

Why Does Undoped FeSe Become a High- T_c Superconductor under Pressure?

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Unlike the parent phases of the iron-arsenide high- T_c superconductors, undoped FeSe is not magnetically ordered and exhibits superconductivity with $T_c \sim 9$ K. Equally surprising is the fact that applied pressure dramatically enhances the modest T_c to ~ 37 K. We investigate the electronic properties of FeSe using ^{77}Se NMR to search for the key to the superconducting mechanism. We demonstrate that the electronic properties of FeSe are very similar to those of electron-doped FeAs superconductors, and that antiferromagnetic spin fluctuations are strongly enhanced near T_c . Furthermore, applied pressure enhances spin fluctuations. Our findings suggest a link between spin fluctuations and the superconducting mechanism in FeSe.

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The discovery of new iron-arsenide (FeAs) high- T_c superconductors [1] has led to a frenzy of research over the last year [2]. The superconducting mechanism still remains enigmatic, but it has become clear that all FeAs superconductors share a salient feature; their undoped parent phase is magnetically ordered in a spin density wave (SDW) state, and the superconducting phase emerges when electron or hole doping suppresses the SDW instability [2]. For example, both undoped LaFeAsO and BaFe₂As₂ have a SDW ground state below $\lesssim 140$ K [3,4], and the superconducting state in LaFeAsO_{1-x}F_x ($T_c \sim 28$ K) [1] and BaFe_{2-x}Co_xAs₂ ($T_c \sim 22$ K) [5] requires 5%–8% of electron doping. Therefore, one could speculate that residual spin fluctuations may be playing a key role in the superconducting mechanism. Alternatively, one could also argue that magnetism and superconductivity are competing against each other.

In view of the possible link or competition between magnetism and superconductivity in FeAs high- T_c superconductors, superconductivity in FeSe ($T_c \sim 9$ K) [6,7] raises interesting questions, and provides important test ground for the ideas to account for high- T_c superconductivity in iron-based systems [8]. We note that the initial discovery identified α -FeSe_{1- δ} with large deficiency $\delta \sim 0.12$ as the superconducting phase [6], which led to a misperception that electron doping by the Se deficiency destroys a SDW ground state and stabilizes superconductivity. However, as some of us have more recently shown, the apparently large δ is caused by oxygen contamination of the Fe ingredient [7]. The actual superconducting phase is the stoichiometric β -Fe_{1.01 \pm 0.02}Se, or equivalently, β -FeSe_{0.99 \pm 0.02} [7], i.e., superconductivity in FeSe does not require electron doping. Furthermore, application of pressure on FeSe raises T_c to as high as ~ 37 K [9–11]. These observations are counterintuitive if we compare the number of electrons at As and Se sites. The nominal ionic state of the FeAs layers is [FeAs]⁻ in the undoped parent

phase with an SDW ground state (e.g., LaFeAsO and BaFe₂As₂), and the As³⁻ sites have eight electrons in the (4s)²(4p)⁶ orbitals. Since a Se atom has one extra electron compared to an As atom, we also expect that eight electrons fill the (4s)²(4p)⁶ orbitals at Se²⁻ sites in the stoichiometric FeSe. This simple electron counting suggests that FeSe should also undergo a SDW rather than superconducting transition if analogies hold between FeAs and FeSe systems. In fact, band calculations suggest that the Fermi surface nesting induces a SDW ground state in undoped FeSe [12]. How different is the stoichiometric FeSe superconductor from electron or hole doped FeAs superconductors? Is T_c as low as ~ 9 K because spin fluctuations associated with the SDW instability are absent? What is the driving mechanism behind the large enhancement of T_c in FeSe under pressure?

In this Letter, we report a ^{77}Se NMR investigation of FeSe. We demonstrate that the electronic properties of the *undoped* FeSe ($T_c \sim 9$ K) share remarkable similarities with *electron-doped* FeAs superconductors. Our measurements of the ^{77}Se spin-lattice relaxation rate, $1/T_1$, in ambient pressure indeed provide evidence for strong enhancement towards T_c of antiferromagnetic spin fluctuations at finite wave vector $\mathbf{q} \neq \mathbf{0}$. This finding suggests that undoped FeSe superconductor is actually on the verge of an SDW ordering. Furthermore, we show that application of hydrostatic pressure *enhances* spin fluctuations as well as T_c . These results strongly suggest that spin fluctuations have a strong link with the superconducting mechanism of FeSe.

Our NMR sample is β -Fe_{1+ δ} Se with a nearly defect free composition of $\delta = 0.01 \pm 0.02$ [7]. For comparison, we also investigated a nonsuperconducting sample with $\delta = 0.03$. From the transport, specific heat, and SQUID measurements, $T_c \sim 9$ K for β -Fe_{1.01}Se, while the upper bound of T_c is 0.4 K for β -Fe_{1.03}Se [7]. Detailed structural studies based on x-ray and neutron diffraction measure-

ments revealed no hint of impurity phases. While conducting NMR measurements at each pressure, we also carried out ac susceptibility measurements at 67.5 MHz using the NMR coil within the high pressure cell. As shown in Figs. 1(a) and 1(b), T_c in zero applied magnetic field ($B_{\text{ext}} = 0$) rises roughly linearly from ~ 9 K in ambient pressure ($P = 0$ GPa) to ~ 14 K (0.7 GPa), ~ 16 K (1.4 GPa), and ~ 22 K (2.2 GPa). We carried out most of the NMR measurements in $B_{\text{ext}} = 8.3$ or 9 T, which has very little effect on T_c except in ambient pressure. We carried out $1/T_1$ measurements by saturating the whole NMR line with comb pulses. We found that the recovery of nuclear magnetization can be fitted with single exponential very well. In $P = 0$ GPa, we used $B_{\text{ext}} = 1.5$ T for $1/T_1 T$ measurements below T_c to minimize the suppression of T_c by B_{ext} ; the results above T_c showed no dependence on B_{ext} .

In Fig. 2, we present representative powder-averaged ^{77}Se NMR line shapes for polycrystalline samples. ^{77}Se has nuclear spin $I = 1/2$ with the nuclear gyromagnetic ratio $\gamma_n/2\pi = 8.118$ MHz/T, hence it is expected to give rise to a single NMR peak at the Zeeman frequency of $f_o \sim (\gamma_n/2\pi)B_{\text{ext}} \sim 67.4$ MHz in $B_{\text{ext}} = 8.3$ T, or $f_o \sim 73.0$ MHz in 9 T. The observed ^{77}Se NMR linewidth of ~ 0.03 MHz in $\beta\text{-Fe}_{1.01}\text{Se}$ is by a factor of ~ 3 narrower than the earlier report for a highly disordered “ $\text{FeSe}_{0.92}$ ” sample [13], and shows very little temperature dependence. We also observed no distribution of $1/T_1$ in the normal state unlike the case of “ $\text{FeSe}_{0.92}$.” These results assure us that our $\beta\text{-Fe}_{1.01}\text{Se}$ sample is homogeneous and nearly defect free. On the other hand, the NMR lineshape of $\beta\text{-Fe}_{1.03}\text{Se}$ is somewhat broader, and becomes more broad at low temperatures without changing the integrated

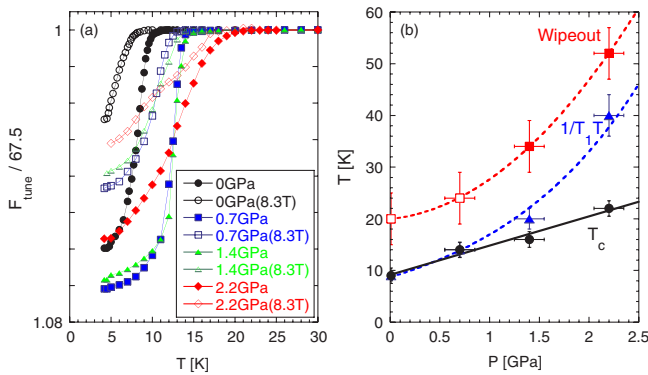


FIG. 1 (color online). (a) ac susceptibility of $\beta\text{-Fe}_{1.01}\text{Se}$ in $B_{\text{ext}} = 0$ and 8.3 T under various pressures. We measured the increase of the tuning frequency $F_{\text{tune}} \sim 1/\sqrt{L(1 + 4\pi\chi')}C$ of the LC tank circuit used for NMR. F_{tune} is normalized by the normal state value, $F_{\text{tune}}(T > T_c) = 67.5$ MHz. Superconducting diamagnetic susceptibility, $\chi' < 0$, enhances F_{tune} . Notice that the vertical axis is reversed. (b) The T - P phase diagram of $\beta\text{-Fe}_{1.01}\text{Se}$. Circles, triangles, and squares represent T_c in $B_{\text{ext}} = 0$ [from Fig. 1(a)], the hump of $1/T_1 T$ (from Fig. 4), and the onset of the loss of the NMR signal intensity [“wipeout”, from Fig. 2(d)], respectively. All lines are guides for the eyes.

intensity. This hints at the presence of defects, which may contribute to the suppression of T_c .

Our results in Fig. 2 show that the actual NMR peak frequency, f , is shifted from f_o . The shift, $\Delta f = f - f_o$, is temperature dependent. We plot the temperature dependence of the Knight shift $K = \Delta f/f_o$ in Fig. 3. The Knight shift arises because B_{ext} polarizes the spin and orbital angular momenta of electrons in proportion to their magnetic susceptibilities, and these induced polarizations exert additional hyperfine magnetic fields on ^{77}Se nuclear spins. Generally, we can express $K = K_{\text{spin}} + K_{\text{chem}}$. The spin contribution $K_{\text{spin}} = A_{\text{hf}}\chi_{\text{spin}}$ is proportional to the spin susceptibility, χ_{spin} , in the FeSe layers (A_{hf} is the hyperfine interaction between electrons and the ^{77}Se nuclear spin). The chemical shift K_{chem} is generally temperature independent and caused by polarized orbital moments. Thus our results in Fig. 3 establish that χ_{spin} of the superconducting FeSe decreases almost linearly with temperature from 480 to ~ 100 K, and then levels off. The observed behavior of χ_{spin} is similar to that of the electron-doped $\text{LaFeAsO}_{1-x}\text{F}_x$ and $\text{Ba}[\text{Fe}_{1-x}\text{Co}_x]_2\text{As}_2$ superconductors [14–17]. In particular, our new results resemble the ^{75}As Knight shift in the optimally electron-doped superconductor $\text{Ba}[\text{Fe}_{0.92}\text{Co}_{0.08}]_2\text{As}_2$ [16,17] ($T_c = 22$ K, $K_{\text{chem}} = 0.2 \sim 0.25\%$ [16] and $A_{\text{hf}} \sim 20$ kOe/ μ_B [18]).

How does χ_{spin} vary with applied pressure P and the concentration x ? Our results in Fig. 3 show that K , hence χ_{spin} , changes little between $P = 0$ and 2.2 GPa. Moreover, the nonsuperconducting $\beta\text{-Fe}_{1.03}\text{Se}$ also exhibits nearly identical χ_{spin} . The inevitable conclusion from these find-

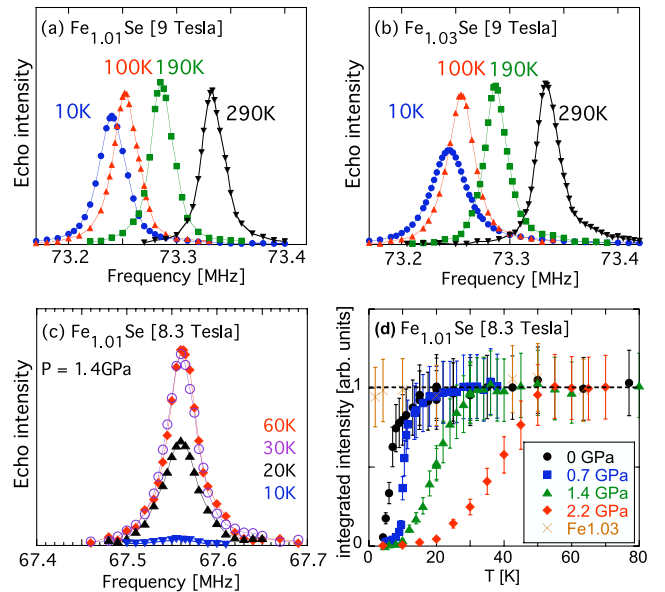


FIG. 2 (color online). Representative ^{77}Se NMR line shapes measured for (a) $\beta\text{-Fe}_{1.01}\text{Se}$ (0 GPa), (b) $\beta\text{-Fe}_{1.03}\text{Se}$ (0 GPa), and (c) $\beta\text{-Fe}_{1.01}\text{Se}$ ($P = 1.4$ GPa). The intensity is corrected for the Boltzmann factor. (d) The temperature dependence of the integrated NMR intensity of $\beta\text{-Fe}_{1.01}\text{Se}$. For comparison, we also show the results for $\beta\text{-Fe}_{1.03}\text{Se}$.

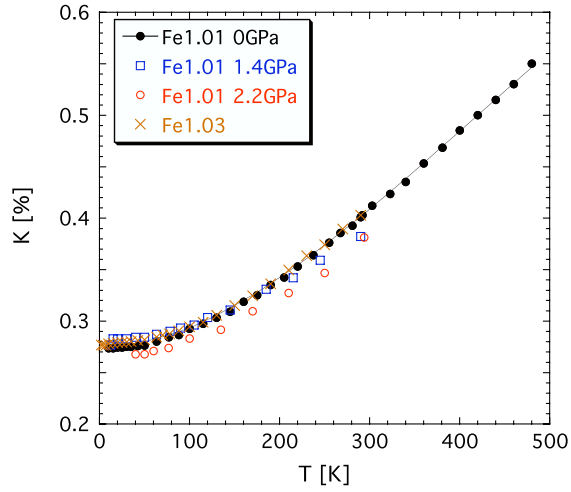


FIG. 3 (color online). The temperature, pressure, and concentration dependencies of ^{77}Se NMR Knight shift $K = K_{\text{spin}} + K_{\text{chem}}$ in the normal state above T_c . K_{spin} is proportional to the uniform spin susceptibility χ_{spin} , and K_{chem} is constant, hence the results reflect the temperature dependence of χ_{spin} .

ings is that the physical parameters that control χ_{spin} (e.g., the density of electronic states, Fe spin-spin exchange interaction J , etc.) may not have a direct link with the superconducting mechanism. Generally, as is well known for high- T_c cuprate superconductors [19], the growth of antiferromagnetic short-range order could suppress χ_{spin} with decreasing temperature. In view of the absence of strong P and x dependencies of χ_{spin} in Fig. 3, it is tempting to conclude that such antiferromagnetic correlations, possibly caused by the nesting of Fermi surfaces [12], may be irrelevant to superconductivity. However, note that χ_{spin} is only a measure of the *uniform* $\mathbf{q} = \mathbf{0}$ response by electron spins to a uniform perturbation B_{ext} . Furthermore, complicated Fermi surface geometry is likely to lead to coexistence of various \mathbf{q} modes of spin excitations in the iron-based superconductors [20], hence χ_{spin} is not necessarily the best probe of magnetic correlations. To explore the potential link between magnetism and the superconducting mechanism, one needs to measure the magnetic response of the nonzero wave-vector modes, $\mathbf{q} \neq \mathbf{0}$.

In Fig. 4, we present the temperature dependence of $1/T_1T \propto \sum_{\mathbf{q}} |A_{\text{hf}}(\mathbf{q})|^2 \chi''(\mathbf{q}, f)$, the nuclear spin-lattice relaxation rate $1/T_1$ divided by temperature T . $A_{\text{hf}}(\mathbf{q})$ and $\chi''(\mathbf{q}, f)$ represent the wave-vector \mathbf{q} -dependent hyperfine form factor [21] and the imaginary part of the dynamical electron spin susceptibility at the NMR frequency $f \sim 67.5$ MHz, respectively. Thus $1/T_1T$ measures the weighted average for various \mathbf{q} -modes of the low frequency spin fluctuations. $1/T_1T$ observed for superconducting $\beta\text{-Fe}_{1.01}\text{Se}$ is strikingly similar to that of the optimally electron-doped $\text{Ba}[\text{Fe}_{0.92}\text{Co}_{0.08}]_2\text{As}_2$ [17]; $1/T_1T$ decreases with T down to ~ 100 K, then begins to increase toward T_c . Since K is nearly temperature independent below 100 K, the latter implies that some $\mathbf{q} \neq \mathbf{0}$

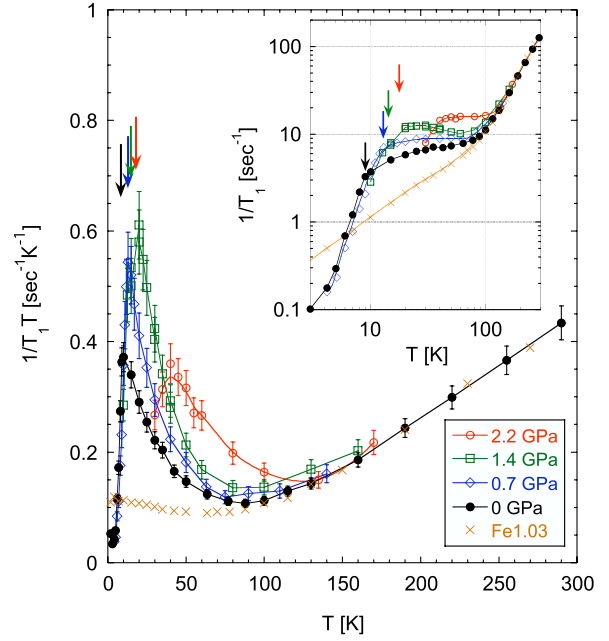


FIG. 4 (color online). $1/T_1T$ for superconducting $\beta\text{-Fe}_{1.01}\text{Se}$ under various pressures, and for nonsuperconducting $\beta\text{-Fe}_{1.03}\text{Se}$ in $P = 0$ GPa. $1/T_1T$ reflects the spin fluctuation susceptibility averaged over various wave-vector modes \mathbf{q} . Inset: A log-log plot of $1/T_1$. Vertical arrows mark (from left to right) T_c for 0, 0.7, 1.4, and 2.2 GPa in the applied magnetic field.

antiferromagnetic modes of spin fluctuations are strongly enhanced toward T_c .

Recalling that removal of a few percent of electrons transforms the superconducting ground state of $\text{Ba}[\text{Fe}_{0.92}\text{Co}_{0.08}]_2\text{As}_2$ into a SDW ordered state [17], the similarities of K and $1/T_1T$ between $\beta\text{-Fe}_{1.01}\text{Se}$ and $\text{Ba}[\text{Fe}_{0.92}\text{Co}_{0.08}]_2\text{As}_2$ lead us to conclude that superconducting FeSe is also in close proximity to a magnetic instability. We also note that $1/T_1T$ measured in 0 and 0.7 GPa shows a sharp peak exactly at $T_c(B_{\text{ext}})$ as determined by the ac susceptibility data presented in Fig. 1(a). This means that superconductivity sets in at T_c after antiferromagnetic spin fluctuations are enhanced, and the opening of the superconducting energy gap suddenly suppresses low frequency spin fluctuations. Unlike typical isotropic BCS s -wave superconductors with a full gap, $1/T_1T$ measured in 0 and 0.7 GPa does not exhibit a Hefel-Slichter coherence peak just below T_c . Instead, as shown in the inset to Fig. 4, $1/T_1$ dives below T_c , exhibiting a power-law-like behavior. This finding is consistent with earlier NMR reports on various iron-based superconductors [13,15,16,22].

A sticky but essential question to address is whether our conclusions in the last two paragraphs imply that (i) antiferromagnetic spin fluctuations are positively linked with the superconducting mechanism, or (ii) antiferromagnetic spin fluctuations are competing with superconductivity. Two pieces of evidence seem to favor scenario (i). First, $1/T_1T$ of $\beta\text{-Fe}_{1.03}\text{Se}$ increases very little

below 100 K, i.e., the enhancement of antiferromagnetic spin fluctuations below 100 K in β -Fe_{1.03}Se, if any, is much weaker than in β -Fe_{1.01}Se. Second, we find that both T_c and spin fluctuations grow under pressure. For example, $1/T_1T$ at 50 K increases from 0.15 sec⁻¹ K⁻¹ in 0 GPa to 0.18 sec⁻¹ K⁻¹ (0.7 GPa), 0.21 sec⁻¹ K⁻¹ (1.4 GPa), and 0.31 sec⁻¹ K⁻¹ (2.2 GPa). If spin fluctuations with $\mathbf{q} \neq \mathbf{0}$ are genuinely competing against the superconducting mechanism, we would expect a suppression of $1/T_1T$ under pressure when T_c rises.

Close inspection of the $1/T_1T$ data reveals that $1/T_1T$ shows a broad hump at ~ 20 K in 1.4 GPa and ~ 40 K in 2.2 GPa. These humps are significantly above $T_c(B_{\text{ext}}) = 14.5$ and 18 K as determined by ac susceptibility measured in identical conditions of B_{ext} and P , hence we cannot attribute the suppression of $1/T_1T$ below these humps to the opening of a superconducting energy gap. Furthermore, we found that the integrated intensity of the NMR signal begins to decrease at temperatures somewhat above these humps (at ~ 34 K in 1.4 GPa and ~ 50 K in 2.2 GPa) as shown in Figs. 2(c) and 2(d). We summarize the T - P phase diagram of β -Fe_{1.01}Se in Fig. 1(b) including these anomalies. Notice that the NMR signal intensity in 1.4 and 2.2 GPa is almost completely wiped out by the time we reach T_c . Thus we need to be somewhat cautious in interpreting the $1/T_1T$ results below these humps, because $1/T_1T$ reflects only some parts of FeSe with observable NMR signals.

The disappearance of paramagnetic NMR signals below a peak of $1/T_1T$ is a typical signature of a magnetic phase transition or spin freezing. If the Fe magnetic moments are statically ordered at lower temperatures, they would exert well-defined static hyperfine fields $B_{\text{hf}} \sim 1.5$ T [18] on ⁷⁷Se nuclear spins and split the NMR lineshape. However, we did not find any additional NMR signals at lower temperatures. Therefore the disappearance of the NMR signals means that (i) glassy slowing of spin fluctuations makes the longitudinal and transverse relaxation times T_1 and T_2 of ⁷⁷Se NMR signals so fast that spin echo cannot form in some parts of FeSe layers, and/or (ii) (nearly) static hyperfine magnetic field B_{hf} has a large distribution. In the case of the SDW ordered phase in lightly electron-doped BaFe₂As₂, B_{hf} has a continuous distribution up to ~ 1.5 T [23]. In the present context, even if these hyperfine fields are static, the ⁷⁷Se NMR linewidth may be as broad as $\gamma_n/2\pi \times B_{\text{hf}} \sim 12$ MHz, i.e., the NMR line may be broadened by a factor of ~ 400 . In any case, these NMR anomalies above T_c strongly suggest that applied pressure above ~ 1.4 GPa enhances spin fluctuations so strongly that a glassy spin freezing takes place in the FeSe layers before bulk superconductivity sets in. We recall that high- T_c cuprate and URu₂Si₂ superconductors exhibit analogous situation in the vicinity of the stripe phase and the hidden ordered phase, respectively [24,25]. In passing, the inhomogeneous electronic properties may be the underlying reason why the superconducting transition in 2.2 GPa becomes broad, as

shown in Fig. 1(a). The results in Fig. 2(d) show that the loss of NMR signal intensity may be also present in 0 and 0.7 GPa somewhat above T_c . However, earlier μ SR measurements did not reveal any static magnetic order in a superconducting specimen of “FeSe_{0.85}” [26]. The rather abrupt loss of the NMR signal below T_c at 0 and 0.7 GPa may merely be due to the Meissner effect, which limits the NMR intensity by shielding the rf pulses for NMR measurements.

To summarize, we have demonstrated that the electronic properties of the stoichiometric FeSe superconductor are very similar to those of optimally electron-doped Ba[Fe_{0.92}Co_{0.08}]₂As₂ high- T_c superconductor. Contrary to an earlier NMR report on a disordered FeSe_{0.92} sample [13], our results for superconducting β -FeSe show no evidence for canonical Fermi liquid above T_c , i.e., the Korringa relation $1/T_1TK^2 = \text{const}$ is not satisfied. Instead, large enhancement of $1/T_1T$ below 100 K indicates that antiferromagnetic spin fluctuations are strongly enhanced toward T_c in FeSe. Application of pressure further enhances both spin fluctuations and T_c , pointing toward a positive link between antiferromagnetic spin fluctuations and the superconducting mechanism.

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