

Magnetic fluctuations under pressure on S-doped FeSe studied via ^{77}Se NMR

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$\text{FeSe}_{1-x}\text{S}_x$ has attracted much attention among iron-based superconductors because the pure sample undergoes nematic and superconducting (SC) phase transitions without magnetism. A pressure-induced antiferromagnetic (AFM) phase emerges upon applying pressure. In the pressure (P)-temperature (T) phase diagram for the 12%-S doped sample, the AFM phase is separated from the nematic phase at around 3.0 GPa, and SC transition temperature (T_c) takes a maximum (~ 30 K). We measured T_1 of ^{77}Se for the 12%-S doped FeSe at 3.0 GPa. We found from $1/T_1T$ that low-energy AFM fluctuations are not so much enhanced under pressure compared with those at ambient pressure. The result suggests changes of topology and nesting of Fermi surfaces during pressurizing process. © 2018 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>). <https://doi.org/10.1063/1.5042570>

I. INTRODUCTION

In iron-based pnictide superconductors such as 1111 and 122 systems, nematicity is inherent in magnetism. The nematic phase followed by the antiferromagnetic (AFM) phase at low temperatures (T) is usually observable in an undoped or a low carrier-doped compound. An iron-based selenide FeSe is a specific compound in the family of iron-based superconductors in the point that it undergoes nematic and superconducting (SC) phase transitions at 90 and 9 K, respectively, without magnetism.^{1,2} The pressure (P)- T phase diagram was obtained from the resistivity measurements.³ FeSe undergoes complex phase transitions upon applying pressure: the nematic phase disappears at 1.5 GPa, and instead an AFM phase with dome structure is induced in the P - T phase diagram. Both the AFM and nematic phases were determined from the variation of the T dependence of the resistivity. The AFM phase overlaps the nematic phase at the boundary in the P - T phase diagram. The two phases coexist in the pressure range between 1 and 2 GPa. The SC phase develops remarkably with increasing pressure above 5 GPa: SC transition temperature (T_c) of 9 K at ambient pressure goes up to 37 K at 6.0 GPa. In this pressure-induced AFM phase, a stripe-type spin configuration with the nesting vector $(\pi, 0)$ has been suggested from NMR measurements,⁴ whereas ^{77}Se line splits into two lines in the nematic phase.⁵ According to the ARPES measurements, the orbital ordering has been suggested under the nematic states, where the degeneracy between d_{xz} and d_{yz} orbitals are resolved.^{6,7} Furthermore, in FeSe, BCS-BEC cross-over has been suggested, where the superconducting gaps and the Fermi energies are of the same order.⁸

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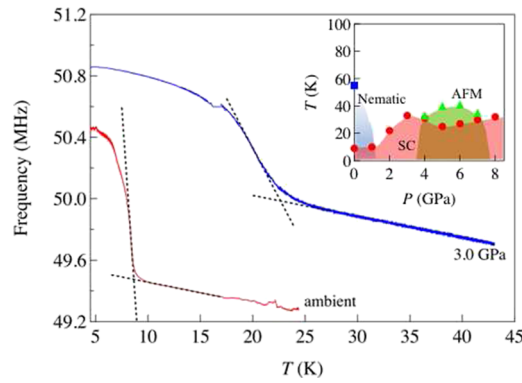


FIG. 1. The AC susceptibility measured using a NMR probe and a network analyzer at 3.0 GPa and ambient pressure for 12%-S doped FeSe under a field of 6.02 T. T_c s are determined from cross points of the dashed lines. The inset shows the pressure vs temperature phase diagram for 12%-S doped FeSe determined from the resistivity measurements.⁹ In the diagram, AFM and SC represent antiferromagnetic and superconducting phases, respectively.

The phase diagram determined from the resistivity dramatically changes by sulfur (S) doping: the pressure-induced AFM phase with the dome structure moves to a higher-pressure regime as the doping level is increased.⁹ As a result, the nematic phase is separated from the AFM phase in the P - T phase diagram, as shown in the inset of Fig. 1. Interestingly, T_c for $x = 0.12$ reaches a maximum (~ 30 K) at the intermediate pressure (~ 3 GPa) where both the nematic and AFM phases are absent. Contrary to the P - T phase diagram, no AFM phases are induced in the x - T phase diagram at ambient pressure. In the x - T phase diagram, the nematic phase is gradually suppressed with increasing the doping level and vanishes at $x = 0.17$, whereas T_c is almost unchanged up to $x = 0.17$, and slightly changes at $x = 0.17$. At this doping level, the nematic quantum critical point has been suggested, toward which nematic fluctuations are enhanced.¹⁰ The Fermi surfaces of the pure FeSe are constructed by one or two hole pockets at Γ point and elliptical electron pockets at M point.^{6,7} An additional hole pocket manifests, and the electron pockets become isotropic with increasing the doping level.⁷

Because the nematic, SC, and AFM phases complicatedly overlap each other in the P - T phase diagram for the pure sample, the 12%-S doped sample is preferred to investigate whether a high T_c under pressure originates from AFM fluctuations. For this purpose, we investigated the electronic state in a microscopic view point using NMR technique for $x = 0.12$ where T_c marks a high value of 25-30 K without the nematic and AFM orderings.

II. EXPERIMENTAL RESULTS

We performed ^{77}Se -NMR measurements at 6.02 T on a single crystal for $x = 0.12$ with the size of about $1.0 \times 1.0 \times 0.5$ mm under a pressure of 3.0 GPa. We used a NiCrAl pressure cell¹¹ and Daphne oil as pressure mediation liquid. We set the crystal in a pressure cell so that the FeSe plane is parallel to the applied field. We measured the relaxation time T_1 by a conventional saturation recovery method. We determined T_c using a network analyzer and the tank circuit of a NMR probe.

The results of the resonance frequency are shown in the main panel of Fig. 1. The resonance frequency changes rather sharply at ambient pressure: T_c determined from the cross point is 8.6 K and that from the onset is 9.8 K. Due to the application of the field, T_c decreases from 8.6 K to 6 K¹² at 6.02 T. The resonance frequency measured at 3.0 GPa exhibits gradual change with decreasing temperature; T_c s determined from the cross point and the onset are 22.8 K and 25.5 K, respectively. Due to the application of the field, T_c decreases from 22.8 K to 22.1 K at 3.0 GPa.

A single ^{77}Se -NMR signal was observed in a paramagnetic state, and it exhibits double-peaks structure in the nematic phase. At ambient pressure, ^{77}Se line splits into two lines below 60 K, which is in good agreement with the nematic transition temperature obtained from the resistivity measurements. While the double-peaks structure has been observed as two well-separated lines for the pure sample in the nematic phase,⁵ the two lines overlap each other for our 12%-doped sample, which implies that Fermi surfaces become isotropic due to S doping.

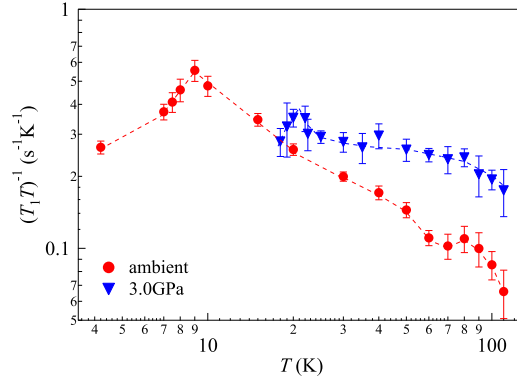


FIG. 2. The relaxation rate $1/T_1$ divided by temperature (T), $1/T_1T$, for ^{77}Se measured at 6.02 T. The peaks correspond to the superconducting transition temperature (T_c) at 6.02 T.

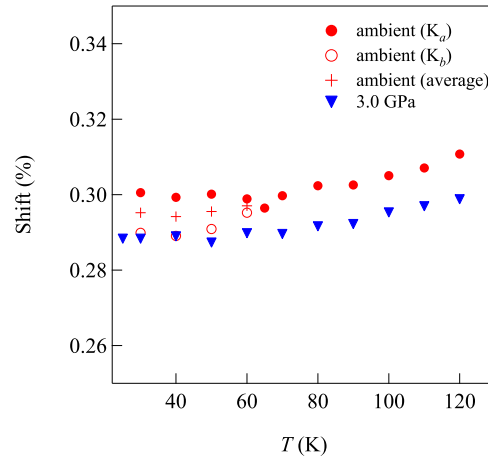


FIG. 3. The T dependence of the ^{77}Se -NMR shift obtained from a two-gaussian fit. The ^{77}Se line at ambient pressure splits into two lines in the nematic phase below 60 K. K_a and K_b represent shifts of higher and lower frequency peaks, respectively.

We measured T_1 for the higher-frequency peak at 6.02 T. Figure 2 shows $1/T_1T$ measured at ambient pressure and 3.0 GPa. The temperatures where $1/T_1T$ takes a peak are in good agreement with T_c s determined from the AC susceptibility measurements at 6.02 T. Below T_c , the signal intensity becomes extremely small, and we were not able to detect the signals below 15 K at 3.0 GPa. $1/T_1T$ at 3.0 GPa shows Curie-Weiss behavior only in a limited temperature region ranging from 30 K to $T_c \sim 22$ K, whereas that at ambient pressure shows the Curie-Weiss behavior in a wide temperature region ranging from the nematic transition temperature (60 K) to T_c (9 K).

As for NMR shifts determined from FFT-NMR spectra, the shift measured at 3.0 GPa qualitatively exhibits similar T dependence to that at ambient pressure, as shown in Fig. 3. The former is quantitatively smaller than the latter in a wide T region, which is attributed to that the density of states and thus the Fermi surfaces change by applying pressure. At ambient pressure, a ^{77}Se line splits into two lines in the nematic phase, however, the average of two lines exhibits the similar T dependence to that at 3.0 GPa where the nematic phase is absent.

III. DISCUSSION

The relaxation rate gives a measure of low-energy spin fluctuations. When wave-vector (q) dependence of the hyperfine interaction is neglected, $1/T_1T$ is expressed as follows:

$$\frac{1}{T_1T} \propto \sum_q \frac{\text{Im} \chi(q, \omega)}{\omega} \quad (1)$$

where ω and $\chi(q, \omega)$ represent the NMR frequency and the dynamical spin susceptibility, respectively.

First, we expected that AFM fluctuations would affect $1/T_1T$ much more at 3.0 GPa than at ambient pressure, because AFM fluctuations would become strong near the AFM phase boundary. A theoretical investigation suggests that the nesting of $q = (\pi, 0)$ corresponding to stripe-AFM fluctuations becomes strong with increasing pressure due to the development of a pocket within the hole pockets at Γ point.¹³ However, the Curie-Weiss behavior was more clearly seen at ambient pressure than at 3.0 GPa in the wide T range. The results of the shift in Fig. 3 indicate that the T dependence of $\chi(q=0)$ is qualitatively unchanged, which implies that the suppression of AFM fluctuations at 3.0 GPa is intrinsic in this system. This unexpected result is not explainable in the case that q dependence of $\chi(q)$ shows continuous change upon applying pressure. Considering that the Fermi surfaces become isotropic^{7,14} and thus the two NMR lines overlap upon S doping, they might exhibit drastic variation in size and shape during pressurizing process. Therefore, the maximum of $\chi(q)$, or the nesting vector of Fermi surfaces may drastically change during pressurizing process, which is a possible explanation why $1/T_1T$ measured at 3.0 GPa exhibit weaker Curie-Weiss behavior than that measured at ambient pressure, despite that the AFM phase boundary is closer to 3.0 GPa than ambient pressure in the P - T phase diagram. It is not certain at present whether the stripe-AFM ordering, which has been observed for the pure FeSe under pressure,⁴ is unchanged with increasing the doping level. This should be clarified using experimental methods on a microscopic level in the AFM phase of the S-doped sample.

Another question is why the AFM phase is absent at ambient pressure despite that the Curie-Weiss behavior is clearly observable. For this question, the nematic and orbital orderings may be deeply associated with the suppression of the AFM ordering.¹³ In $\text{FeSe}_{1-x}\text{S}_x$ system, the AFM phase tends to manifest apart from the nematic phase despite that there is some overlap at low S-doping and pressure regimes, which gives prominent difference from FeAs systems such as 122, 111, 1111 systems. At ambient pressure, the AFM ordering may be suppressed due to the nematic ordering or fluctuations despite that strong AFM fluctuations remain. Thus, the nematicity would be competing with the AFM ordering in this system. It is important to clarify the relationship between the nematicity and AFM fluctuations.

Considering that the superconductivity exhibits a high T_c near the AFM phase, AFM fluctuations would have strong effect on the formation of superconductivity, however, prominent Curie-Weiss behavior was not observed in our experiments at 3.0 GPa. To clarify the relationship between low-energy AFM fluctuations and the superconductivity, systematic investigations at a wide pressure range and detailed information about the Fermi surfaces are needed.

IV. SUMMARY

We measured T_1 of ^{77}Se for 12%-S doped FeSe at 3.0 GPa and compared the results with those at ambient pressure. We confirmed from $1/T_1T$ and the AC susceptibility measurements that T_c is enhanced from 8.6 K to 22.8 K by applying a pressure of 3.0 GPa. Low-energy AFM fluctuations measured from $1/T_1T$ are not so much enhanced under pressure compared with those at ambient pressure, despite that the Curie-Weiss behavior is observed only in a limited temperature region ranging from 30 K to $T_c \sim 22$ K. The result suggests changes of topology and nesting of Fermi surfaces during pressurizing process.

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