Two different superconducting states and possible antiferromagnetic quantum critical points in S-doped FeSe under pressure

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We performed $^{77}$Se-NMR measurements on FeSe$_{1-x}$S$_x$ ($x=0.12$) up to 3.0 GPa at an applied magnetic field of 6.02 T, and found that the superconducting (SC) phase exhibits a remarkable double-dome structure in the pressure($P$)-temperature($T$) phase diagram which is hidden at 0 T. From the relaxation rate $1/T_1$ divided by $T$, $1/T_1/T$, a Lifshitz transition may occur at 1.0 GPa, and the dominant nesting vector could change due to topological changes in Fermi surfaces. In other words, two types of antiferromagnetic (AFM) fluctuations would exist in the $P$-$T$ phase diagram. We conclude that the SC double domes in 12%-S doped FeSe consist of two SC states each of which correlates to a different type of AFM fluctuation. Furthermore, the strong AFM fluctuation at ambient pressure could originate from a possible hidden AFM quantum critical point.

Recently, iron chalcogenides, so-called 11 systems, have received much attention because of their unique phase diagrams. In particular, FeSe undergoes nematic and superconducting (SC) transitions at 90 and 9 K, respectively, without any magnetism at ambient pressure [1], while an antiferromagnetic (AFM) phase exists in most iron based superconductors, such as undoped or low carrier doped 1111 and 122 systems [2]. The pressure ($P$)- temperature ($T$) phase diagram for FeSe has been obtained from the resistivity measurements [2]: the nematic phase disappears at 1.5 GPa, and an AFM phase with a dome structure is induced in the $P$-$T$ phase diagram instead. The AFM phase overlaps the nematic phase at the boundary in the $P$-$T$ phase diagram. The SC phase develops remarkably as pressure increases above 1.5 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 [1]. A theoretical investigation proposed that an inner hole-like pocket appears due to increasing pressure and it would make the AFM ordering with the ($\pi, 0$) nesting [3]. More information about the Fermi surfaces at ambient pressure has been obtained from the angle resolved photo emission spectroscopy (ARPES) [6–12]. The Fermi surfaces of the pure FeSe are constructed by a hole-like pocket at the $\Gamma$ point and elliptical electron-like pockets at the M point. Several experiments suggest orbital ordering under the nematic states, where the degeneracy between $d_{xz}$ and $d_{yz}$ orbitals is resolved [6, 9].

The phase diagram determined from the resistivity dramatically changes with sulfur (S) doping [13]: the pressure-induced AFM phase with the dome structure moves to a higher pressure region as the doping level is increased. As a result, the nematic phase is segregated from the AFM phase in the $P$-$T$ phase diagram. Interestingly, $T_c$ for $x=0.12$ reaches a maximum ($\sim$30 K) at the intermediate pressure ($\sim$3 GPa) where both the nematic and AFM phases are absent (see the inset of Fig.1). Contrary to the $P$-$T$ phase diagram, no AFM phases are induced in the $x$-$T$ phase diagram at ambient pressure [14–16]. An additional hole-like pocket emerges, and the electron-like pockets become isotropic as the doping level is increased [14, 16–18]. Because the nematic, SC, and AFM phases overlap each other in a complex manner in the $P$-$T$ phase diagram for the pure sample, the 12%-S doped sample is preferred for the investigation of the origin of a high $T_c$ under pressure.

In the present work, we revealed the double-dome structure of the SC phase which is hidden at 0 T from $^{77}$Se-NMR measurements on 12%-S doped FeSe under an applied field. We found that each of these two domes correlates to a different type of AFM fluctuation. In addition, we argue that the strong AFM fluctuation observed at ambient pressure could originate from a possible hidden AFM quantum critical point (QCP).

We performed $^{77}$Se-NMR measurements at 6.02 T up to 3.0 GPa on a 12%-S doped single crystal with dimensions of about $1.0 \times 1.0 \times 0.5$ mm. We used a NiCrAl pressure cell [20] and Daphne oil as pressure mediation liquid. We placed the crystal in the pressure cell so that the FeSe plane was parallel to the applied field.

First, we determined $T_c$ from AC susceptibility measurements using the tank circuit of a NMR probe at both
FIG. 1. The relaxation rate $1/T_1$ divided by temperature ($T$), $1/T_1 T$, for $^{77}$Se measured at 6.02 T up to 3.0 GPa. The dashed and solid lines are the guides for the eyes. (a), (b) $1/T_1 T$ at low and high pressures, respectively. (c) Expansion of $1/T_1 T$ for Figs.1a and 1b at low $T$ below 60 K. The inset shows the phase diagram obtained from the resistivity measurements [13].

TABLE I. $T_c$ measured at 0 T and 6.02 T up to 3.0 GPa.

| Pressure (GPa) | $T_c$ at 0 T (K) | $T_c$ at 6.02 T (K) |
|---------------|-----------------|-------------------|
| ambient       | 9.8             | 6.5 [19]          |
| 1.0           | 8.8             | 2 [19]            |
| 2.0           | 15.5            | 14.2              |
| 3.0           | 25.5            | 24.1              |
FIG. 2. (a) $T$ dependence of the $^{77}$Se-NMR shift at several pressures. The black crosses represent the average of two lines in the nematic phase. The black arrows represent $T_c$. The inset shows the $T$ dependence of the shift at ambient pressure. The split lines are obtained from two Gaussian fits determined from a single Gaussian fit. The gray arrows show the nematic transition points determined from onsets of the upturn.

The $^{77}$Se-NMR shifts are also consistent with the scenario that two different SC states form the double-dome-like SC phase in the $P$-$T$ phase diagram at 6.02 T. In the SC phase, the shift decreases with decreasing $T$. Contrary to the shift at ambient pressure, it exhibits a remarkable drop at $T_c$ at 2.0 GPA and 3.0 GPA. While the data points to detect the SC gap symmetry are few, this difference may reflect the two different SC phases. From the above, two different SC phases exist in FeSe$_{1-x}$S$_x$ $(x = 0.12)$ under pressure, and thus, SC-SC transition may occur. Recently, the STM and STS measurements imply two distinct pairing states in the $x$-$T$ phase diagram [23, 24]. It is uncertain that the SC-SC transitions in the $P$-$T$ and $x$-$T$ diagrams are the same at present.

We propose a possible hidden AFM QCP, (2). In FeSe systems, the AFM fluctuation is very strong at magnetic order [12, 18]. Taking these topological changes into account, in S doped FeSe under pressure, remarkable changes of the Fermi surfaces and the dominant nesting vector could occur. The NMR spectra reflect these topological changes as mentioned. Thus, two types of AFM fluctuations (colored in green in Fig.3a) imply that the Lifshitz transition occurs and the dominant nesting vector changes around 1.0 GPA. The $P$ dependence of $T_c$ correlates to this change in the topology, which can be clearly seen in Fig.3a.

As we will discuss below, our results imply that (1) two distinct SC states in FeSe$_{1-x}$S$_x$ $(x = 0.12)$ form the double-dome structure in the $P$-$T$ phase diagram under the applied magnetic field and that (2) a hidden AFM QCP exists at ambient pressure.

First, we discuss the former, (1). At first glance, $T_c$ seems to be suppressed by the nematic fluctuations around a nematic QCP and seems to increase at higher pressures because the SC state is free from the suppression. From the FWHM (Fig[2a]), however, the nematic fluctuation would exist up to 2.0 GPA whereas an anomaly of $T_c$ emerges at 1.0 GPA (Fig[3a]). It is possible that a Lifshitz transition causes the anomaly in $T_c$ at 1.0 GPA. Considering the $P$ and $T$ dependence of $1/T_1T$ (Fig[3a]), AFM fluctuations seem to correlate to $T_c$. To understand the relationship between the AFM fluctuations and the SC phase, the evolution of the Fermi surfaces and the nesting vector upon S doping and the application of pressure should be taken into account. From the ARPES and quantum oscillation measurements, the electron-like pockets at M point become isotropic with S doping and a Lifshitz transition may occur [16, 17, 24]. Furthermore, the theoretical investigation suggests that the additional hole-like pocket emerges at the $\Gamma$ point under pressure [5, 18]. Both S doping and the application of pressure would make the electron pockets isotropic [12, 18]. Taking these topological changes into account, in S doped FeSe under pressure, remarkable changes of the Fermi surfaces and the dominant nesting vector could occur. The NMR spectra reflect these topological changes as mentioned. Thus, two types of AFM fluctuations (colored in green in Fig[3a]) imply that the Lifshitz transition occurs and the dominant nesting vector changes around 1.0 GPA. The $P$ dependence of $T_c$ correlates to this change in the topology, which can be clearly seen in Fig[3a].

Next, we discuss a possible hidden AFM QCP, (2). In FeSe$_{1-x}$S$_x$, the AFM fluctuation is very strong at ambient pressure despite the absence of magnetic order, which is an open problem at present [4, 27]. Herein, we propose a possible explanation for this phenomenon. Fig[3b] shows the $P$ dependence of the Weiss temperature $\theta$ determined from a Curie-Weiss fit:

$$\frac{1}{T_1T} \sim a + \frac{b}{T - \theta}$$

where $a$ and $b$ are assumed to be coefficients independent of $T$. In general, $\theta = 0$ K at QCP. In Fig[3] $\theta$ takes 0 K near 0 GPA and 2.6 GPA. The latter is accountable as the QCP of the pressure-induced AFM phase, although the value is smaller than that suggested from the resistivity measurements [12]. It is important to ascertain why $\theta$ takes 0 K near 0 GPA where no magnetism is observed. A possible explanation is that another AFM phase would exist in an imaginary negative pressure region. Application of hydrostatic negative pressure is unrealistic. In terms of lattice expansion, however, isovalent substitutions can give a clue for understanding the unexpected...
FIG. 3. (a) Phase diagram and magnetic fluctuations in FeSe$_{1-x}$S$_x$ ($x = 0.12$). The inverted triangle and circles represent $T_c$ at 0 T and 6.02 T, respectively. The value of $1/T_1 T$ is superimposed in the phase diagram by a colored contour. The black squares represent the long and short range nematic transitions observed in pure FeSe and FeSe$_{1-x}$S$_x$ could originate from a possible hidden AFM QCP. Interestingly, the $P$ dependence of the Weiss temperature in the low pressure region seems to have some correlations with the nematic transition temperature (see Fig.3).

Assuming that the hidden QCP exists, the phase diagram is reminiscent of that for LaFeAsO$_{1-x}$H$_x$, where two SC domes are sandwiched between two AFM phases [33, 34]. Fig. 3 shows a schematic phase diagram of FeSe$_{1-x}$S$_x$. The double dome structure of the SC phase is sandwiched between two separated AFM phases. The hidden QCP and the unique phase diagram are first suggested from our present NMR measurements on S-doped FeSe, where the nematic phase is segregated from the AFM phase. Because there is no way to apply hydrostatic negative pressure, this phase diagram is speculative. To clarify this, systematic investigations with wider $x$ and $P$ ranges are needed. However, it is certain that we obtained clues for understanding the SC pairing mechanism in iron-based superconductors.

In summary, we have demonstrated that two different SC states form the double-dome-like SC phase in FeSe$_{1-x}$S$_x$ ($x = 0.12$) under pressure. The Lifshitz transition may occur around 1.0 GPa where $T_c$ is strongly suppressed. Thus, an unexpected $P$ and $T$ dependence of $1/T_1 T$ reflects topological changes in Fermi surfaces, that is, the dominant nesting vector below 1.0 GPa is different from that above 1.0 GPa. In addition, the Weiss temperature $\theta$ takes 0 K near 0 GPa, which implies that another AFM QCP exists. In nature, the SC phase in FeSe$_{1-x}$S$_x$ ($x = 0.12$) has the double-dome-like structure, and is sandwiched between two AFM phases, similar to the case of LaFeAsO$_{1-x}$H$_x$.

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