TOPICAL REVIEW

Magnetic excitations in iron chalcogenide superconductors

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Received 8 October 2012
Accepted for publication 8 October 2012
Published 13 December 2012
Online at stacks.iop.org/STAM/13/054302

Abstract

Nuclear magnetic resonance and neutron scattering experiments in iron chalcogenide superconductors are reviewed to make a survey of the magnetic excitations in FeSe, FeSe$_{1-x}$Te$_x$, and alkali-metal-doped $A_x$Fe$_{2-y}$Se$_2$ ($A = $ K, Rb, Cs, etc). In FeSe, the intimate relationship between the spin fluctuations and superconductivity can be seen universally for the variations in the off-stoichiometry, the Co-substitution and applied pressure. The isovalent compound FeTe has a magnetic ordering with different wave vector from that of other Fe-based magnetic materials. The transition temperature $T_c$ of FeSe increases with Te substitution in FeSe$_{1-x}$Te$_x$ with small $x$, and decreases in the vicinity of the end member FeTe. The spin fluctuations are drastically modified by the Te substitution. In the vicinity of the end member FeTe, the low-energy part of the spin fluctuation is dominated by the wave vector of the ordered phase of FeTe; however, the reduction of $T_c$ shows that it does not support superconductivity. The presence of same wave vector as that of other Fe-based superconductors in FeSe$_{1-x}$Te$_x$ and the observation of the resonance mode demonstrate that FeSe$_{1-x}$Te$_x$ belongs to the same group as most of other Fe-based superconductors in the entire range of $x$, where superconductivity is mediated by the spin fluctuations whose wave vector is the same as the nesting vector between the hole pockets and the electron pockets. On the other hand, the spin fluctuations differ for alkali-metal-doped $A_x$Fe$_{2-y}$Se$_2$ and FeSe or other Fe-based superconductors in their wave vector and strength in the low-energy part, most likely because of the different Fermi surfaces. The resonance mode with different wave vector suggests that $A_x$Fe$_{2-y}$Se$_2$ has an exceptional superconducting symmetry among Fe-based superconductors.

Keywords: NMR, neutron scattering, Fe-chalcogenides

1. Introduction

An exchange of pnictogen for chalcogen successfully opened new route in the research of Fe-based superconductors [1]. Iron chalcogenide superconductors are represented by $\beta$-FeSe (transition temperature $T_c = 8$ K), FeSe$_{1-x}$Te$_x$ ($T_c = 14$ K), and the alkali-metal-doped system $A_x$Fe$_{2-y}$Se$_2$ ($A = $ K, Rb, Cs, etc: $T_c = 32$ K) [1–4]. In addition, recent reports of $T_c > 40$ K in $A$Fe$_2$Se$_2$ ($A = $ Li, Na, etc) and (LiNH$_2$)$_x$Fe$_2$Se$_2$ demonstrate the further potential in iron chalcogenide superconductors [5, 6]. Such variety in materials is a characteristic of Fe-based superconductors. Their superconductivity mechanism is still controversial; the spin-fluctuation scenario yields $s^\pm$ symmetry in most of Fe-based superconductors [7–10]; however, for instance in $K_x$Fe$_{2-y}$Se$_2$, different superconducting (SC) symmetries
have been proposed by different theoretical approaches [11–18]. On the other hand, the orbital-fluctuation scenario gives $s^\pm$ symmetry [19, 20]. Substitution or doping of elements drastically changes the electronic/magnetic states of the systems, resulting in different Fermi surfaces and wave vectors in the magnetic correlations. Thus iron chalcogenide superconductors offer an excellent system for extensive research to elucidate the SC mechanism of Fe-based superconductors.

In this review paper, we focus on several characteristic results of nuclear magnetic resonance (NMR) and neutron scattering measurements to see the relationship between the spin fluctuations and superconductivity. Our reanalyzed NMR data are also added in this paper. NMR is a microscopic probe sensitive to spatial inhomogeneity, which is a benefit to the investigation of the substituted or doped systems. The nuclear spin lattice relaxation rate $1/T_1$ reflects the low-energy part of the spin fluctuations, and low-energy excitation of the SC quasiparticles. On the other hand, neutron scattering directly probes the energy dependence of the spin fluctuations, and the wave vector of the magnetic correlations. The observation of the magnetic resonance confirms the spin-mediated superconductivity and indicates the origin of the spin fluctuation. In section 2, we review FeSe and FeSe$_{1−x}$Te$_x$, where magnetic character is changed by Te content, but the spin fluctuation relevant to superconductivity has the same origin as in most other Fe-based superconductors. In this section, the antiferromagnetic (AF) wave vector is indicated by the folded Brillouin zone notation. In section 3, we review the results for $A_xFe_{2−x}Se_2$ which has a higher $T_c$. The behavior of $1/T_1$, Korrinya relation and the resonance mode suggest that the magnetic character of $A_xFe_{2−x}Se_2$ is considerably different from that of FeSe and other Fe-based systems. The AF wave vector is indicated by the unfolded Brillouin zone notation in $A_xFe_{2−x}Se_2$.

2. Magnetic and superconducting properties in FeSe and FeSe$_{1−x}$Te$_x$

2.1. Spin fluctuations in FeSe

$\beta$-FeSe was the first iron chalcogenide superconductor that exhibited $T_c \sim 8$ K [1]. Its crystal structure is simple and is composed of FeSe layers. Owing to the lack of large single crystals, neutron scattering experiments have not been satisfactory in investigations of the magnetic excitation, and therefore we start reviewing NMR results with FeSe. FeSe possesses a simple structure; however, this system has a delicate problem with stoichiometry [21]. Figure 1 shows $^{77}$Se-NMR spectra for two samples that were prepared by the solid-state reaction method via two different routes [22]. Since Se has a nuclear spin $I = 1/2$ and zero nuclear quadrupole moment, the spectral width depends on the magnetic inhomogeneity. The actual composition of FeSe#1 is determined to be FeSe$_{0.92}$ with Se deficiency [23, 24]. The synthesis process is known to influence the stoichiometry of the sample [21], and the improved sample FeSe#2 should be more stoichiometric. The composition of the sample made via a similar procedure to that of FeSe#2 was confirmed as FeSe$_{0.985}$ from energy-dispersive x-ray spectroscopy. The sample FeSe#1 was reacted at 680 °C, whereas the sample FeSe#2 was reacted at 1100 °C and then annealed at 400 °C for 200 h [22]. Apparently the spectral width is narrower in FeSe#2 than FeSe#1 by a factor of $\sim 3$, indicating a good homogeneity of the former sample [25]. The full-width at half-maximum of FeSe#2 is $\sim 37$ Oe, which is comparable to that of Fe$_{1.01}$Se [26]. A similar comparison can be found in [27].

The difference in the stoichiometry significantly influences the electronic state of the system. Figure 2 shows the recovery curves to evaluate the nuclear spin lattice relaxation time $T_1$ for two samples. The relaxation of FeSe#2 is about twice faster than FeSe#1. For $I = 1/2$ of $^{77}$Se the recovery should follow a single exponential function. This is indeed observed at high temperatures, but not at 10 K due to the spatial inhomogeneity of the spin fluctuations. We used two kinds of fitting methods to evaluate $T_1$. First one is the fitting by two components in $T_1$ as follows:

$$m(t) = \frac{M_0 - M(t)}{M_0} = A_S \exp\left(-\frac{t}{T_{1S}}\right) + A_L \exp\left(-\frac{t}{T_{1L}}\right).$$

(1)

As shown in figure 2(a), the fast component becomes dominant in the high-quality sample, increasing from 60% in FeSe#1 to 75% for FeSe#2. Second fitting is a stretch type as follows:

$$m(t) = \frac{M_0 - M(t)}{M_0} = A \exp\left(-\left(\frac{t}{T_1}\right)^\alpha\right).$$

(2)

The value $\alpha = 1$ corresponds to the homogeneous case, and $\alpha$ is slightly closer to 1 for FeSe#2 ($\alpha = 0.65$) than FeSe#1 ($\alpha = 0.6$). These results suggest that the fast relaxation is intrinsic for homogeneous FeSe, as confirmed for the almost
Figure 2. Recovery curves for two samples. Two figures present two procedures to evaluate $T_1$: (a) the two-components fitting and (b) the stretch fitting.

Figure 3. Temperature dependences of $1/T_1 T$ for Fe$_{1.01}$Se and Fe$_{1.03}$Se. For Fe$_{1.01}$Se, $1/T_1 T$ under pressure is also plotted. The development of $1/T_1$ is distinct at low temperatures in the SC sample. (Reproduced with permission from [26] © 2009 American Physical Society.)

Figure 4. Temperature dependences of $1/T_1 T$ for FeSe#1, FeSe#2 and non-superconducting (Fe$_{0.9}$Co$_{0.1}$)Se. Electron doping strongly suppresses the spin fluctuations.

stoichiometric Fe$_{1.01}$Se [26]. Figure 3 shows the temperature dependence of $1/T_1 T$ for Fe$_{1.01}$Se and an off-stoichiometric Fe$_{1.03}$Se measured by Imai et al [26]: $1/T_1 T$ in FeSe$_{1.01}$ strongly increases toward low temperatures, while it remains constant in Fe$_{1.03}$Se which does not show superconductivity. Figure 4 is the same plot for FeSe#1(FeSe$_{0.92}$), FeSe#2(more stoichiometric) and non-superconducting (Fe$_{0.9}$Co$_{0.1}$)Se [25, 28], where only the fast component is displayed at low temperatures for FeSe. FeSe#1 and #2 exhibit a development of $1/T_1 T$ toward low temperatures, while it disappears in the non-superconducting (Fe$_{0.9}$Co$_{0.1}$)Se similarly to Fe$_{1.03}$Se in figure 3. Superconductivity in FeSe is accompanied by the development of $1/T_1 T$ toward low temperatures.

In all the samples used for figures 3 and 4, on the other hand, $1/T_1 T$ shows a large temperature variation above ~100 K. This behavior is commonly seen in the electron-doped Fe-based superconductors [29], and is understood as the effect of the band structure [30]. The suppression of this temperature dependence at high temperatures in (Fe$_{0.9}$Co$_{0.1}$)Se indicates that a high density of states is removed from the Fermi level, ensuring that cobalt doping works as an electron doping. Weak but certain suppression from FeSe#2 to FeSe#1 indicates that Se deficiency also works as the electron doping. The relationship between the carrier doping and the development of $1/T_1 T$ at low temperatures demonstrates that the electron doping significantly changes the spin fluctuations through a modification in the nesting properties.
Figure 5 shows the temperature dependence of Knight shift. The behavior at low temperatures differs from that of 1/T1T and indicates the presence of q \neq 0 spin fluctuations. (Reproduced with permission from [26] © 2009 American Physical Society.)

Figure 5 shows the temperature dependence of Knight shift [26]. The large variation at high temperatures originates in the band structure near the Fermi level as seen in 1/T1T. Knight shift is almost constant at low temperatures, and 1/T1T which drastically increases toward low temperatures. Generally the temperature-dependent spin part of Knight shift, Ks, and 1/T1T are expressed as follows:

\[ K_s = A_s \chi(q = 0, \omega = 0), \]

\[ \frac{1}{T_1T} = \frac{2\gamma_n^2 k_B}{(\gamma_e h)^2} \sum_q A^2 \chi''(q, \omega \rho_n) \rho_n, \]

where \( A_s \) and \( A_q \) are hyperfine coupling constants, and \( \gamma_e \) (\( \gamma_n \)) is a nuclear (electronic) gyromagnetic ratio, \( \omega \rho_n \) is an NMR frequency, of the order of tens of MHz. The gradual decrease of Knight shift with decreasing temperature indicates the suppression of the spin susceptibility \( \chi(0,0) \). Thus the development of 1/T1T at low temperatures possibly originates in the \( q \neq 0 \) component in the dynamical susceptibility. The presence of superconductivity accompanied by the \( q \neq 0 \) spin fluctuation suggests that the AF spin fluctuations are relevant to the superconductivity in FeSe. This close relationship has been confirmed under pressure as well [26, 31], as shown in figure 3. From NMR measurements in Fe-based systems, the AF wave vector has been discussed from the anisotropy of 1/T1 using a single crystal [32–35]; however, the data have not been obtained thus far in FeSe owing to the lack of a large single crystal.

2.2. Magnetic order and magnetic structure in FeTe

Since single crystals of FeSe\(_{1-x}\)Te\(_x\) became available, neutron scattering measurements have been performed extensively in FeSe\(_{1-x}\)Te\(_x\). Bao et al [36] first reported the magnetic structure of Fe\(_{1+y}\)Se\(_{1-x}\)Te\(_x\). In Fe\(_{1+y}\)Te with \( y > 0.12 \) (\( y < 0.12 \)), the long-range AF ordering at \( \sim 70 \text{ K} \) is accompanied by a structural transition from a high-temperature tetragonal phase to a low-temperature monoclinic (low-temperature orthorhombic) phase [37, 38]. Unlike other AF parent compounds of Fe-based superconductors such as 1111- and 122-type compounds, in which the AF order is characterized by the ordering wave vector \( Q = (\delta, 0, \frac{1}{2}) \) (folded Brillouin zone notation), the non-superconducting Fe 11 sample magnetically orders at \( Q = (\delta, 0, \frac{1}{2}) \) [36, 39] (figure 6). In the orthorhombic phase, \( \delta \) varies with the amount of excess Fe in the interstitial sites (\( y \)), and it is fixed to \( \frac{1}{2} \) in the monoclinic phase. The ordered moment for Fe in Fe\(_{1+y}\)Te (\( y \sim 0.09 \)) is reported to be 1.86(2) \( \mu_B \) [36, 40], which is larger than the that of 0.8\( \mu_B \) in LaFeAsO [41] and 0.87(3)\( \mu_B \) in BaFe\(_2\)As\(_2\) [42]. These unique magnetic properties provide an important opportunity to study the universal relation between spin correlations and superconductivity in Fe-based superconductors.

Xu et al [43] claimed that the long-range AF order, which is characterized by the commensurate in-plane wave vector \( Q = (\frac{1}{2}, 0) \), competes with superconductivity, while the short-range order with \( Q = (\frac{1}{2}, \frac{1}{2}) \) induced by Se-doping coexists with the bulk superconductivity. The appearance of superconductivity, concomitant with the change of the wave vector with Se substitution, is a strong evidence for the correlation between the superconductivity and the character of magnetic order.
2.3. Evolution of spin fluctuations in FeSe$_{1-x}$Te$_x$

In cuprate oxide superconductors, the doping evolution of spin correlation provides an important clue for understanding the role of magnetism in high-$T_c$ mechanism. For example, the appearance of 'spin resonance' in the SC state is a direct evidence for $d$-wave symmetry, which is expected in the SC mechanism with spin fluctuations. To clarify the character of the dynamical magnetic properties of the parent material and the SC compounds in iron chalcogenides, Iikubo et al [40] performed inelastic neutron scattering measurements on Fe$_{1.086}$Te and Fe$_{1.086}$Se$_{0.25}$Te$_{0.75}$ powders. As shown in figure 7(b), non-superconducting Fe$_{1.086}$Te exhibits a pronounced magnetic fluctuation around $|\mathbf{Q}| \approx 0.9$ Å$^{-1}$ which is slightly smaller than the absolute value of $|\mathbf{Q}| = 0.97$ Å$^{-1}$ for $\mathbf{Q} = (\frac{1}{2}, 0, \frac{1}{2})$ (folded Brillouin zone notation). On the other hand, SC Fe$_{1.086}$Se$_{0.25}$Te$_{0.75}$ shows a magnetic fluctuation at $|\mathbf{Q}| = 1.2$ Å$^{-1}$ (figure 7(a)), which is close to the absolute value for $\mathbf{Q} = (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ or $(\frac{1}{2}, \frac{1}{2}, 0)$ at higher energies. These results suggest that the dynamical property also evolves when the system enters into the SC phase with Se substitution, and that the AF fluctuations characterized by the 2D vector $\mathbf{Q} = (\frac{1}{2}, \frac{1}{2})$ are common among Fe-based superconductors. Subsequently, $Q$-resolved measurements on a single crystal more directly showed the evolution of spin fluctuations (see figures 10(a) and (b)). Magnetic correlation with $\mathbf{Q} = (\frac{1}{2}, 0, 0)$ would be associated with the carrier localization, and the bulk superconductivity emerges with the suppression of the $\mathbf{Q} = (\frac{1}{2}, 0)$ correlation. Spin fluctuations with in-plane wave vector $\mathbf{Q} \approx (\frac{1}{2}, \frac{1}{2})$ could be a response originated from the Fermi surface nesting, since $\mathbf{Q}$ corresponds to the nesting vector between the cylinder-like electron and hole Fermi surfaces.

Even more importantly, in the SC phase, a 'spin resonance' appears in the magnetic excitation spectrum. Figures 8(a) and (b) show the spin excitation spectra of FeSe$_{0.4}$Te$_{0.6}$ ($T_c = 14$ K) at 1.5 and 30 K, respectively, measured by Qiu et al [45]. The difference between these figures clearly indicates the enhancement of intensity at $\sim 6.5$ meV ($= 5.3 \, k_B T_c$) in the SC state. As shown in figure 8(c), an additional signal develops below $T_c$. Qiu et al demonstrated that the resonance feature is consistent with a two-band model (see figure 8(d)) for $s^\pm$ superconductivity. Furthermore, Wen et al [46] clarified that in SC FeSe$_{0.4}$Te$_{0.6}$ the magnetic field effect on the spin resonance is characterized by the appearance of a resonance intensity at a lowered $T_c$ of 12 K and the reduction of low-temperature signal. In figure 9, the bulk magnetic susceptibility and the resonance intensity measured at 0 and 7 T are plotted as a function of temperature. The concomitant suppression of superconductivity and the resonance peak by an external magnetic field simply suggests the intimate relation between the two, and is consistent with the picture that the resonance is related to quasiparticle scattering in the SC state as pointed out by Wen et al.

To gain further insight into the nature of spin correlations, high-energy inelastic neutron scattering measurements were...
Figure 8. Spin excitation spectra of FeSe$_{0.4}$Te$_{0.6}$ at (a) 1.5 K and (b) 30 K. (c) The difference between 1.5 and 30 K spectra, and (d) corresponding resolution-convoluted intensity difference from the model calculation. (Reproduced with permission from [45] © 2009 American Physical Society.)

Figure 9. (a) Magnetic susceptibility in $H = 0.0005$ T (red symbols) and 7 T (blue symbols). (b) Resonance intensity at $Q = (\frac{1}{2}, \frac{1}{2}, 0)$. (Reproduced with permission from [46] © 2010 American Physical Society.)

performed. Lipscomben et al [47] reported the spin excitation spectrum of non-SC Fe$_{1.05}$Te with increasing energy transfer. The evaluated dispersion throughout the Brillouin zone was analyzed by a Heisenberg Hamiltonian with anisotropic ferromagnetic nearest-neighbor (NN) and isotropic AF next-nearest-neighbor (NNN) exchange couplings. Lipscomben et al found that the amplitude of NNN interaction and its direction are similar to those in CaFe$_2$As$_2$, while the NN coupling in these two systems is quite different. This finding suggests that the fundamental physics is the same in Fe$_{1.05}$Te and CaFe$_2$As$_2$, and the AF NNN coupling, which can cause $s^\pm$-wave paring [9], plays an important role for the appearance of superconductivity in the iron pnictides and iron chalcogenides.

In the SC FeTe$_{0.51}$Se$_{0.49}$, the magnetic peaks disperse away from $Q = (\frac{1}{2}, \frac{1}{2}, 0)$ toward $Q = (1, 0)$ with increasing energy transfer as depicted in figure 10(c) [48]. A similar tendency was observed in the spin-glass phase of FeTe$_{0.72}$Se$_{0.27}$ [49]. Interestingly, high-energy excitations persist around $Q = (1, 0)$ with no evidence for dispersion away from this wave vector, similar to the steep high-energy dispersion in the nearly AF metal Cu$_{0.95}$V$_{0.05}$, although the spin excitation is characterized by $Q = (\frac{1}{2}, \frac{1}{2})$ [50].

Next we consider the NMR results for FeSe$_{1-x}$Te$_x$. Independent measurements have been performed by Shimizu et al [51] ($x = 0.5$), Michioka et al [52] ($x = 0.67$) and Arcon et al [53] ($x = 0.58$) [51–53]. Figure 11 shows the temperature dependence of Knight shift reported by Hara et al [54], at the Se site and the Te site for FeSe$_{1-x}$Te$_x$ with a wide range of $x$. The data including $1/T_i$ (shown in figure 12) are qualitatively consistent with those obtained by the other groups [51–53]. In all the samples, the Knight
Figure 10. Constant-energy plots of the magnetic excitation spectrum at an energy transfer of 61 meV for Fe\textsubscript{1+y}Te\textsubscript{1−x}Se\textsubscript{x} with (a) \(x = 0.27\) and (b) \(x = 0.49\). (c) Dispersion of the magnetic excitations in Fe\textsubscript{1+y}Te\textsubscript{1−x}Se\textsubscript{x}, where (rlu) stands for reciprocal lattice unit. (Reproduced with permission from [48] © 2010 Nature Publishing Group.)

Figure 11. Temperature dependence of Knight shift for FeSe\textsubscript{1−x}Te\textsubscript{x} (\(x = 0, 0.6\) and 0.8). The absolute value in the normal state increases as increase Te. (Reproduced from [54] © 2011 The Physical Society of Japan.)

Figure 11. Temperature dependence of Knight shift for FeSe\textsubscript{1−x}Te\textsubscript{x} (\(x = 0, 0.6\) and 0.8). The absolute value in the normal state increases as increase Te. (Reproduced from [54] © 2011 The Physical Society of Japan.)

shift gradually decreases with decreasing temperature and drops below \(T_c\); it comprises the spin part corresponding to the spin susceptibility \(\chi(0, 0)\) and temperature-independent orbital (chemical) part. If the orbital parts are estimated as the extrapolated values toward 0 K due to the spin-singlet pairing then the orbital part is almost independent of Te doping. The spin part in the normal state has a large value in Te-rich samples, indicating that \(\chi(0, 0)\) increases with Te doping level.

Temperature dependences of \(1/T_{1}T\) for FeSe\textsubscript{1−x}Te\textsubscript{x} are shown in figure 12 [54]. Comparison of Se-NMR (a and b) and Te-NMR (c and d) results reveals that \(1/T_{1}T\) in the normal state increases with Te doping. The fast components of \(1/T_{1}T\) for FeSe and FeSe\textsubscript{0.2}Te\textsubscript{0.8} increase significantly toward low temperatures, indicating the critical fluctuation toward the magnetic ordering, whereas \(1/T_{1}T\) for the intermediate FeSe\textsubscript{0.6}Te\textsubscript{0.6} with higher \(T_c\) is nearly temperature independent. The absence of the critical behavior in FeSe\textsubscript{0.4}Te\textsubscript{0.6} is consistent with the result by Shimizu et al [51] for FeSe\textsubscript{0.5}Te\textsubscript{0.5} and Arčon et al [53] for FeSe\textsubscript{0.42}Te\textsubscript{0.58}. Shimizu et al [51] observed the development of spin fluctuations under pressure in FeSe\textsubscript{0.5}Te\textsubscript{0.5} accompanied by an increase
Figure 12. Temperature dependences of $1/T_1 T$ for FeSe$_{1-x}$Te$_x$. The solid (open) squares indicate the fast (slow) component in $1/T_1$ estimated by fitting with equation (1). (Reproduced from [54] © 2011 The Physical Society of Japan.)

Figure 13. Temperature dependence of $1/T_1$ in the SC state for two different samples. $T_1$ is obtained by the stretch function with fixed $\alpha$. Data for FeSe#1 are taken from [24].
2.4. Superconducting symmetry in FeSe$_{1-x}$Te$_x$

Most of Fe-based superconductors possess isotropic multiple SC gaps. Similarly to other Fe-based superconductors, the isotropic multigap has been proposed in Se-deficient FeSe, from the penetration depth and the thermal conductivity [56, 57], and also in FeSe$_{1-x}$Te$_x$ from ARFES ($x = 0.7$) and scanning tunneling microscopy (STM) ($x = 0.5$) results [58, 59]. On the contrary, the presence of node has been proposed from a recent STM measurement using FeSe film as an intrinsic property in the stoichiometric FeSe [60]. In the NMR measurements of FeSe, $1/T_1$ showed the lack of coherence peak and a $T^3$ dependence similar to that of the La 1111 system [24]. As shown in figure 13, the temperature dependence of $1/T_1$ obeys $T^3$ behavior below $T_c$ for FeSe#1 with Se deficiency and FeSe#2, which is expected to be more stoichiometric. The difference in the SC gap symmetry cannot be seen between two samples in this temperature range. However, the $1/T_1 \propto T^3$ behavior in this temperature region can be reproduced by either the typical line-node model or the s$^\pm$ model [61]. (The fitting result by the s$^\pm$ model is shown in figure 14(c).) Further, low-temperature measurements are required to distinguish these SC symmetries experimentally from $1/T_1$.

The evolution of the SC gap with Te doping was investigated by $1/T_1$ measurements. Figure 14 shows the temperature dependence of $1/T_1$ for FeSe$_{1-x}$Te$_x$, where $T_1$ was estimated by the stretch fitting while fixing the parameter $\alpha$ in expression (2). In all the samples, $1/T_1$ shows the power-law-like behavior below $T_c$, consistent with the measurements for other doping levels [51, 52]. The $T^3$ dependence has been confirmed for FeSe, while larger power-law exponents are observed with increasing Te doping: $\sim T^3 − T^6$ for FeSe$_{0.4}$Te$_{0.6}$ and $\sim T^7$ for FeSe$_{0.2}$Te$_{0.8}$. The strong temperature dependence of $T_1$ below $T_c$ has been reported by Arcon et al [53] in FeSe$_{0.42}$Te$_{0.58}$. Fitting by the $s^\pm$ model for these systems is shown in figure 14(c), and the obtained parameters are summarized in table 1, where the smearing factor by impurity scattering, $\eta$, which gives $T_1 T$ = con st at low temperature, is ambiguously determined owing to the insufficient low-temperature data.

The estimated gaps for FeSe and FeSe$_{0.4}$Te$_{0.6}$ agree well with the estimations in FeSe by $\mu$SR ($\Delta_1/k_B T_c = 2.25$ and $\Delta_2/k_B T_c = 0.55$) [56], in FeSe$_{0.55}$Te$_{0.45}$ by the optical conductivity ($\Delta_1/k_B T_c = 4.2$ and $\Delta_2/k_B T_c = 2.1$) [62] and in Fe$_{1.03}$Se$_{0.7}$Te$_{0.3}$ by angle-resolved photoemission spectroscopy (ARPES) ($\Delta_1/k_B T_c = 3.5$) [58]. The gap for FeSe$_{0.2}$Te$_{0.8}$ seems to be overestimated. This might indicate that the low-energy part of ($\frac{1}{2}$, 0) spin fluctuations which dominates $1/T_1$ is strongly suppressed in the SC state.

Figure 15 shows the Te doping dependences measured by NMR. $T_c$ has a broad maximum at around $x = 0.5$–0.6 and is suppressed when approaching FeTe. However the spin part of Knight shift and $1/T_1 T$ at $T_c$ increase monotonously with $x$ up to $x = 0.8$. This contrasts the close relationship between $T_c$ and $1/T_1 T$ observed under pressure [26, 31, 51], suggesting that the dominant spin fluctuations in FeSe$_{0.2}$Te$_{0.8}$, that is, ($\frac{1}{2}$, 0) spin fluctuation, is not relevant to superconductivity. The evolution of $K_c$ indicates that the density of states at the Fermi level increases with increasing $x$, which should be relevant to the increase in $T_c$ and the modification to the strong-coupling regime in the Te-doped system.
**Table 1.** The SC gap parameters obtained by fitting with the $s^\pm$ model (figure 14(c)).

|       | $T_c$ (K) | $\Delta_1/k_B T_c$ | $\Delta_2/k_BT_c$ | $N_1/(N_1+N_2)$ | $\eta$     |
|-------|-----------|---------------------|-------------------|-----------------|------------|
| FeSe  | 8.0       | 2.5                 | 0.8               | 0.7             | 0.12 $\Delta_J$ |
| FeSe$_{0.4}$Te$_{0.6}$ | 13.0     | 3.5                 | 1.9               | 0.7             | 0.015 $\Delta_J$ |
| FeSe$_{0.2}$Te$_{0.8}$ | 10.0     | 5.5                 | 2.5               | 0.85            | 0.015 $\Delta_J$ |

3. Spin fluctuations and superconducting symmetry in $A_x$Fe$_{2-y}$Se$_2$

Alkali-metal-doped $A_x$Fe$_{2-y}$Se$_2$ is a unique example among the Fe-based superconductors [4], which differs from FeSe in many aspects. The most interesting and important feature is the different Fermi surface from other Fe-based superconductors studied by ARPES [63–65]. The disappearance of hole pockets at the $\Gamma$ point yields the exclusion of $s^\pm$ wave for the SC symmetry, because the nesting vector is modified from $(1/2,0)$ (unfolded Brillouin zone notation in this section). The nodeless $d$ wave and nodal $d$ wave have been proposed by a nesting scenario [11–15], while the robustness of $s$-wave has been pointed out by a strong-coupling scenario taking into account the next-nearest neighbor exchange interaction [16–18]. On the other hand, an $s^{++}$ wave mediated by the orbital fluctuations is another candidate [14]. Another feature is the presence of an AF phase with a high transition temperature, and the phase segregation between a paramagnetic (PM) phase and the AF phase [66–69]. Many experimental results suggest that the PM phase is a minor phase compared with a majority AF phase [67–69]. NMR is an effective tool to investigate each phase separately.

Figure 16 shows the temperature dependences of $1/T_1$ and $1/T_2 T$ for K$_x$Fe$_{2−y}$Se$_2$. $1/T_2$ shows a gradual increase with temperature, in a strong contrast to FeSe. (Reproduced with permission from [70] © 2011 American Physical Society.)

Figure 15. Te doping dependences of (a) $T_c$, (b) $K_1$, value at $T_c$, (c) $1/T_2 T$ of the fast component at $T_c$, and (d) the SC gap estimated by the $s^\pm$ model. The AF ordering in FeTe has a different wave vector from that of the magnetic correlation in other Fe-based superconductors.
shows the temperature dependences of $1 \chi_{(i)}$ in K$_{x}$Fe$_{2-y}$Se$_{2}$. This indicates that magnetic fluctuations along the $c$-axis are stronger than those in the $ab$ plane at the As site [32–35], and does not contradict to the presence of ($\frac{1}{4}$, $\frac{1}{2}$) fluctuations [73]. The contribution of different spin fluctuations to superconductivity has been demonstrated by the inelastic neutron scattering measurements performed by Park et al and Friemel et al [74, 75] on Rb systems. They have observed a resonance mode at $Q = (0.5, 0.25, 0)$ as shown in figure 19. It clearly develops below $T_c$ as shown in figure 19(e). The Q value is close to the theoretically predicted $Q = (0.5, 0.3125, 0)$ [13]. This wave vector is in strong contrast to that of other Fe-based superconductors, and it was also reconfirmed in other $A_x$Fe$_{2-y}$Se$_2$ systems [76, 77].

Figure 20 shows the temperature dependences of $1/T_1$ down to 1.6 K for $H \parallel ab$ and the results calculated by several models [73]. The field-independent $T_1T \sim \text{const}$ behavior below ~5 K originates in the pair breaking via scattering by impurity or defect. The residual density of state (RDOS) at the Fermi level is estimated at ~6% of the density of states just above $T_c$. This value is comparable to those of some other Fe-based superconductors with isotropic multigap [78, 79]. The lines in figure 20 are calculated using three different models [73]. The normalized density of states near the Fermi level for each model ($N(E)/N_0$) is displayed in the right part of figure 20. The data can be fitted well with the models A and B. The gap value in model A is almost consistent with the ARPES results [63, 80, 81], where two gaps with $\Delta_1 \sim 10$ meV ($= 3.6 k_B T_c$) and $\Delta_2 \sim 7$ meV ($= 2.5 k_B T_c$) are suggested to open at the different Fermi pockets, the $M$ point and $Z$ point. The authors have observed the isotropic gap even in the Fermi pocket at the $Z$ point, objecting the $d$-wave symmetry [80, 81]. The absence of the coherence peak and the RDOS in $1/T_1$, and also the resonance mode indicate a sign-changing order parameter.

4. Conclusions

In FeSe, the development of AF spin fluctuations is essential for the occurrence of superconductivity, and the intimate relationship are also valid under pressure. Inelastic neutron scattering in FeSe$_{1-x}$Te$_x$ demonstrates that the wave vector...
of spin fluctuation relevant to superconductivity is $Q = (\frac{1}{2}, \frac{1}{2})$ same as that of other Fe-based superconductors (the folded Brillouin zone notation). This spin fluctuation is considered to yield $s^\pm$-wave symmetry, and the $1/T_1$ values are well reproduced by $s^\pm$-wave with the gap-sizes consistent with other experiments. Similar to Te doping, the different wave vector of $Q = (\frac{1}{2}, 0)$ develops toward the magnetically ordered state. This ($\frac{1}{2}, 0$) fluctuation dominates the low-energy part of the spin fluctuations in Te-rich compounds, whereas $T_c$ rather decreases, suggesting no relevance of the ($12, 0$) fluctuation to superconductivity. The magnetic resonance mode in FeSe$_{1-x}$Te$_x$ also demonstrates that the spin fluctuations relevant to superconductivity are ($\frac{1}{2}, \frac{1}{2}$) correlations.

In $A_xFe_{2-y}Se_2$, the low-energy spin fluctuations are weak, and their wave vector is not of $Q = (\frac{1}{2}, 0)$ (the unfolded Brillouin zone notation). The resonance mode has been observed at $(0.5, 0.25, 0.5)$, which differs from the position in other Fe-based superconductors. In this mode, the $s^\pm$-wave, which is the same as in other Fe-based
Figure 20. Temperature dependence of $1/T_1$ in $H \parallel ab$ for $K_{x}Fe_{2-y}Se_2$. The curves are calculated from the SC gap models displayed in the right panel. (Reproduced from [73] © 2012 The Physical Society of Japan.)

superconductors, should be excluded. The temperature dependence of $1/T_1$ is reproduced by the SC gaps suggested by the ARPES experiments, indicative of the isotropic multigap in $A_{x}Fe_{2-y}Se_{2}$.

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