate superconductors is interpreted as evidence for \(d\)-wave pairing. Such observations have been reported in many iron-based superconductors \([34–40]\), and has been interpreted as a indication of \(s^\pm\) symmetry on separate Fermi surfaces \([11,43]\). However, the orbital symmetries of these studies may not be applicable in K\(_x\)Fe\(_{2−x}\)Se\(_2\), where the presence of a hole band at the center of the Brillouin zone has not been confirmed despite a number of ARPES investigations. Further, a nodeless gap has been suggested in one ARPES study \([23]\). We note here that our data are obtained in a high magnetic field, and thus that measurements at much lower fields will be required to exclude the possibility that K\(_x\)Fe\(_{2−y}\)Se\(_2\) may in fact be a system with a field-suppressed coherence peak, as has been found in A\(_3\)C\(_{60}\) superconductors \([40]\).

We turn next to 1/\(T_1^7\) in the normal state. As shown in Fig. 3, 1/\(T_1^7\) is isotropic with field orientation and increases with temperature above \(T_c\). In inset (a) we show 1/\(T_1^7 T\) for both samples. This quantity is almost \(T\)-independent over a substantial range above \(T_c\), before increasing rapidly at higher temperatures. For a Fermi liquid, 1/\(T_1 T\) is a constant depending on the density of states at the Fermi level. Further, a Fermi liquid satisfies the Korringa relation, 1/(\(T_1 T\))\(^{0.5}\) \(\propto K_x\), where the spin part of the Knight shift is given by \(K_x(T) = K(0) - K_c\) and the chemical shift \(K_c\) is temperature-independent. We show in Fig. 4 the relation between 1/(\(T_1 T\))\(^{0.5}\) and \(K(T)\) for S1 in the temperature range between 30 K and 140 K. The linear dependence demanded by the Korringa relation is obvious. The gradient \(k\) in Fig. 4 appears in the Korringa ratio, \(S = (4\pi k_B/h)(\gamma_n/\gamma_e)^2/k^2 = (4\pi k_B/h)(\gamma_n/\gamma_e)^2 T_1 T K_c^2\). From our data, \(S \approx 0.8 - 1.5\) between 30 K and 140 K, which falls in the range for a canonical Fermi liquid with no strong ferromagnetic (\(S \gg 1\)) or antiferromagnetic (\(S \ll 1\)) spin fluctuations \([47,49]\). Our data therefore indicate strongly a rather conventional Fermi-liquid state for the conduction electrons in K\(_x\)Fe\(_{2−y}\)Se\(_2\) above \(T_c\).

Before leaving Fig. 4 we comment briefly that the \(K\)-axis intercept yields \(T_7 \approx 0.08\). Usually \(K_c\) can be obtained directly in the superconducting state, where \(K_x(T)\) approaches zero as \(T \to 0\). In Fig. 2(c), the flattening of \(T_7\) below 15 K indicates a higher value, \(T_7 \approx 0.13\%\); this latter method may, however, overestimate \(T_7\) because \(T_7\) can be enhanced by the high NMR field used in our experiments. Above \(T_c\), activated increases of \(K\) and 1/\(T_1\) with increasing temperature have been observed in some iron pnictide superconductors, and have been interpreted as a pseudogap state \([50]\). We stress that our \(T_7\) data for K\(_x\)Fe\(_{2−y}\)Se\(_2\) can be fitted by the simple function \(K(T) = a + bT^2\) up to 300 K [Fig. 2(b)], with parameters \(a \approx 0.23\%\) and \(b \approx 6 \times 10^{-6}\%/K^2\). It is currently not clear whether this increase of \(T_7\) with temperature can be caused by a band effect or by a magnetic correlation effect \([50,51]\). The Knight shift of 0.74% at room temperature is to our knowledge the largest yet measured among the iron-based superconductors.

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**FIG. 3:** (color online) Temperature-dependence of the spin-lattice rate 1/\(T_1^7\) for both samples. Inset (a): data shown as 1/\(T_1^7 T\). Inset(b): 1/\(T_1^7\) shown on logarithmic axes at low temperatures. Solid lines indicate different types of power-law dependence (1/\(T_1 \sim T^n\)), while the dotted line is a fit to an activated form 1/\(T_1^7 = A\exp(\Delta/k_B T)\) (see text).

**FIG. 4:** (color online) Korringa plot of 1/(\(T_1^7 T\))\(^{0.5}\) against \(T_7\) with temperature as an implicit parameter. The solid line represents the Korringa relation.

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In the binary iron superconductor FeSe, strong antiferromagnetic spin fluctuations, with a Curie-Weiss upturn in $1/T_1T \sim 1/(T + \Theta)$, are indicated \[4\]. It has been argued that these spin fluctuations are responsible for superconductivity. A similar Curie-Weiss upturn in $1/T_1T$ has also been reported in many iron pnictide superconductors, \[9, 50, 52–56\]. These are in contrast to our $K_xFe_2-xSe_2$ samples, where no upturn of $1/T_1T$ is detected. However, we caution that our measurements cannot exclude antiferromagnetic spin fluctuations at the wave vector $q = (\pi, \pi)$, because these would cancel at the Se site due to its location at the center of the Fe square \[17\]. We note in this context that low-energy spin fluctuations are also rather weak in the overdoped $LaFeAsO_1-xF_x$ compound, while $T_c$ is reasonably high ($T_c \approx 40$ K at 3 GPa pressure) \[57\]. In summary, we have performed $^{77}$Se Knight shift and $1/T_1T$ measurements on single crystals of the iron-based superconductor $K_xFe_2-xSe_2$. The Knight shift demonstrates bulk singlet superconductivity. However, no coherence peak is observed under the measurement field. We find Fermi-liquid behavior above $T_c$, which further indicates an absence of strong low-energy spin fluctuations on the Se site in the normal state. Our experimental evidence for singlet superconductivity with no coherence peak and no clear evidence of spin fluctuations on the Se site constitutes essential ingredients in formulating a complete understanding of this newest family of iron selenide superconductors. Such an understanding would in turn contribute to unravelling the mystery of high-$T_c$ superconductivity in general.

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\[\text{[54x338]}\] T

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