The discovery of high-temperature superconductivity in iron pnictides has attracted a lot of research interests. Recently, high-temperature superconductivity is also observed in the ternary iron selenide AₙFe₂₋ₓSe₂ (A=K, Rb, Cs, etc.) with Tc ~ 32 K, which is much higher than that of the binary iron selenide α-Fe₁₋ₓSe at the ambient pressure. Compared with other iron-based superconductors, K₀.₈Fe₂₋ₓSe₂ shows distinctive properties. First, iron vacancy seems to heavily electron doped while the hole band is absent. Theoretically, a band insulator, and possibly with magnetic correlations, has been suggested in stoichiometric AFe₂Se₂. However, evidence of antiferromagnetic (AFM) spin fluctuations are not obvious.

These observations immediately lead to the question whether the superconducting properties of KₓFe₂₋ₓSe₂ are the same as that of the iron pnictides and α-Fe₁₋ₓSe, where the AFM spin fluctuations and interband interactions are believed important for the superconductivity. In K₀.₈Fe₂₋ₓSe₂, a large isotropic gap is suggested by the ARPES, and preliminary NMR data give a bulk evidence of singlet pairing. So far the superconducting properties are not intensively investigated in the ternary iron selenides, and more work is necessary in order to gain better understanding on the mechanism of the superconductivity.

In this paper, we report our ⁷⁷Se NMR Knight shift (⁷⁷Kₐ) and spin lattice relaxation rate (1/⁷⁷T₁) studies on high quality K₀.₈Fe₂₋ₓSe₂ single crystals (Tc ranging between 29.5-32 K). Below Tc, the Knight shift decreases with T. However, the 1/⁷⁷T₁ does not show a coherence peak. In fact, the SLRR decreases rapidly down to Tc/2, which can be fit with a single isotropic gap Δ ≈ (3.8 ± 0.5)kBTc. These data gives bulk evidence for a strongly coupled superconductor with a singlet pairing and an isotropic gap. Below Tc/2, however, the Kₐ ceases to decrease with T, and the 1/⁷⁷T₁ shows a 1/⁷⁷T₁ ∼ T² behavior. We discuss these low-temperature behaviors with possible intrinsic low energy excitations, or vortex core contributions.

The K₀.₈Fe₂₋ₓSe₂ single crystals were synthesized by the flux-growth method. For this NMR study, two large single crystals (S1 and S2) with a dimensions of 3×2×0.5mm³ is chosen for the measurements. Sample S1 was also used for the normal state studies reported elsewhere. Sample S2, from the same batch, is moderately grounded into small pieces to gain better RF penetration (see Fig. 1 for the susceptibility data). The ⁷⁷Se Knight shift and the spin-lattice relaxation rate (SLRR) measurements were performed under a 12 Tesla magnetic field, and the superconducting transition is observed at 29.5 K for S1 and 31 K for S2 under field. We compared the data for sample S1 with $H//ab$ and $H//c$.
$H//c$, and for sample S2 primarily sampling the spectra with $H//ab$. The Knight shift $K_n(T)$ is obtained from $K_n(T) = (f - f_0)/f_0$, where $f_0 = \gamma B$ is the calculated frequency, and $f$ is the measured frequency of spectral maximum. The SLRR is deduced from the spin recovery after an inversion pulse, with the spectra collected with a CPMG sequence $((\pi/2)_z - \pi_y - echo - \pi_y - echo...)$ to maximize the signal-to-noise ratio. Our spin recovery data is well fit by the single exponential function $I(t)/I(0) = 1 - be^{-t/T}$. In general, the Knight shift is proportional to the electron density of states on the Fermi surface, which decrease below $T_c$. The spin-lattice relaxation rate $1/T_1$ is in the superconducting state are correlated with the normal state $1/T_1n$ by 

$$\frac{T_{1n}^{-1}}{T_{1s}^{-1}} = \frac{2}{k_BT} \int_{0}^{\infty} \left[ \frac{N_S(E, \Delta)}{N_0(E)} \right]^2 f(E)(1 - f(E)) dE \quad (1)$$

where $N_S(E, \Delta)$ and $N_0(E)$ are the electron density of states in the normal state and in the superconducting state respectively, and $f(E)$ is the Fermi-Dirac distribution function with $f(E) = 1/(e^{E/k_BT} + 1)$.

The temperature dependence of the Knight shift $^{77}K_n$ for two samples with different field orientations are shown in Fig. 2. Above $T_c$, the Knight shift is isotropic, and decreases gradually as temperature drops. Below $T_c$, the Knight shift drops faster with field along the $ab$-plane ($^{77}K_n^{ab}$) than with field along the $c$-axis ($^{77}K_n^c$) for sample S1, indicating an anisotropic $H_C2$. The $^{77}K_n^{ab}$ are consistent for sample S1 and S2, and we primarily discuss the results of sample S2 in the following. In general, the Knight shift $K_n(T)$ is written as $K_n(T) = K_c + K_s(T)$, where $K_c$ is the chemical shift and $K_s(T)$ is the contribution from the spin part. Our analysis on $^{77}K_n(T)$ in the normal state gives a constant $^{77}K_c$ of $\approx 0.05\%$, and the $K_s(T)$ changing with temperature.

A large decrease of $K_n$ is clearly seen from $T_c$ down to $T_c/2$, which suggests that the system is primarily a singlet superconductor. This is consistent with most iron arsenide superconductor. For comparison, the decrease of $K_n$ has not been reported by $\alpha$-FeSe system below $T_c$ to our knowledge.

In order to gain more insight on the pairing symmetry, the low-energy excitations are studied by the spin-lattice relaxation rate, as shown in Fig. 3 The SLRR is isotropic above $T_c$ and anisotropic below $T_c$, and we only discuss $1/T_1^{ab}$ for sample S2 with $H//ab$. Above $T_c$, the SLRR is consistent with a canonical Fermi liquid with $^{77}T_1^{ab}K_n^{2}$ as a constant. Below $T_c$, the $1/T_1^{ab}$ drops quickly with temperature. As shown in Fig. 3(b), two orders of magnitude difference in the SLRR is seen in a large temperature range from $T_c$ down to $T_c/2$. The temperature dependence is close to a power-law behavior with $1/T_1^{ab} \sim T^6$, as shown in Fig. 3. Such a rapid decrease is much faster than the $1/T_1 \sim T^3$, which suggests that the line node is absent or not obvious in $K_{0.8}Fe_{2-x}Se_2$.

For conventional superconductors, the superconducting gap $\Delta(T)$ increases from zero as temperature drops below $T_C$, which produces a Hebel-Slichter coherence peak from $T_c$ down to 0.8 $T_c$. In $K_{0.8}Fe_{2-x}Se_2$, our data does not show evidence of a coherence peak. The absence of the coherence peak draws a similarity to other iron-based superconductors, which will be discussed later.

For an isotropic singlet superconductor, the SLRR far below $T_c$ (Eq. 1) can be simplified $1/T_1 \sim e^{-\Delta/k_BT}$, where $\Delta$ is the superconducting gap. We fit the $1/T_1^{ab}$ with a constant gap slightly below $T_c$, and $\Delta \approx 10.8 \pm 2$ mev is obtained as shown by the fit in Fig. 3(b). Such a large value produces $\Delta/k_BT \approx 3.8$, over
two times of the BCS value $\Delta/k_B T_c = 1.75$. Our obtained value is very close to the ARPES data\textsuperscript{25}, and gives the bulk evidence for a strongly coupled, isotropic superconductor. Here we assumed that the gap opens quickly with temperature to get the full value of $\Delta(0) \sim 4k_BT_c$ about 2 Kelvin below $T_c$, so that the coherence peak diminishes naturally.

In all, the temperature behavior of the Knight shift and the SLRR from $T_c$ down to $T_c/2$ suggest a strongly coupled, singlet superconductivity with an isotropic gap, which is similar to other iron pnictides\textsuperscript{11-14}. From our data, we cannot give direct evidences for multiple superconducting gaps in $K_{0.8}Fe_2Se_2$. However, multiple gaps with close values in different bands should lead to a single gap behavior in the SLRR. Furthermore, the absence of the Hebel-Slichter coherence peak, well known in other iron pnictide superconductors, may be an indirect evidence for multiple gaps with strong impurity scattering effect\textsuperscript{24}.

For iron pnictides, an $s\pm$ gap symmetry has been suggested due to the interband interactions between the electron band and the hole band\textsuperscript{25-28}. Antiferromagnetic spin fluctuations are probably also important for the superconductivity in both the iron pnictides\textsuperscript{22} and the $\alpha$-FeSe system\textsuperscript{24}. In $K_{0.8}Fe_2Se_2$, however, the hole band is not observed in the center of the Brillouin zone due to heavy electron doping. The AFM fluctuations are not observed by NMR studies\textsuperscript{23}. Then the issue rises how to connect the pairing symmetry with the band structure and the spin fluctuations in $K_{0.8}Fe_2Se_2$, since the superconducting properties are similar for different compounds. It is possible that other types of spin fluctuations are effective to the superconductivity\textsuperscript{16,17}.

Below $T_c/2$, the temperature behavior of the Knight shift and the SLRR are unexpected. In principle, $\rho(T)$ should drop to $K_c \approx 0.5\%$ as $T \rightarrow 0$ (or $K_c(T) \rightarrow 0$) for a singlet superconductor. However, the spin-part of the Knight shift $K^c/T^c$ below $T_c/2$ levels off with a residual value of 0.09\% (Fig. 2), by taking off our estimated value of $K_c \approx 0.05\%$. Currently we are not aware whether the large residual $K_c$ as $T \rightarrow 0$ is intrinsic, or possibly due to vortex contributions.

The SLRR also shows a slower decrease with $1/T^2$ below $T_c/2$ (Fig. 3). In fact, such behavior has also been reported in various iron-based superconductors. If we assume the low temperature behavior is intrinsic, low energy excitations are expected to raise the Knight shift and the SLRR rate. Such small value may indicate small gap minimum on the Fermi surface. Applying a two-gap function for the $1/T^2$, a second gap of $\Delta_2 \sim 0.25T_c$ with a very low electron density of states ($\sim 0.1\%$) is obtained. Alternatively, these behaviors could also be caused by vortex core contribution\textsuperscript{30}, which is unlinked to the superconductivity regions. Measurements under different fields may be helpful to verify if the vortex contributions exists.

To summarize, our NMR Knight shift study on $K_{0.8}Fe_2Se_2$ has shown the bulk evidence of singlet superconductivity. The spin-lattice relaxation data further support a strongly coupled superconductor with an isotropic gap $\Delta \approx 3.8k_BT_c$. The coherence peak is not observed in the SLRR, and may be an indirect evidence for unconventional superconductivity. These observation draw a lot of similarities of the pairing symmetry among $K_{0.8}Fe_2Se_2$ and other iron-based superconductors, although their respective band structure and the magnetic correlations seem to be very different. We also observed a level off of the Knight shift and a low-power behavior of the SLRR below $T_c/2$, which are not understood.

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