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Superconductivity of highly spin-polarized electrons in FeSe probed by $^{77}$Se NMR

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A number of recent experiments indicate that the iron-chalcogenide FeSe provides the long-sought possibility to study bulk superconductivity in the cross-over regime between the weakly coupled Bardeen-Cooper-Schrieffer (BCS) pairing and the strongly coupled Bose-Einstein condensation (BEC). We report on $^{77}$Se nuclear magnetic resonance experiments of FeSe, focused on the superconducting phase for strong magnetic fields applied along the c axis, where a distinct state with large spin polarization was reported. We determine this high-field state as bulk superconducting with high spatial homogeneity of the low-energy spin fluctuations. Further, we find that the static spin susceptibility becomes unusually small at temperatures approaching the superconducting state, despite the presence of pronounced spin fluctuations. Taken together, our results clearly indicate that FeSe indeed features an unusual field-induced superconducting state of a highly spin-polarized Fermi liquid in the BCS-BEC crossover regime.

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I. INTRODUCTION

The discovery of superconductivity in iron-based materials in 2008 opened a new avenue for the exploration of unusual superconducting states and phenomena in multiband superconductors, with wide possibilities for tuning the electronic ground states by variation of the material composition and the ensuing thermodynamic parameters [1–4]. At present, the binary iron-chalcogenide FeSe attracts a lot of research interest [5–15]. As to the Fermi-surface topology and energy scales in this material, there is one shallow hole pocket at the $\Gamma$ point, and at least one electron pocket at the $M$ point, both with remarkably small Fermi energies ($\varepsilon_F^h \approx 3$ meV and $\varepsilon_F^e \approx 10$ meV, respectively) [6,16]. The superconducting gap energies are $\Delta_1 = 2.5$ meV and $\Delta_2 = 3.5$ meV, resulting in an unusually high ratio $\Delta/\varepsilon_F \approx 1$ and $\approx 0.3$ for the electron and hole bands, respectively [6].

Despite its structural simplicity, FeSe yields a wealth of interesting phenomena. For example, a nematic transition, presumably induced by orbital ordering, occurs at about 90 K, where the $C_4$ rotational symmetry is broken, while the translational symmetry is preserved [8–11,17]. A drastic increase of $T_c$ can be achieved via hydrostatic pressure or when growing thin films on specific substrates [18–20].

Further, very recently compelling evidence for the appearance of a Fulde-Ferrell-Larkin-Ovchinnikov (FFLO) state was found when the applied magnetic field is aligned parallel to the $ab$ plane [15]. On the other hand, for fields perpendicular to the planes, the observation of an unusual superconducting phase with extremely high spin polarization, dubbed B phase, was reported based on measurements of thermal transport properties [21,22]. Close to the upper critical field of superconductivity, all three relevant energy scales, i.e., those of the Fermi energy, the superconducting gap, and the Zeeman interaction, are of comparable magnitude, the combined action of which may lead to a significant modification of the underlying electronic system. For that reason, the condensation of electron pairs in the B phase is proposed to take place in the BCS (Bardeen-Cooper-Schrieffer)–BEC (Bose-Einstein-condensate) crossover regime, which bridges the two fundamental theories for the condensation of attractively coupled fermions. In this crossover regime, the average interparticle distance approaches the size of the interacting pairs, i.e., $k_F\xi \approx 1$, where $k_F$ is the Fermi wave vector and $\xi$ is the superconducting coherence length [21]. The resulting ground state is a strongly interacting superfluid out of which new states of matter may emerge. The manifestation of preformed pairs with an associated pseudogap, existing at temperatures much higher than the actual condensation temperature, is a hallmark of the BCS-BEC crossover [23]. As the intrinsic energy scales in materials usually place the electronic
interactions strictly in either the BCS or the BEC limit, little is known about bulk superconductivity in the crossover regime.

In this paper, we present $^{77}$Se nuclear magnetic resonance (NMR) data of a high-quality single crystal of FeSe. The parameter range of our study covers magnetic fields between 5 and 16 T applied along the crystallographic $c$ axis, and temperatures between 0.3 and 40 K. Our work mainly focuses on the electronic properties at low temperatures and close to the upper critical field of superconductivity, where the existence of the B phase was reported, thus investigating the local dynamic properties across the A-B transition in FeSe at the BCS-BEC crossover regime.

II. EXPERIMENTAL METHODS

The NMR coil with a vapor-grown FeSe single crystal [24], with dimensions of approximately $5.0 \times 2.0 \times 0.04$ mm$^3$, was mounted on a single-axis rotator and placed directly in liquid $^3$He inside a top-loading cryostat in a 16 T high-resolution magnet. The $^{77}$Se NMR spectra were recorded using a commercial solid-state spectrometer with a 500 W power amplifier and a standard Hahn spin-echo pulse sequence. The $^{77}$Se Knight shift, linewidth, and $T_1$ relaxation time were either measured in a top-tuned resonator configuration, using a typical $\pi/2$ pulse duration $t_{\pi/2} = 16$ $\mu$s and a power attenuation $\theta_2 = 20$ dB, or in a bottom-tuned configuration, using $t_{\pi/2} = 29$ $\mu$s and $\theta_2 = 36$ dB, with both configurations giving consistent results. The temperature-dependent intensity of the $^{77}$Se NMR spectra, as shown in the inset of Fig. 1, was measured in the bottom-tuned resonator configuration, using a $\pi/2$ pulse duration $t_{\pi/2} = 5$ $\mu$s and a power attenuation of 20 dB. Further details on the nutation response of the $^{77}$Se nuclear magnetization are provided in the Supplemental Material [25]. The orientation of the magnetic field parallel to the crystallographic $c$ axis was adjusted with an accuracy of about $\pm 2^\circ$ by probing the anisotropic frequency shift of the $^{77}$Se spectra. To determine the superconducting phase diagram of our sample, we monitored frequency changes of the complex radio-frequency (RF) reflection coefficient $S_1$ at the NMR tank circuit, using a vector network analyzer. Here, the detuning of the resonance frequency indicates a relative change of sample volume penetration by the probing RF field.

The nuclear spin-lattice relaxation rate is defined as $1/T_1 \propto \sum_{q,n,m} F_{nm}(q)\chi''_{nm}(q, f_{\text{res}})/f_{\text{res}}$, with $n, m = x, y, z$. Here, $F_{nm}$ denotes the hyperfine form factors and $\chi''_{nm}$ is the imaginary part of the dynamic electronic susceptibility. $T_1$ was measured via the saturation-recovery method and determined by fitting $M_r(\tau) = M_0[1 - \exp\left( - (\tau / T_1)\right)]$ to the recovery of the nuclear magnetization after saturation, where $\beta$ is a stretching exponent that accounts for a distribution of relaxation times.

III. RESULTS AND DISCUSSION

The obtained results from the RF reflection measurements, shown in Fig. 1 as blue circles, are in very good agreement with previously reported data for the boundary of the A phase [21]. The characteristic temperatures and magnetic fields that determine the boundary of the A phase were extracted at intersection points of linear fits to the data above and below the respective slope changes in the temperature- and field-dependent sweeps, see Fig. 2(a). As shown in Fig. 2(a), in the temperature-dependent sweeps at fields corresponding to the A phase, the transition from the normal to the superconducting state is manifested as a pronounced change of slope, and we find $T_c = 8.7$ K at 0 T. At 14 T, however, upon crossing the transition to the B phase, no pronounced feature is observed.

In the field-dependent sweeps at low temperatures [see Fig. 2(b)], the resonance frequency at first monotonically decreases due to vortex formation in the Shubnikov phase and shows a maximum at about 12.6 T and 0.3 K and at about 12.4 T and 1.0 K, closely below the transition between the A and B phase. The appearance of this maximum is attributed to an order-disorder transition of the vortex lattice, as was observed also by magnetic-torque measurements of FeSe, see Supplemental Material of Ref. [21]. Further, weak features in the data in Figs. 2(a) and 2(b), such as the kink at 10 T and 1 K in Fig. 2(a), are attributed to a principal lack of background compensation in the S11 RF reflection measurements.

Similar to the S11 RF reflection experiments, a change of the RF volume penetration at the transition to the superconducting state can be probed via the intensity of the NMR spectra, as seen in the inset of Fig. 1. At 11 T, the NMR intensity decreases by about 10% below $T_c = 2.6$ K due to vortex formation and drops abruptly at around 0.5 K. The latter feature is attributed to a highly nonmonotonic temperature dependence of the surface resistance below $T_c$, as revealed...
the study of iron-based superconductors [27–30]. Hence, the 
77Se Knight shift and linewidth in FeSe are very sensitive to 
any static local-field contribution. We determine the Knight 
shift from the first spectral moment of our data, using a 
nuclear gyromagnetic ratio \(\gamma(77\text{Se})/2\pi = 8.13 \text{ MHz/T}\). The 
77Se NMR spectra yield a typical linewidth (FWHM) of about 
3 kHz, in line with previously reported results [8,9]. We take 
the FWHM as a very conservative error for the Knight-shift 
data, see Fig. 2.

For precise determination of the 77Se Knight shift, the 
magnetic field was repeatedly calibrated with a 63Cu NMR 
reference during the experiments. For all fields, the tempera-
ture dependence of the Knight shift shows no noticeable 
change below 30 K, see Fig. 2(c). It increases only for 
\(T \gtrsim 30 \text{ K}\), consistent with previous reports [8,9]. In particular, 
the 77Se NMR spectra recorded at 0.3 K, deep in the supercon-
ducting state, yield, within error bars, no decrease of the shift 
within the whole field range of our measurements, including 
the transition between A and B phase [Fig. 2(d)]. This is quite 
surprising, since, in a spin-singlet superconductor, a reduction 
of the local spin susceptibility, driven by the formation of 
Cooper pairs, occurs when approaching zero field at tempera-
tures much smaller than \(T_c\). Therefore, we conclude that the 
observed Knight shift of about 1300 ppm is purely of orbital 
origin and that the static uniform electronic spin susceptibility 
in FeSe is extremely small at temperatures approaching the 
superconducting state.

This finding is further corroborated by the very small 
linewidth and purely Lorentzian NMR lineshape in the whole 
parameter range of our study. Any finite contribution from 
local susceptibilities would, with the large 77Se hyperfine 
coupling mentioned above, immediately lead to Gaussian line 
broadening. Also, the linewidth of the Redfield pattern, 
resulting from a periodic array of local orbital magnetization in 
the vortex lattice, is estimated to be much smaller than the 
linewidth of the 77Se spectra in the high-field regime of our 
study [31]. A recent study of anisotropic spectral properties 
in the superconducting state of FeSe reports results in agree-
ment with our findings, as well as a rather small suppression 
of the Knight shift and inhomogeneously broadened spectra 
below \(T_c\) for in-plane fields [32]. With the given hyperfine 
coupling and linewidth, we estimate the upper limit of the 
uniform static susceptibility for fields parallel \(c\) to about 
\(2 \times 10^{-5} \text{ emu}/(\text{G mol})\). Further, our findings confirm that the 
splitting of the 77Se line, observed for fields applied along the 
\(ab\) planes and interpreted as a microscopic signature of 
nematic order in FeSe, stems from the anisotropic orbital 
polarization in the orbital-ordered domains [8,9]. A study by 
means of 77Se NMR and microscopic modeling on detwinned 
FeSe in the nematic state reports that the static magnetic 
susceptibility at the wave vector \(q = 0\) is mainly of orbital 
character, whereas the spin part dominates at \(q = (\pi, 0)\) and 
\((0, \pi)\), in agreement with our observations [33].

Next, we turn to the discussion of the low-energy spin 
fluctuations. As shown in Fig. 3(a), for \(T > 10 \text{ K}\), 
\(1/T_c T\) is only weakly field dependent, in good agreement with previous 
results [6,8,9,34]. For decreasing \(T < 10 \text{ K}\) and \(\mu_0 H < 13 \text{ T}\), 
we find a decrease of \(1/T_c T\) clearly starting from well above 
\(T_c\). These results are in line with recent reports of pre-formed 
Cooper pairs and associated pseudogap behavior, leading to
a depletion of the density of states above the superconducting condensation temperature \([6,34]\). The pseudogap sets in below about 10 K, whereas the spin part of the Knight shift decreases already at higher temperatures [see Fig. 2(c)], finally becoming smaller than the spectroscopic linewidth below 30 K. Consequently, the decrease of the static spin susceptibility is not related to the pseudogap formation.

Upon crossing the superconducting transition, \(1/T_1T\) drops further—without showing any feature that might be associated with \(T_c\)—and levels off at about 2 K at 11 T and 3 K at 8 T, in good agreement with the vortex liquid-solid transition indicated by the peak fields obtained from the torque data reported by Kasahara et al. [21], as well as our RF reflection measurements. At lower temperatures, \(1/T_1T\) is almost constant and increases with magnetic field. For higher magnetic fields, at 13 T, the relaxation rate does not decrease below \(T_c\), and finally, at 15 T, despite the transition to superconductivity as probed by the abrupt decrease of the NMR signal intensity [cf. inset of Fig. 1], \(1/T_1T\) even monotonically increases towards lowest temperatures. These observations are in line with a field-driven suppression of the pseudogap, being associated with preformed pairs of the superconducting condensate, as predicted for the BCS-BEC crossover regime \([6,23]\).

In Fig. 3(b), the temperature dependence of the stretching exponent \(\beta\) is shown for 11 and 15 T. In the normal-conducting state, we find \(\beta \approx 1\), indicating a single \(T_1\) and correspondingly a spatially homogeneous electronic state in the whole sample volume. At 11 T, when entering the A phase, \(\beta\) becomes smaller than unity below \(T_c\), in line with the presence of a vortex lattice with superconducting regions and vortex cores with increased quasiparticle density. In stark contrast, at 15 T, in the B phase, \(\beta\) remains close to unity at temperatures below \(T_c\), evidencing a spatially homogeneous electronic state.

The field dependence of \(1/T_1T\) at 0.3 K (Fig. 4), deep in the superconducting state, is determined both by the structure of the vortex lattice and the gradual suppression of the superconducting gap amplitudes. Again, the presence of a vortex lattice gives rise to a spatial variation of quasiparticle densities, yielding a distribution of \(T_1\) relaxation times with \(\beta\) becoming smaller than unity \([31,35]\). Towards high fields, the superconducting gap amplitudes decrease, and the vortex density with the corresponding volume fraction of the normal-conducting vortex cores increases. In consequence, the overall \(T_1\) distribution sharpens, and \(\beta\) approaches unity.

The field dependence of \(1/T_1T\) yields two transitional regimes at around 11 and 14 T, respectively. As was reported from measurements of the thermal Hall coefficients, the transverse thermal conductivity changes sign at around 12 T and 0.59 K, indicating that the quasiparticles that determine the thermal conduction change from electronlike to holelike \([22]\). The clear change in the field dependence of \(1/T_1T\) at around 11 T is likely driven by the same phenomenon, namely, a field-driven closure of the smaller, anisotropic gap on the electron pocket. Here, the field-dependent increase of \(\beta\) shows a monotonic variation of the spatial dependence of the low-energy quasiparticle density.

The second change of the field dependence of \(1/T_1T\) occurs around \(\mu_0H^* \approx 14 T\), which gives evidence of a field-driven transition to a distinct bulk superconducting state, in very good agreement with features found in previous reports based on thermodynamic quantities \([21,22]\). Above 14 T, in the B phase, the field dependence of \(1/T_1T\) becomes approximately linear with a significantly smaller slope, without saturation up to 16 T. More importantly, the stretching exponent \(\beta\) saturates close to unity above 14 T, evidencing
spatially homogeneous low-energy quasiparticle excitations. Since the magnetic-torque measurements show no anomaly at $\mu_0 H^2$, a Lifshitz transition or spin-density wave order as driving mechanism for the transition to the B phase are very unlikely [21].

Finally, we comment on the compatibility of our results with an FFLO state underlying the B phase [21,22]. The spectroscopic signature of a spatially inhomogeneous superconducting state, as predicted by FFLO, with coupled modulated local susceptibility, would be an inhomogeneous broadening of the spectral line. This was observed in NMR studies of the FFLO states in the organic superconductors $\kappa$-(ET)$_2$Cu(NCS)$_2$ [36] and $\beta''$-(ET)$_2$SF$_5$CH$_2$CF$_2$SO$_3$ [37]. However, as $K_s$ is smaller than the $^{77}\text{Se}$ linewidth in FeSe, a corresponding modulation would not be resolved. As to the dynamic properties, a spatially inhomogeneous superconducting state would give rise to a local variation of the quasiparticle densities and result in a stretched relaxation, unless strong mechanisms of nuclear spin diffusion are at play. However, spatial inhomogeneities arising from an FFLO state are in contrast to our observations of $\beta = 1$ for the B phase. We, therefore, may exclude a simple FFLO state as origin for the B phase.

IV. SUMMARY

In summary, RF volume penetration and $^{77}\text{Se}$ NMR measurements of the static and low-energy dynamic susceptibility of single-crystalline FeSe at fields between 5 and 16 T and temperatures down to 0.3 K reveal that the high-field B phase represents a distinct bulk superconducting state of a highly spin-polarized Fermi liquid with nonlinear RF response of the surface conductivity. The B phase yields, within our experimental resolution, no spatial modulation of either the density of low-energy quasiparticle excitations or the static local susceptibility, as evidenced by a nonstretched spin-lattice relaxation and the absence of a discernible inhomogeneous line broadening, respectively. Rather, $1/T_1 T$ increases monotonically towards low temperatures and increasing fields in the B phase, which sets it apart from standard BCS bulk superconductivity with gapped excitations. Further, measurements of the orbital part of the NMR Knight shift deep in the superconducting state reveal that the static spin susceptibility in FeSe becomes extremely small below 30 K, despite the presence of pronounced spin fluctuations. In line with previous results, $1/T_1 T$ reveals a gapped behavior of the low-energy spin fluctuations already well above $T_c$ in a wide field range, indicating pseudogap formation due to preformed Cooper pairs, which underlines the unusual superconductivity of FeSe in the BCS–BEC crossover regime.

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[1] Y. J. Kamihara, T. Watanabe, M. Hirano, and H. Hosono, J. Am. Chem. Soc. 130, 3296 (2008).
[2] D. Johnston, Adv. Phys. 59, 803 (2010).
[3] G. R. Stewart, Rev. Mod. Phys. 83, 1589 (2011).
[4] A. Chubukov and P. Hirschfeld, Phys. Today 68(6), 46 (2015).
[5] F.-C. Hsu, J.-Y. Luo, K.-W. Yeh, T.-K. Chen, T.-W. Huang, P. M. Wu, Y.-C. Lee, Y.-L. Huang, Y.-Y. Chu, D.-C. Yan, and M.-K. Wu, Proc. Natl. Acad. Sci. USA 105, 14262 (2008).
[6] S. Kasahara, T. Yamashita, A. Shi, R. Kobayashi, Y. Shimoyama, T. Watashige, K. Ishida, T. Terashima, T. Wolf, F. Hardy, C. Meingast, H. v. Löhneysen, A. Levchenko, T. Shibauchi, and Y. Matsuda, Nat. Commun. 7, 12843 (2016).
[7] P. Bourgeois-Hope, S. Chi, D. A. Bonn, R. Liang, W. N. Hardy, T. Wolf, C. Meingast, N. Doiron-Leyraud, and L. Taillefer, Phys. Rev. Lett. 117, 097003 (2016).
[8] S. H. Baek, D. V. Efremov, J. M. Ok, S. J. Kim, J. V. D. Brink, and B. Büchner, Nat. Mater. 14, 210 (2015).
[9] A. E. Böhmer, T. Araii, F. Hardy, T. Hattori, T. Iye, T. Wolf, H. v. Löhneysen, K. Ishida, and C. Meingast, Phys. Rev. Lett. 114, 027001 (2015).
[10] Q. Wang, Y. Shen, B. Pan, Y. Hao, M. Ma, F. Zhou, P. Steffens, K. Schmalzl, T. R. Forrest, M. Abdel-Hafiez, X. Chen, D. A. Charéeve, A. N. Vasilyev, P. Bourges, Y. Sidis, H. Cao, and J. Zhao, Nat. Mater. 15, 159 (2016).
[11] F. Wang, S. A. Kivelson, and D.-H. Lee, Nat. Phys. 11, 959 (2015).
[12] J. M. Ok, C. I. Kwon, Y. Kohama, J. S. You, S. K. Park, J. H. Kim, Y. J. Jo, E. S. Choi, K. Kindo, W. Kang, K. S. Kim, E. G. Moon, A. Gurevich, and J. S. Kim, Phys. Rev. B 101, 224509 (2020).
[13] V. Grinenko, R. Sarkar, P. Materne, S. Kamusella, A. Yamamshita, Y. Takano, Y. Sun, T. Tamegai, D. V. Efremov, S.-L. Drechsler, J.-C. Orain, T. Goko, R. Scheuermann, H. Luetkens, and H.-H. Klauss, Phys. Rev. B 97, 201102(R) (2018).
[14] J. Li, B. Lei, D. Zhao, L. P. Nie, D. W. Song, L. X. Zheng, S. J. Li, B. L. Kang, X. G. Luo, T. Wu, and X. H. Chen, Phys. Rev. X 10, 011034 (2020).
[15] S. Kasahara, Y. Sato, S. Licciardello, M. Čulo, S. Arsenijević, T. Ottenbros, T. Tominaga, J. Böker, I. Eremin, T. Shibauchi, J. H. V. Löhneysen, and C. Meingast, Phys. Rev. B 91, 014504 (2020).
[16] T. Terashima, N. Kikugawa, A. Kiswandhi, E.-S. Choi, J. S. Brooks, S. Kasahara, T. Watashige, H. Ikeda, T. Shibauchi, Y. Matsuda, T. Wolf, A. E. Böhmer, F. Hardy, C. Meingast, H. V. Brooks, S. Kasahara, T. Watashige, H. Ikeda, T. Shibauchi, Y. Matsuda, T. Wolf, A. E. Böhmer, F. Hardy, C. Meingast, H. V. Brooks, S. Kasahara, T. Watashige, H. Ikeda, T. Shibauchi, Y. Matsuda, T. Wolf, A. E. Böhmer, F. Hardy, C. Meingast, H. V. Brooks, S. Kasahara, T. Watashige, H. Ikeda, T. Shibauchi, Y. Matsuda, T. Wolf, A. E. Böhmer, F. Hardy, C. Meingast, H. V.
Löhneysen, M. T. Suzuki, R. Arita, and S. Uji, Phys. Rev. B. 90, 144517 (2014).

[17] A. E. Böhmer and C. Meingast, C. R. Phys. 17, 90 (2016).

[18] S. Medvedev, T. M. McQueen, I. A. Troyan, T. Palasyuk, M. I. Eremets, R. J. Cava, S. Naghavi, F. Casper, V. Ksenofontov, G. Wortmann, and C. Felser, Nat. Mater. 8, 630 (2009).

[19] S. He, J. He, W. Zhang, L. Zhao, D. Liu, X. Liu, D. Mou, Y.-B. Ou, Q.-Y. Wang, Z. Li, L. Wang, Y. Peng, Y. Liu, C. Chen, L. Yu, G. Liu, X. Dong, J. Zhang, C. Chen, Z. Xu et al., Nat. Mater. 12, 605 (2013).

[20] J.-F. Ge, Z.-L. Liu, C. Liu, C.-L. Gao, D. Qian, Q.-K. Xue, Y. Liu, and J.-F. Jia, Nat. Mater. 14, 285 (2015).

[21] S. Kasahara, T. Watashige, T. Hanaguri, Y. Kohsaka, T. Yamashita, Y. Shimoyama, Y. Mizukami, R. Endo, H. Ikeda, K. Aoyama, T. Terashima, S. Uji, T. Wolf, H. v. Löhneysen, T. Shibauchi, and Y. Matsuda, Proc. Natl. Acad. Sci. USA 111, 16309 (2014).

[22] T. Watashige, S. Arsenijević, T. Yamashita, D. Terazawa, T. Onishi, L. Opherden, S. Kasahara, Y. Tokiwa, Y. Kasahara, T. Shibauchi, H. v. Löhneysen, J. Wosnitza, and Y. Matsuda, J. Phys. Soc. Jpn. 86, 014707 (2017).

[23] M. Randeria and E. Taylor, Annu. Rev. Condens. Matter Phys. 5, 209 (2014).

[24] A. E. Böhmer, F. Hardy, F. Eilers, D. Ernst, P. Adelmann, P. Schweiss, T. Wolf, and C. Meingast, Phys. Rev. B 87, 180505(R) (2013).

[25] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevB.104.014504 for $^{77}$Se NMR nutation and thermal-conductivity experiments in the normal and superconducting states, as well as more details on the spectroscopic properties.

[26] M. Li, N. R. Lee-Hone, S. Chi, R. Liang, W. N. Hardy, D. A. Bonn, E. Girt, and D. M. Broun, New J. Phys. 18, 082001 (2016).

[27] N. Terasaki, H. Mukuda, M. Yashima, Y. Kitaoka, K. Miyazawa, P. M. Shirage, H. Kito, H. Eisaki, and A. Iyo, J. Phys. Soc. Jpn. 78, 013701 (2009).

[28] K. Kitagawa, N. Katayama, K. Ohgushi, M. Yoshida, and M. Takigawa, J. Phys. Soc. Jpn. 77, 114709 (2008).

[29] K. Kitagawa, N. Katayama, K. Ohgushi, and M. Takigawa, J. Phys. Soc. Jpn. 78, 063706 (2009).

[30] S.-H. Baek, H.-J. Grafe, F. Hammerath, M. Fuchs, C. Rudisch, L. Haranega, S. Aswartham, S. Wurmehl, J. v. d. Brink, and B. Büchner, Eur. Phys. J. B 85, 159 (2012).

[31] N. J. Curro, Rep. Prog. Phys. 72, 026502 (2009).

[32] I. Vinograd, S. P. Edwards, Z. Wang, T. Kissikov, J. K. Byland, J. R. Badger, V. Taufour, and N. J. Curro, arXiv:2102.09090.

[33] R. Zhou, D. D. Scherer, H. Mayaffre, P. Toulouse, M. Ma, Y. Li, B. M. Andersen, and M.-H. Julien, npj Quantum Mater. 5, 93 (2020).

[34] A. Shi, T. Arai, S. Kitagawa, T. Yamanaka, K. Ishida, A. E. Böhmer, C. Meingast, T. Wolf, M. Hirata, and T. Sasaki, J. Phys. Soc. Jpn. 87, 013704 (2018).

[35] D. C. Johnston, Phys. Rev. B 74, 184430 (2006).

[36] J. A. Wright, E. Green, P. Kuhns, A. Reyes, J. Brooks, J. Schlueter, R. Kato, H. Yamamoto, M. Kobayashi, and S. E. Brown, Phys. Rev. Lett. 107, 087002 (2011).

[37] G. Koutroulakis, H. Kühne, J. A. Schlueter, J. Wosnitza, and S. E. Brown, Phys. Rev. Lett. 116, 067003 (2016).
Superconductivity of highly spin-polarized electrons in FeSe probed by $^{77}$Se NMR: Supplemental Material

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Nutation response of the $^{77}$Se nuclear magnetization.

As described in the main text, the response of the screening currents to the amplitude of the RF excitation pulses yields a highly unusual behavior in the superconducting states of FeSe. This is manifested when comparing the measurements of the low-power RF reflection coefficient $S_{11}$ via a vector network analyzer with the results of the high-power RF excitation by the NMR pulses.

As a crucial procedure for most NMR experiments, the nutation response of the nuclear magnetization, i.e., the dependence of the NMR signal intensity on the parameters of the excitation pulses, needs to be determined. Since the nutation angle of the nuclear magnetization is linear proportional to the duration and amplitude of the excitation pulses, the nutation may be characterized via the parameters $t_{\pi/2}$, the $\pi/2$ pulse duration of a Hahn spin-echo sequence with $\pi/2 - \tau - \pi$, as well as $\theta$, which denotes the power attenuation of the 0 dBm RF signal before feeding the pulses into the power amplifier. It is straightforward to show that, for a $\pi/2$ nutation of the nuclear magnetization, resulting in a maximum intensity of the NMR signal, the relation between $\theta_{\pi/2}$ and $t_{\pi/2}$ follows the form

$$\theta_{\pi/2} = 20 \log_{10} \left( \frac{2\omega_1(0)t_{\pi/2}}{\pi} \right),$$

where $\omega_1(0) = \gamma N \sqrt{P_0/P_1} H_1$. Here, $P_0$ and $P_1$ are the non-attenuated and attenuated output pulse-power levels of the RF amplifier, respectively, and $H_1$ denotes the amplitude of the RF field acting on the sample.

Comprehensive $^{77}$Se nutation data of FeSe were recorded in a bottom-tuned resonator configuration at 5 K and 11 T as well as 15 T in the normal-conducting regime [Figs. S1 (a) and (c)], and at 0.3 K and 11 T, deep in the A phase [Fig. S1 (b)], as well as at 0.3 K and 15 T, in the B phase [Fig. S1 (d)]. In Figs. S1 (a) - (d), the dashed black lines represent the $\theta_{\pi/2}$ curves according to Eq. (1). The maximum signal intensity follows these modeled $\theta_{\pi/2}$ curves very well in the normal-conducting regime at 5 K, yielding a weak decrease of signal intensity towards smaller RF amplitudes and increasing pulse durations. In contrast,

**FIG. S1.** Nutation response of the $^{77}$Se nuclear magnetization in FeSe, i.e., dependence of the integrated real-part NMR intensity on the RF pulse length $t_{\text{pulse}}$ and the attenuation $\theta$ of the transmitted RF pulses, using a 500 W power amplifier. Here, larger values of $\theta$ correspond to smaller RF field amplitudes $H_1$. Compared are data for the normal-conducting regime in (a) and (c) with the behavior in the superconducting states of (b) the A phase and (d) the B phase. The sampling steps are $\Delta \theta = 4$ dB and $\Delta t_{\text{pulse}} = 4$ ms at 11 T and 2 ms at 15 T, respectively. The dashed black lines represent the $\pi/2$ condition, i.e., the trace of maximum signal intensity according to Eq. (1).

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at 0.3 K, the intensity is strongly suppressed for small $\theta_{\pi/2}$ and short pulse durations $t_{\pi/2}$. Thus, a significant RF volume penetration may be achieved by using relatively small pulse amplitudes, which is in contrast to the usual procedure, where the amplitude of RF pulses needs to be increased for better sample penetration in the superconducting state. On the other hand, using a high transmitted power results in a strong intensity drop at the transition from the normal to the superconducting state, as shown in the inset of Fig. 1 in the main text.

**FIG. S2.** Waterfall diagrams of normalized $^{77}$Se NMR real-part spectra (a) for various temperatures at 13 T and (b) for various fields at 0.3 K. Vertical offsets of the spectral baselines are proportional to the respective temperatures or magnetic fields. The spectra recorded at temperatures corresponding to the normal-conducting state are shown as black curves, those for temperatures and fields according to the superconducting A and B phases are shown in blue and orange, respectively. A Lorentzian function is fitted to the spectrum at 0.3 K and 13 T, and shown as red dashed line in (a) to demonstrate the purely Lorentzian line shape of the $^{77}$Se spectra. In both (a) and (b), the red triangles represent the first spectral moment.

**FIG. S3.** Numerical full width at half maximum of the $^{77}$Se real part NMR spectra as shown in Fig. S2 (b), both in absolute (kHz) and relative (ppm) units.

**NMR spectra.**

The $^{77}$Se NMR spectra were either measured in a top-tuned resonator configuration, using a typical $\pi/2$ pulse duration $t_{\pi/2} = 16 \mu s$ and a power attenuation $\theta_{\pi/2} = 20$ dB, or in bottom-tuned configuration, using $t_{\pi/2} = 29 \mu s$ and $\theta_{\pi/2} = 36$ dB. These low-power parameters were chosen to ensure optimal RF volume penetration, compare Fig. S1. Since the $^{77}$Se NMR linewidth of our FeSe single crystal is very small (2-3 kHz) at all temperatures and fields, this rather long $t_{\pi/2}$ yields no modulation of the spectral properties. As a sanity check, the spectra were measured for different sets of $t_{\pi/2}$ and $\theta_{\pi/2}$ at selected temperatures and fields, yielding very consistent results. The spectra yield a Lorentzian line shape [see also the fit to the spectrum at 13 T and 0.3 K in Fig. S2 (a)] in the whole parameter range of our investigations. At 0.3 K and fields below 9 T, the lineshape is less defined (but still sharp when considering the horizontal scale) due to a relatively small signal-to-noise ratio per single spectrum. As can be seen from the spectra and as discussed in the main text, the change of Knight shift with field or temperature variation is negligible in the whole parameter range of our study. The numerical full width at half maximum (FWHM) data of the $^{77}$Se real-part NMR spectra as a function of field, determined from the spectra in Fig. S2 (b), are shown in Fig. S3. We observe a sub-linear increase of the absolute linewidth with increasing magnetic field, which yields no notable slope change at 14 T, the transition regime between the A and B phases. This is less than the linear field dependence from typical effects of Pauli susceptibility, and in contrast to effects expected from vortex-lattice contributions, which would yield a decrease of linewidth with increasing field. Presumably, the observed change of linewidth is determined by either microscopic or macroscopic dilute paramagnetic effects that give rise to...
local field variations of the order of 100 \( \mu \text{T} \).

**Thermal-conductivity measurements.**

Measurements of the in-plane thermal conductivity \( \kappa \) were performed on a FeSe single crystal taken from the same batch as the sample for the NMR experiments, using the standard steady-state method for low temperatures. The results of the temperature-dependent thermal conductivity divided by temperature are shown in Fig. S4 (a) for different magnetic fields applied parallel to the crystallographic \( c \) axis. At \( T_c = 9 \) K, the temperature-dependent \( \kappa/T \) at zero field yields a clear deviation from the linear behavior in the high-temperature regime, marking the onset of superconductivity. With increasing magnetic field, the slope change at \( T_c \) becomes less pronounced. In a similar fashion, the field dependence of \( \kappa/T \) yields a kink-like feature at the transition between the superconducting and normal conduction regime, as shown in Fig. S4 (b).

![FIG. S4. (a) Temperature dependence of the in-plane thermal conductivity divided by temperature at different magnetic fields applied parallel to the \( c \) axis. The solid lines are linear fits to the temperature regime above \( T_c \) at the respective fields. (b) Field dependence of \( \kappa/T \) at different temperatures. The slope change at fields in the range of 10.6 to 12.2 T is attributed to the onset of superconductivity.](image)

From the field-dependent measurements of \( \kappa/T \) at various low temperatures as shown in Fig. S5, we find the appearance of a cusp-like feature, yielding an almost temperature-independent maximum at \( H^* = 14.3 \) T. The amplitude of this maximum decreases with increasing temperatures, and approaches zero for temperatures above 1.4 K. This observation is in excellent agreement with the results reported in ref. [1].

Finally, the superconducting phase diagram for fields parallel to the \( c \) axis is constructed from the features in the \( \kappa/T \) data presented in Figs. S4 and S5. The results are in very good agreement with the phase diagram reported by Kasahara et al. [1]. The boundary of the A phase, and also the almost temperature-independent, cusp-like feature at the transition between A and B phase at about 14 T could be very well reproduced, confirming the excellent quality of the sample material for our studies. We note that the electrical resistivity and magnetic torque data in ref. [1] clearly show the formation of bulk superconductivity in the parameter range of the B phase (compare open grey symbols in Fig. 1 in the main text).

![FIG. S5. Dependence of \( \kappa/T \) on fields parallel to the \( c \) axis at various temperatures in a semi-logarithmic plot. The transition between the A and B phases manifests as an almost temperature-independent, cusp-like feature at \( H^* = 14.3 \) T.](image)

![FIG. S6. Superconducting phase diagram of FeSe for fields applied parallel to the \( c \) axis, constructed from the features in Figs. S4 and S5.](image)
[1] S. Kasahara, T. Watashige, T. Hanaguri, Y. Kohsaka, T. Yamashita, Y. Shimoyama, Y. Mizukami, R. Endo, H. Ikeda, K. Aoyama, T. Terashima, S. Uji, T. Wolf, H. v. Löhneysen, T. Shibauchi, and Y. Matsuda, Proc. Natl. Acad. Sci. USA 111, 16309 (2014).