Unconventional Superconductivity in the Novel Layered Superconductor Fe(Te-Se) Investigated by $^{125}$Te NMR on the Single Crystal

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We have performed $^{125}$Te NMR on a single crystal of the novel layered superconductor Fe$_{1.04}$Te$_{0.67}$Se$_{0.33}$ for the first time. The spin parts of the Knight shifts for both $H//a$, $H//c$ are suppressed in the superconducting state, indicating the spin singlet superconductivity. At superconducting state, $1/T_1$ shows the power-law behavior ($\sim T^3$) without any coherent peaks. Observations of the residual density of state and the $T^3$-law indicate the presence of the line node in the superconducting gap. In the normal state, $1/T_1T$ which probes the $\mathbf{q}$-summation of spin fluctuations enhances at low temperatures. Our results suggest that the superconductivity in Fe$_{1+y}$Te$_{1-x}$Se$_x$ is stabilized by the growth of the antiferromagnetic spin fluctuations as well as in FeSe.

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Since recent discoveries of iron based superconductors with the superconducting transition temperature ($T_c$) being 55 K in the highest cases [1, 2, 3, 4], many studies have been done to search new materials with high $T_c$ and to clarify the mechanism of superconductivity. In such investigations, the superconductivity was discovered with $T_c = 8$ K in the $\alpha$-FeSe system [5]. The $\alpha$-FeSe has a simple layered structure, in which the tetragonal FeSe layers stack continuously along the $c$-axis without insertion of another layers. However, the presence of Se defects are discussed in the report of the discovery of the superconductivity [6], Williams et al. indicated that the stoichiometric FeSe is the most preferable for the superconductivity [6], since the excess irons should suppress the superconductivity [7]. In the next stage, superconductivity in Se-substituted (maximum $T_c = 14$ K [8, 9]) and S-substituted (maximum $T_c = 10$ K [10]) systems at the Te sites in FeTe which is isostuctural with the superconducting FeSe were discovered. Fang et al. presented that the end member $\alpha$-FeTe shows a magnetic phase transition at 65 K and the superconductivity of Fe$_{1-x}$Te$_x$Se$_x$ occurs when the magnetic phase transition is suppressed by the increase of $x$ [8]. Because these Fe chalcogenide systems FeSe and Fe$_{1-x}$Te$_x$Se$_x$ layers have the simplest structure of stacked quasi-two dimensionally, we can regard them as important key compounds to clarify the intrinsic properties of Fe-based superconductors.

In all Fe-based superconductors, the superconductivity occurs in the vicinity of the magnetic phase. Therefore, the magnetic fluctuations are thought to play an important role in the Fe-based superconductors. NMR is a powerful probe to investigate low energy excitations of fluctuated spins. Imai et al. presented that in almost stoichiometric FeSe, the relaxation rate divided by temperature $(1/T_1T)$ which is proportional to the $\mathbf{q}$-summation of the imaginary part of the dynamical spin susceptibility $\chi(q)$ is enhanced at low temperatures [11]. In a slightly Fe-rich Fe$_{0.99}$Se$_{0.01}$ sample, the short $T_1$ component $1/T_1$ST also shows the enhancement with decreasing temperature together with almost constant $1/T_1LT$ of the long $T_1$ component $12, 13$. From a point of view of electron spin fluctuations, there would be two-types in Fe-based superconductors: one shows the enhancement of $1/T_1T$ at low temperatures and the other does not show such the enhancement. The former includes the 122-system (e.g. Ba$_{1-x}$K$_x$Fe$_2$As$_2$) [14, 15, 16, 17], and the 11-system (e.g. FeSe) [11, 13], and the latter the 1111-system (e.g. LaFeAsO$_{1-x}$F$_x$) [18, 19, 20]. Even if there are some differences in each compound, it should be quite natural to consider that all the Fe based superconductors have the same superconducting mechanism. It is therefore very important to investigate the spin fluctuations and the antiferromagnetic quantum criticality of the Fe based superconductors. Our purpose is to clarify the role of spin fluctuations from the antiferromagnetic FeTe to superconducting Fe$_{1+y}$Te$_{1-x}$Se$_x$ systematically. In this letter we present $^{125}$Te NMR studies in the single crystal Fe$_{1.04}$Te$_{0.67}$Se$_{0.33}$ for the first time.

The Te site in antiferromagnet FeTe can be substituted by Se in all the composition range [8, 9], and excess irons are doped in the other Fe site as nonstoichiometric Fe$_{1+y}$Te$_{1-x}$Se$_x$ [21, 22]. Since there is a variety of nonstoichiometry, characterizations of samples are so important.

The single crystal of Fe$_{1.04}$Te$_{0.67}$Se$_{0.33}$ was prepared by the self-flux method in an evacuated quartz tube. The sample used for NMR measurements is the same as the previous report [23]. The sample was characterized by X-ray diffraction, and the compositions were determined by energy dispersive spectroscopy. The crystal axes were also decided by Laue photographs. All NMR measurements were carried out by using spin-echo method with a standard phase coherent-type NMR pulsed spectrometer applying the magnetic field $H$ parallel to the $a$ or $c$-axis. NMR spectra were measured with sweeping mag-

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magnetic field in a constant NMR frequency. The nuclear spin-lattice relaxation time ($T_1$) was measured by inversion recovery method. $^{125}$Te nucleus with the nuclear spin $I = 1/2$ has the nuclear gyromagnetic ratio $\gamma = 13.454$ MHz/T. The magnetic field was calibrated by using reference signals of $^2$D in D$_2$O and $^{125}$Te in TeCl$_4$aq.

In the Fe$_{1+5}$Te$_2$Se$_{1-x}$ system, excess irons are thought to suppress the superconductivity, e.g., the upper critical field ($H_{c2}$), and this situation is similar to the case of Fe$_{1+5}$Se$_2$.[2, 23] Fe$_{1.04}$Te$_{0.67}$Se$_{0.33}$ shows large superconducting volume fraction while Fe$_{1.12}$Te$_{0.72}$Se$_{0.28}$ shows small fraction.[22] From the results of the electric resistivity measurements, both samples show the onset $T_c = 15$ K, while the critical temperature estimated from zero resistivity in Fe$_{1.04}$Te$_{0.67}$Se$_{0.33}$ is higher than that in Fe$_{1.12}$Te$_{0.72}$Se$_{0.28}$.[22]

Figure 1 shows the field-swept $^{125}$Te NMR spectra of Fe$_{1.04}$Te$_{0.67}$Se$_{0.33}$. In Fig. 1(a), we show the spectra in the normal state in a constant frequency $\nu = 107.7$ MHz (at about 8 T). In both conditions of $H//a$ and $H//c$, the central frequencies of the spectra increase with decreasing temperature. The linewidth is about three times broader than that in Fe$_{1.01}$Se[11], indicating distribution of the local electronic state around Te caused by the Se-substitution as well as the presence of excess irons. In our preliminary investigations, the linewidth of the NMR spectrum decreases with the decrease of the amount of excess irons which produce nearly-localized Curie-Weiss-like temperature dependence in the magnetic susceptibility. The spectra around and below $T_c$ are shown in Fig. 1(b). As well as the normal state, the central frequencies for both $H//a$ and $H//c$ increase slightly with the decrease of temperature. Below $T_c$ the spin-echo intensity of the NMR spectrum is markedly weakened. The linewidth of the spectrum increases with decreasing temperature accompanied by the decrease of the London penetration depth $\lambda$.

We show the temperature dependence of the Knight shift $^{125}K$ in Fe$_{1.04}$Te$_{0.67}$Se$_{0.33}$ in Fig. 2 with the Knight shift of $^{77}$Se nucleus $^{77}K$ for comparison. In the normal state, both $^{125}K$ and $^{77}K$ decrease with decreasing temperature, similar to the case with Fe$_{1.01}$Se[11]. The uniform spin susceptibility ($\chi$) in Fe$_{1+5}$Te$_{1-x}$Se$_x$ frequently shows Curie-Weiss-like behavior at low temperatures, and the Curie constant depends on the amount of the excess irons, $\delta$.[23] In the case of the sample which contains very few excess irons, $\chi$ does not show such the Curie-Weiss-like behavior, and decreases with decreasing temperature with scaled to $K$. This behavior of the intrinsic spin susceptibility is characteristic of the case with itinerant antiferromagnets, i.e., $\chi_0$ is suppressed by the growth of $\chi(q)$[11, 22, 26].

Figure 2 shows Knight shifts plotted against the uniform susceptibility (so called $K-\chi$ plot) of $^{77}$Se and $^{125}$Te nuclei in Fe$_{1.04}$Se$_{0.33}$Te$_{0.67}$ with temperature as an implicit parameter. As discussed above, when the amount of excess irons is small, $\chi$ does not show the Curie-Weiss
like enhancement and decreases with decreasing temperature similar to $K$. The $K$ -- $\chi$ plots show good linearity as seen in Fig. 3. From the slopes, we estimated hyperfine coupling constants as $A_{//a} = 36.3$ kOe/$\mu_B$, $A_{//c} = 48.8$ kOe/$\mu_B$ and $A_{//c} = 28.5$ kOe/$\mu_B$. The temperature dependent $K$ and $\chi$ originate in the spin part. Next, we consider the temperature-independent terms of $K$ and $\chi$. In general, the chemical shift of $^{125}$Te nucleus is large, sometimes up to 0.3 %, and is by a factor of ~2 larger than that of $^{77}$Se nucleus which is located in the same chemical surroundings [27]. From the ordinary ratio of chemical shifts in $^{125}$Te and $^{77}$Se, we can roughly estimate the chemical shifts in Fe$_{1.04}$Te$_{0.67}$Se$_{0.33}$ as $^{125}CS \sim 0.25\%$ and $^{77}CS \sim 0.12\%$, and then $\chi_{orb}$ can be estimated as $\sim 4.5 \times 10^{-4}$ emu/mol as shown in Fig. 3.

In the superconducting state, both $^{125}K_a$ and $^{125}K_c$ decrease with decreasing temperature. From the roughly estimated chemical shifts in Fe$_{1.04}$Se$_{0.33}$Te$_{0.67}$, which gives us proper estimation of $\chi_{orb}$, the spin part of the Knight shift $K_{spin}$ seems to be completely suppressed in the ground state for both magnetic field directions, indicating the spin-singlet superconductivity. Since the spectrum shape changes at low temperatures, we need detailed studies at more low field.

In Fig. 4 we present the temperature dependence of the $^{125}$Te nuclear spin-lattice relaxation rate ($1/T_1$) in Fe$_{1.04}$Te$_{0.67}$Se$_{0.33}$ for both conditions of $H//a$ and $H//c$. The recovery of the nuclear spin momentum cannot be explained with single $T_1$ component, and was fitted with the sum of two $T_1$ components of single-exponential. This is similar to the case with FeSe$_{0.92}$ [13] while nearly stoichiometric Fe$_{1.01}$Se does not show any distributions of $T_1$ [11]. In the normal state, we estimated short and long components of $T_1$ by fitting the recoveries to two $T_1$ components of single-exponential for recovery curves measured at about $H \sim 8$ T. The main part of the recovery comes from the short $T_1$ component with the fraction of ~80%. In the superconducting state, we also measured $T_1$ at more lower field ($H \sim 4.3$ T). The recovery curves below $T_c$ have large distribution of $T_1$ due to contributions of superconducting and vortex sites, and cannot be fitted with two components. In these regions, we estimated $T_1$ from the main component of the recovery curves, then the main component of $T_1$ below 8 K is slowest component which should come from the intrinsic superconductivity.

In the normal state, the relaxation rates of both short and long $T_1$ components, $1/T_1S$ and $1/T_1L$, decrease with decreasing temperature, and the anisotropy is small. For the main short $T_1$ component, $1/T_{1S,H//a}$ is about 20 % larger than $1/T_{1S,H//c}$. $1/T_{1S,H//a}$ and $1/T_{1S,H//c}$ are proportional to $(\delta h_a)^2 + (\delta h_c)^2$ and $(\delta h_a)^2 + (\delta h_a)^2$, respectively, where $\delta h_a,c$ are local magnetic fluctuations. Taking it into account that $A_{//c}$ is larger than $A_{//a}$, the anisotropy of $1/T_1$ can be qualitatively explained by the anisotropy of the hyperfine coupling constant estimated from $K$ -- $\chi$ plots.

Below $T_c$, $1/T_1$ decreases roughly proportional to $T^3$ without coherent peak, resulting in an anisotropic superconductivity with line node. At low temperatures, the slope seems to close with $T$-linear due to the residual
The tendency of the enhancement of $1/T_1 T$ at low temperatures is similar to the case with Fe$_{1.01}$Se$_{0.67}$.

In the earlier reported neutron diffraction, an incommensurate $(\delta \pi, \delta \pi)$ short-range magnetic ordering was observed even in the superconducting Fe$_{1.080}$Te$_{0.67}$Se$_{0.33}$, and $\delta$ can be tunable with the amount of excess iron [22]. The spin fluctuations with incommensurate $q$ are expected to give a finite $A(q)$ at any crystal sites. Therefore, the enhancement of $1/T_1 T$ in our result may be probed as the similar spin fluctuations revealed by neutron diffraction. In our preliminary measurements, the absolute value of $1/T_1 T$ in Fe$_{1.04}$Te$_{0.67}$Se$_{0.33}$ is larger than that in Fe$_{1.12}$Te$_{0.72}$Se$_{0.28}$ which has larger amount of excess iron and shows very small amount of superconducting volume fraction. Therefore, the increase of excess iron should decrease the density of states (DOS) at Fermi surface. By the density function calculations, the curious valence state Fe$^{+}$ is predicted to occur in excess iron sites, i.e., Fe(II) sites in Fe$_{1.04}$Te with nearly localized strong magnetic moment [28]. The role of excess iron is not only pair breaking magnetic scattering at the superconducting state but also causes reduction of DOS by electron doping, making the superconducting state unstable. Since the superconductivity strongly relates to the magnetic instability, the magnetic fluctuations proved by $1/T_1 T$ are thought to be the driving force and origin of superconductivity in this Fe based system.

We measured $^{125}$Te NMR on the single crystal of the novel layered superconductor Fe$_{1.04}$Se$_{0.33}$Te$_{0.67}$. We found that the superconducting gap has the line node with the spin singlet superconducting pairing. We also found that the magnetic fluctuations have an important role for the occurrence of the superconductivity.

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