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# Persistent Correlation between Superconductivity and Antiferromagnetic Fluctuations near a Nematic Quantum Critical Point in $\text{FeSe}_{1-x}\text{S}_x$

P. Wiecki,<sup>1</sup> K. Rana,<sup>1</sup> A. E. Böhmer,<sup>1,2</sup> Y. Lee,<sup>1</sup> S. L. Bud'ko,<sup>1</sup> P. C. Canfield,<sup>1</sup> and Y. Furukawa<sup>1</sup>

<sup>1</sup>*Ames Laboratory, U.S. DOE and Department of Physics and Astronomy, Iowa State University, Ames, Iowa 50011 USA*

<sup>2</sup>*Karlsruhe Institute of Technology, Institut für Festkörperphysik, 76021 Karlsruhe, Germany*

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We present  $^{77}\text{Se}$ -NMR measurements on  $\text{FeSe}_{1-x}\text{S}_x$  samples with sulfur content  $x = 0, 9, 15$  and 29%. Twinned nematic domains are observed in the NMR spectrum for all samples except  $x = 29\%$ . The NMR spin-lattice relaxation rate shows that antiferromagnetic (AFM) fluctuations are initially enhanced between  $x = 0\%$  and  $x = 9\%$ , but are strongly suppressed for higher  $x$  values. The observed behavior of the AFM fluctuations parallels the superconducting transition temperature  $T_c$  in these materials, providing strong evidence for the primary importance of AFM fluctuations for superconductivity, despite the presence of nematic quantum criticality in the  $\text{FeSe}_{1-x}\text{S}_x$  system.

PACS numbers:

Critical fluctuations of an ordered phase found in the proximity to unconventional superconductivity have frequently been discussed as a source of superconducting pairing [1–4]. In the iron-based superconductors [5, 6], superconductivity (SC) is found in the vicinity of two types of long-range order: the stripe-type antiferromagnetic (AFM) order and the nematic order, which breaks the in-plane rotational symmetry while preserving time reversal symmetry. While dynamical AFM fluctuations are well known to support SC, experimental and theoretical studies have suggested that nematic fluctuations may also be important for high- $T_c$  SC [7–9].

In this context, FeSe has emerged as a key material since it undergoes a nematic phase transition from a tetragonal to an orthorhombic structure at  $T_s \approx 90$  K and develops superconductivity below  $T_c \approx 8.5$  K, but does not display static magnetic ordering [10–12]. This suggests an opportunity to study the behavior of  $T_c$  near a nematic quantum critical point (QCP) isolated from a magnetic QCP. The nematic phase can be suppressed by pressure application, with  $T_s$  reaching 32 K at  $p = 1.5$  GPa. However, an AFM ordered state emerges above  $p = 0.8$  GPa [13, 14] and merges with the nematic state above  $p = 1.7$  GPa [15]. Non-monotonic behavior of  $T_c$  is seen near the onset of the magnetic order [16], but overall  $T_c$  is strongly enhanced up to 37 K at  $p = 6$  GPa [17–19]. While early nuclear magnetic resonance (NMR) measurements connected the enhancement of  $T_c$  to enhanced spin fluctuations under pressure [20], the recently revealed complexity of the phase diagram raises new questions. Notably, the role of nematic fluctuations in the superconductivity remains unclear.

The nematic phase can also be suppressed by S substitution in  $\text{FeSe}_{1-x}\text{S}_x$  at ambient pressure, with the nematic phase disappearing around  $x \approx 17\%$ . Importantly, no long-range magnetic order can be observed at ambient pressure, which implies an isolated nematic QCP [21].  $T_c$  initially increases slightly to  $T_c \approx 10$  K at  $x \approx 10\%$  [22] from  $T_c \approx 8.5$  K at  $x = 0$ , but then decreases, reach-

ing  $T_c \approx 5$  K by  $x = 29\%$ . The application of pressure induces magnetic order in S substituted samples [23, 24].

Recent results have highlighted the rich interplay between magnetic, nematic and superconducting orders in  $\text{FeSe}_{1-x}\text{S}_x$ . Elastoresistivity measurements found that nematic fluctuations diverge near the nematic QCP near  $x \approx 17\%$  [21]. The full three-dimensional  $T$ - $p$ - $x$  dependent phase diagram revealed strongly enhanced  $T_c$  in regions lacking both nematic and AFM long-range orders [24]. Although several studies have suggested that  $T_c$  seems to not correlate with nematicity in  $\text{FeSe}_{1-x}\text{S}_x$  [21, 24–26], nematic fluctuations have been shown to strongly impact the SC pairing interactions [27]. Similarly, the SC gap structure is highly anisotropic in the  $ab$  plane [28], suggesting that nematicity is involved in the SC. However, no direct measurements of the concentration dependence of magnetic fluctuations have been reported yet.

Since magnetic fluctuations are considered to be one of the key ingredients for the appearance of SC in iron pnictides, it is crucial to reveal how magnetic fluctuations vary with S substitution in  $\text{FeSe}_{1-x}\text{S}_x$ . NMR is an ideal tool for the microscopic study of low-energy magnetic fluctuations in correlated electron systems. Here, we carried out  $^{77}\text{Se}$  NMR measurements to investigate static and dynamic magnetic properties of  $\text{FeSe}_{1-x}\text{S}_x$ . Our NMR data clearly show that stripe-type AFM fluctuations are initially slightly enhanced by S doping up to  $x \approx 10\%$  from  $x = 0$  but are strongly suppressed thereafter, particularly beyond the nematic dome above  $x \approx 17\%$ . This behavior shows a strong correlation with  $T_c$ , providing clear evidence for the primary importance of AFM fluctuations over critical nematic fluctuations for SC in  $\text{FeSe}_{1-x}\text{S}_x$ .

The crystals were grown using chemical vapor transport as outlined in Refs. [29, 30]. The four different S-content crystals used are  $x = 0$  ( $T_s = 90$  K,  $T_c = 8.5$  K),  $x = 0.09$  ( $T_s = 68$  K,  $T_c = 10$  K),  $x = 0.15$  ( $T_s = 45$  K,  $T_c = 8$  K), and  $x = 0.29$  ( $T_c = 5$  K).  $^{77}\text{Se}$

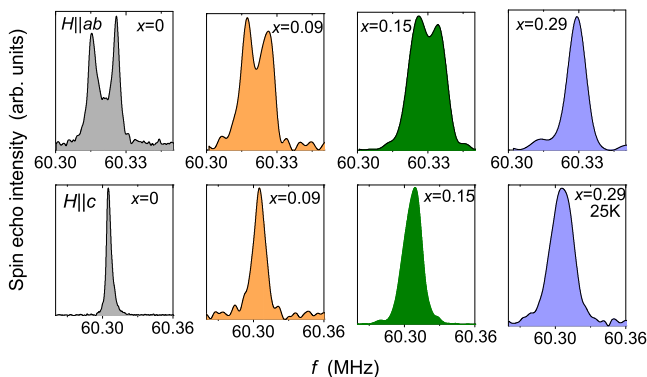


FIG. 1: Representative NMR spectra with  $H||ab$  (upper panels) and  $H||c$  (lower panels) at  $T = 20$  K (unless otherwise specified) for indicated S concentrations  $x$ .

NMR measurements have been carried out under a fixed magnetic external field of  $H = 7.4089$  T applied either along the  $c$  axis or in the  $ab$  plane ( $[110]$  direction in the high- $T$  tetragonal phase). The  $ab$  plane orientation of the  $x = 29\%$  crystals was not precisely controlled. At the NMR field with  $H||ab$ , we observed  $T_c(H) = 6.8$  K ( $x = 0$ ),  $7.8$  K ( $x = 0.09$ ),  $7.25$  K ( $x = 0.15$ ) and  $\leq 1.5$  K ( $x = 0.29$ ). Further experimental details are described in the Supplemental Material (SM) [30].

In FeSe, the single peak observed in the  $H||ab$  NMR spectrum at high  $T$  splits into two peaks below  $T_s$  due to nematic order, where the two peaks originate from twinned nematic domains [34–36]. Representative NMR spectra at 20 K for both field directions are shown in Fig. 1. Splittings of the  $H||ab$  spectra below  $T_s$  are also observed in FeSe $_{1-x}$ S $_x$  for all samples in which a nematic

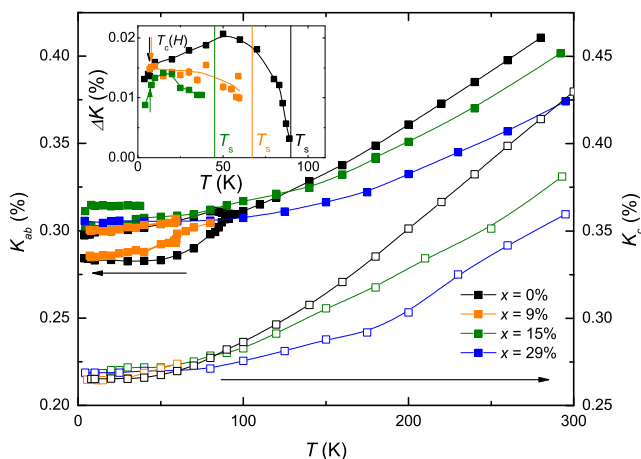


FIG. 2:  $T$  dependence of the NMR shift  $K$  for indicated  $x$  for  $H||ab$  (filled symbols) and  $H||c$  (open symbols). Inset: Splitting  $\Delta K$  of the  $H||ab$  NMR spectrum. Vertical lines represent  $T_s$  from resistivity [30]. Arrows in inset represent  $T_c(H)$  from *in situ* ac-susceptibility [30].

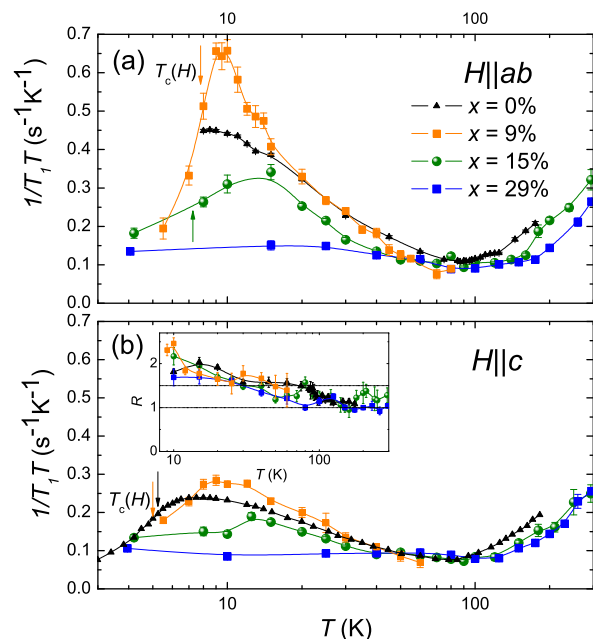


FIG. 3:  $T$  dependence of  $1/T_1 T$  for  $H||ab$  (upper panel) and  $H||c$  (lower panel) for indicated  $x$ . Arrows denote observed  $T_c(H)$  from *in situ* ac-susceptibility [30] (not shown for  $x = 0\%$   $H||ab$ ). For S-doped samples, missing arrows indicate  $T_c(H) < 4.0$  K. Inset: The  $T$  dependence of  $R = T_{1,c}/T_{1,ab}$  above  $T_c$ . Data for  $x = 0\%$  ( $ab$  plane average  $1/T_1 T$  and  $R$  at  $H = 9$  T) from Ref. 35. Data for  $x = 0\%$  ( $H||c$  at  $H = 7$  T) from Ref. 53.

transition was seen by resistivity [30].

The  $T$  dependence of the NMR shift  $K$  is shown in Fig. 2. As in FeSe, all  $K$  values increase monotonically with increasing  $T$ .  $K_{ab}$  is greater than  $K_c$  for all samples with almost no  $x$  dependence at low  $T$ . On the other hand, the high- $T$  value of  $K$  shows a large concentration dependence, where  $K$  decreases with increasing  $x$ .

The inset of Fig. 2 shows the  $T$  and  $x$  dependence of the  $H||ab$  spectral splitting  $\Delta K$  (the difference of the NMR shifts of the two peaks), which is a measure of the local nematic order parameter [34]. For FeSe,  $\Delta K$  increases sharply below  $T_s$  and shows a broad maximum near  $\sim 50$  K, as reported previously [34, 36, 37]. In contrast to FeSe,  $\Delta K$  for  $x = 9\%$  and  $x = 15\%$  does not exhibit this maximum. While the  $\Delta K$  of the  $x = 0\%$  and  $x = 9\%$  samples show no clear kinks at  $T_c$ , the  $x = 15\%$  sample shows a noticeable drop in the SC state. In the S-doped samples, we could not resolve the splitting all the way up to the bulk  $T_s$  identified by resistivity measurements [30], likely due to the broadening of the two individual lines (see Fig. 1) by microscopic disorder from dopants and/or small variations in the local S composition. Due to the broad spectra relative to FeSe, no clear evidence for the local nematicity above  $T_s$ , observed in FeSe from FWHM measurements [36, 38], could be found.

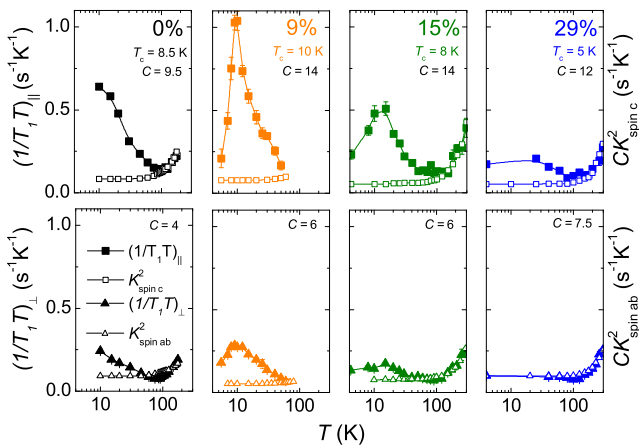


FIG. 4: Comparison of  $1/T_1T$  (left axes, filled symbols) with  $CK_{\text{spin}}^2$  (right axes, open symbols) for indicated  $x$ . The upper panels compare  $1/T_{1,\parallel}T$  to  $CK_{\text{spin},c}^2$ , while the lower panels compare  $1/T_{1,\perp}T$  to  $CK_{\text{spin},ab}^2$ . The empirical value of  $C$  (in units of  $10^4\text{s}^{-1}\text{K}^{-1}$ ) for each panel is indicated.

We now discuss the behavior of the low-energy magnetic fluctuations from NMR spin-lattice relaxation rate ( $1/T_1$ ) data.  $1/T_1T$  data are shown in Fig. 3 [39]. In general,  $1/T_1T$  is related to the dynamical magnetic susceptibility as  $1/T_1T \sim \gamma_N^2 k_B \sum_{\mathbf{q}} |A(\mathbf{q})|^2 \chi''(\mathbf{q}, \omega_N) / \omega_N$ , where  $A(\mathbf{q})$  is the wave-vector  $\mathbf{q}$  dependent form factor and  $\chi''(\mathbf{q}, \omega_N)$  is the imaginary part of  $\chi(\mathbf{q}, \omega_N)$  at the Larmor frequency  $\omega_N$  [40]. Above  $\sim 100$  K,  $1/T_1T$  shows a similar  $T$  dependence as  $K(T)$  which measures the uniform susceptibility  $\chi(\mathbf{q} = 0)$ . In contrast, below  $\sim 100$  K a strong upturn of  $1/T_1T$  is observed which is not seen in  $K(T)$ . The enhancement of  $1/T_1T$  at low  $T$  is therefore attributed to the growth of AFM spin fluctuations with  $\mathbf{q} \neq 0$ . The AFM fluctuations appear below  $\sim 100$  K for all samples, but the enhancement of the AFM fluctuations shows a strong  $x$  dependence.

In order to characterize the AFM fluctuations, we plotted the ratio  $R \equiv (1/T_1T)_{ab}/(1/T_1T)_c$  as shown in the inset of Fig. 3(b). According to previous NMR studies performed on Fe pnictides and related materials [41–46],  $R$  depends on the wavevector of the spin correlations. Assuming isotropic spin correlations, one expects  $R = 1.5$  for stripe-type,  $R = 0.5$  for Néel-type.  $R \approx 1$  at high  $T$  and increases to  $R > 1.5$  starting below  $\sim 100$  K. The value of  $R$  observed here at low  $T$  is consistent with stripe-type spin correlations. The  $T$  dependence of  $R$  is independent of  $x$  within experimental error, indicating no change in the character of magnetic fluctuations with doping.

To discuss magnetic fluctuations in more detail, it is convenient to isolate the component-resolved hyperfine field (HF) fluctuations from the measured  $1/T_1$  data.  $1/T_1$  probes the  $\mathbf{q}$  sum of fluctuations of HF at  $\omega_N$  perpendicular to the applied field according to  $(1/T_1)_{H\parallel i} =$

$\gamma_N^2 \sum_{\mathbf{q}} [|H_j^{\text{hf}}(\mathbf{q}, \omega_N)|^2 + |H_k^{\text{hf}}(\mathbf{q}, \omega_N)|^2]$ , where  $(i, j, k)$  are mutually orthogonal directions and  $|H_j^{\text{hf}}(\mathbf{q}, \omega)|^2$  represents the  $\mathbf{q}$ -dependent power spectral density of the  $j$ -th component of HF at the nuclear site. Therefore, we define the quantities  $1/T_{1,\perp} \equiv (1/T_1)_{H\parallel c} = 2\gamma_N^2 \sum_{\mathbf{q}} |H_{ab}^{\text{hf}}(\mathbf{q}, \omega_N)|^2$  and  $1/T_{1,\parallel} \equiv 2(1/T_1)_{H\parallel ab} - (1/T_1)_{H\parallel c} = 2\gamma_N^2 \sum_{\mathbf{q}} |H_c^{\text{hf}}(\mathbf{q}, \omega_N)|^2$  [33]. Note that, for simplicity, we have neglected any  $ab$ -plane anisotropy due to nematicity ( $H_a^{\text{hf}} = H_b^{\text{hf}} \equiv H_{ab}^{\text{hf}}$ ). Thus defined,  $1/T_{1,\perp}$  ( $1/T_{1,\parallel}$ ) directly measures the  $ab$  ( $c$ ) component of HF fluctuations  $\sum_{\mathbf{q}} |H_{ab}^{\text{hf}}(\mathbf{q}, \omega_N)|^2$  ( $\sum_{\mathbf{q}} |H_c^{\text{hf}}(\mathbf{q}, \omega_N)|^2$ ).

In Fermi liquid systems, one expects that  $1/T_1T \propto K_{\text{spin}}^2$ . Here  $K_{\text{spin}} = K - K_0$ , where  $K_0$  is the  $T$ -independent chemical shift (see [30]).  $K_{\text{spin}}$  probes the uniform  $\mathbf{q} = 0$  susceptibility according to  $K_{\text{spin},i} = A_{ii}\chi_{ii}(\mathbf{0})$ , where  $A_{ii}$  is the hyperfine coupling constant. Therefore, to examine the contribution of  $\mathbf{q} \neq 0$  correlations one can compare  $1/T_1T$  to  $K_{\text{spin}}^2$ . The quantities  $1/T_{1,\parallel}T$  and  $1/T_{1,\perp}T$  should be compared to  $K_{\text{spin},c}^2$  and  $K_{\text{spin},ab}^2$ , respectively [33]. The experimentally observed  $1/T_1T$  can then be decomposed into  $\mathbf{q} = 0$  and AFM ( $\mathbf{q} \neq 0$ ) components as  $1/T_1T = (1/T_1T)_{\text{AFM}} + (1/T_1T)_{\mathbf{q}=0}$ . We have  $(1/T_1T)_{\mathbf{q}=0} = CK_{\text{spin}}^2$ , where  $C$  is a proportionality constant determined empirically from the high  $T$  data [30].

In Fig. 4, we compare the angle-resolved pairs of  $1/T_1T$  and  $CK_{\text{spin}}^2$ . Above  $\sim 100$  K, it is clear that  $1/T_1T \approx CK_{\text{spin}}^2$ , indicating that the  $T_1$  relaxation is driven by the  $\mathbf{q} = 0$  component. In contrast, the difference between  $1/T_1T$  and  $CK_{\text{spin}}^2$  can be clearly seen below  $\sim 100$  K and is attributed to the contribution of AFM fluctuations,  $(1/T_1T)_{\text{AFM}}$ . Relative to FeSe, spin fluctuations are enhanced at  $x = 9\%$ , slightly suppressed at  $x = 15\%$  and strongly suppressed for  $x = 29\%$ . The  $x$  dependence of the AFM fluctuation enhancement closely parallels the  $x$  dependence of  $T_c$ , which shows a slight enhancement between  $x = 0\%$  and  $x = 9\%$  and is suppressed at higher doping levels. The suppression of magnetic fluctuations for  $x \geq 15\%$  is consistent with ARPES data [47].

In all cases, we find that  $1/T_{1,\parallel}T > 1/T_{1,\perp}T$  at low  $T$ , indicating that  $\sum_{\mathbf{q}} |H_c^{\text{hf}}(\mathbf{q}, \omega_N)|^2$  is greater than  $\sum_{\mathbf{q}} |H_{ab}^{\text{hf}}(\mathbf{q}, \omega_N)|^2$ . The HF at the Se nuclear site is determined from the magnetic moments on the Fe sites by the hyperfine coupling tensor. Since the stripe-type AFM fluctuations produce the HF fluctuations at the Se site through off-diagonal components of the hyperfine coupling tensor [6, 48], the fact that  $|H_c^{\text{hf}}|^2$  is greater than  $|H_{ab}^{\text{hf}}|^2$  shows that the  $ab$ -plane polarized stripe-type AFM fluctuations are more developed than the corresponding  $c$ -axis polarized fluctuations, similar to the  $\text{BaFe}_2\text{As}_2$  system [33].

Within an itinerant picture, the change in the AFM correlations with doping would be associated with a change in the nesting condition due to modification of

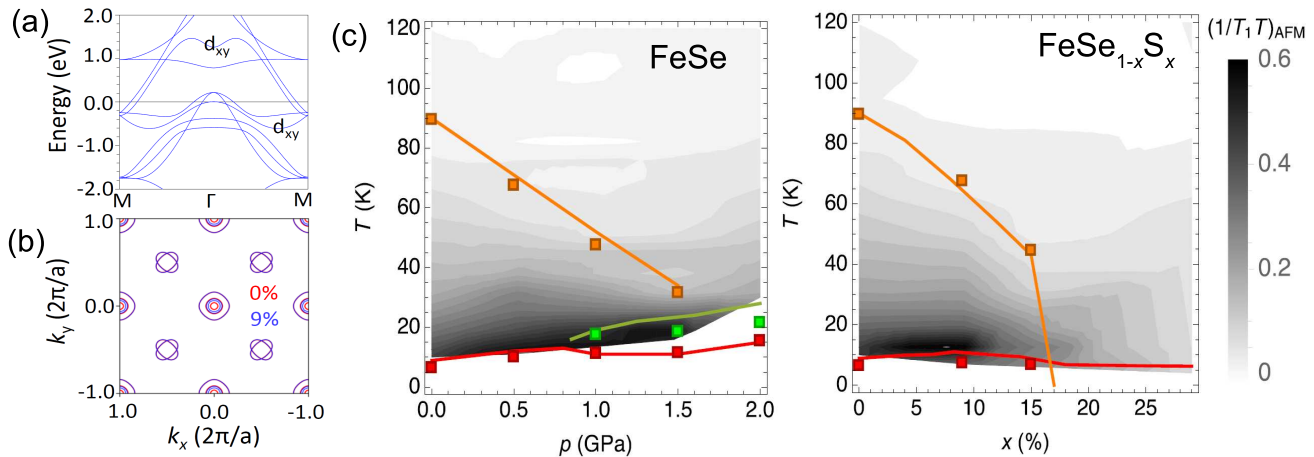


FIG. 5: (a) Band dispersion of FeSe in the tetragonal phase, with bands of  $d_{xy}$  orbital character indicated. (b) Cross-sections of the Fermi surface in the tetragonal phase at  $k_z = 0$  for  $x = 0\%$  (red) and  $x = 9\%$  (blue). (c) Comparison of AFM fluctuations in FeSe under pressure [36] (left panel) and  $\text{FeSe}_{1-x}\text{S}_x$  (right panel). Here, the AFM contribution to  $1/T_1T$  is defined by  $(1/T_1T)_{\text{AFM}} \equiv (1/T_1T) - (1/T_1T)_{q=0}$  using  $H\parallel ab$  data [30]. Solid lines show  $T_s$  (orange),  $T_N$  (green) and  $T_c$  (red) from resistivity at  $H = 0$  [13, 16, 23, 47]. Data points show  $T_s$ ,  $T_N$  and  $T_c(H)$  from NMR under  $H \sim 7.4$  T (this work and [36]). Note  $T_c(H)$  for  $x = 29\%$  is less than 1.5 K.

the Fermi surface with S substitution. To understand the band structure of  $\text{FeSe}_{1-x}\text{S}_x$ , we performed electronic structure calculations [49] using the full-potential linearized augmented plane wave method [50] with a generalized gradient approximation [51]. Here we calculate the band structure for the tetragonal phases in  $\text{FeSe}_{1-x}\text{S}_x$  using an FeSe unit cell, adopting chemical pressure effects on the  $a$  and  $c$  lattice parameters. The calculated band dispersion is shown in Fig. 5(a), which is in good agreement with the previous report [25]. The calculated Fermi surface has three hole pockets around the  $\Gamma$  point and two electron pockets at the  $M$  point along the  $[110]$  direction (Fig. 5(b)). We find that the size of the smallest of the three hole pockets, originating from the  $d_{xy}$  orbital, is increased by S doping. In contrast, the other pockets, originating from  $d_{yz}$  and  $d_{zx}$  orbitals, do not change. These results continue to hold for a 1% reduction of the chalcogen height, which also occurs by S doping [24]. Thus the  $d_{xy}$  orbital can be considered to play an important role in AFM spin correlations and also in the appearance of SC in  $\text{FeSe}_{1-x}\text{S}_x$ .

Finally let us comment on the temperature dependence of  $1/T_1T$  observed in  $x = 9\%$  and  $x = 15\%$  (see Fig. 3). For  $x = 0\%$ , the maximum of  $1/T_1T$  has been reported to occur close to  $T_c$  [34, 37]. However, for  $x = 9\%$  and  $x = 15\%$ , we find that the maximum of  $1/T_1T$  instead occurs well above  $T_c(H)$ , as determined by our *in situ* ac-susceptibility measurements [30]. At  $x = 9\%$ , we find  $T_c(H\parallel ab) = 7.8$  K and  $T_c(H\parallel c) = 5.0$  K, while  $1/T_1T$  peaks at  $\sim 9$  K for both  $H$  directions. At  $x = 15\%$ , we find  $T_c(H\parallel ab) = 7.25$  K and  $T_c(H\parallel c) \leq 4.0$  K. However, for both  $H$  directions,  $1/T_1T$  peaks at  $\sim 12 - 15$  K. These results imply a suppression of magnetic fluctuations

just above  $T_c$  in the S-doped samples. The effect is more apparent for  $H\parallel c$  data. Furthermore, the  $T$  difference between  $T_c$  and the peak of  $1/T_1T$  appears to increase with doping. Similar behavior has been observed in FeSe and discussed in terms of a possible SC fluctuation effect [52, 53]. Reductions of  $1/T_1T$  above  $T_c$  have been observed in  $\text{LaFeAsO}_{1-x}\text{F}_x$  [42, 54] and  $\text{Ca}(\text{Fe}_{1-x}\text{Co}_x)_2\text{As}_2$  [55] where pseudogap behavior has been discussed. Detailed  $H$ -dependent measurements on the S-doped samples will be needed to confirm the origin of the suppression of  $1/T_1T$ .

Our main results are summarized in the phase diagram of Fig. 5(c), which shows a contour plot of the AFM contribution to  $1/T_1T$  as a function of  $x$  and  $T$ . For comparison, a similar plot for FeSe under pressure is also shown. In both cases, the bulk nematic order is suppressed. In FeSe, AFM fluctuations are roughly independent of pressure or slightly enhanced [36]. In  $\text{FeSe}_{1-x}\text{S}_x$ , the AFM fluctuations are strongly suppressed by S doping after an initial slight enhancement for  $x \approx 9\%$  where the AFM fluctuations are strongly correlated with  $T_c$ . In contrast, nematic fluctuations are most strongly enhanced near the nematic QCP at  $x \approx 17\%$  [21] and show no correlation with  $T_c$ . These NMR results clearly demonstrate the primary importance of AFM fluctuations to SC in  $\text{FeSe}_{1-x}\text{S}_x$ , and help to disentangle the roles of magnetic and nematic fluctuations in iron-based superconductors in general.

*Note added.* Quite recently a different  $x$  dependence of  $T_c$  has been reported in  $\text{FeSe}_{1-x}\text{S}_x$  crystals where  $T_c$  keeps increasing up to  $x \sim 0.15$  [56]. It is interesting to perform NMR measurements to investigate how the magnetic fluctuations change in the crystals. This would

be a future project.

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