Pressure Induced Static Magnetic Order in Superconducting FeSe$_{1-x}$

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We report on a detailed investigation of the electronic phase diagram of FeSe$_{1-x}$ under pressures up to
1.4 GPa by means of ac magnetization and muon-spin rotation. At a pressure $\simeq 0.8$ GPa the nonmagnetic
and superconducting FeSe$_{1-x}$ enters a region where static magnetic order is realized above T_c and bulk
superconductivity coexists and competes on short length scales with the magnetic order below T_c. For
even higher pressures an enhancement of both the magnetic and the superconducting transition tempera-
tures as well as of the corresponding order parameters is observed. These exceptional properties make
FeSe$_{1-x}$ to be one of the most interesting superconducting systems investigated extensively at present.

The phase diagram of the recently discovered Fe-based
high-temperature superconductors (HTS) [1] share a com-
mon feature with cuprates and heavy fermions. The parent
compounds of the Fe-based HTS, such as, LnOFeAs
(Ln = La, Ce, Pr, Sm) [2–9], AFe$_2$As$_2$ (A = Ba, Sr, Ca)
[10–13] and Fe(SeTe) [14,15] exhibit long-range static
magnetic order. Upon doping or application of pressure
(chemical or external), magnetism is suppressed and super-
conductivity emerges. Recent investigations revealed,
however, that the structurally most simple binary com-
pound FeSe$_{1-x}$ is an exception of this rule [16]. Different
from the other Fe-based HTS, FeSe$_{1-x}$ did not seem to
exhibit static magnetic order for pressures up to about
30 GPa [16]. Yet, short-range spin fluctuations, which are
strongly enhanced towards T_c, were observed [17]. The
superconducting transition temperature of FeSe$_{1-x}$ was
found to increase continuously to $\simeq 37$ K at 7–9 GPa.
For higher pressures a decrease is observed with $T_c \simeq$
6 K approaching 20 GPa [16,18]. Subsequent experiments
with finer pressure steps revealed, however, a local mini-
mum on $T_c(p)$ at 1.5 GPa of unexplained nature [19].

In this Letter we report on a detailed study of the
evolution of the superconducting and magnetic properties
of FeSe$_{1-x}$ as a function of pressure and temperature
through a combination of ac susceptibility and muon-spin
rotation (μSR) techniques. Two samples with the nominal
composition FeSe$_{0.94}$ and FeSe$_{0.98}$ were investigated. The
obtained phase diagram of FeSe$_{1-x}$ was found to be sepa-
rated into three distinct regions. At low pressures, $0 \leq p \lesssim$
0.8 GPa, the samples are nonmagnetic and T_c increases
monotonically with increasing pressure. In the intermedi-
ate pressure region, $0.8 \leq p \lesssim 1.0$ GPa, $T_c(p)$ decreases
with increasing pressure and static magnetism develops. In
this region of the phase diagram the superconducting and
the magnetic order parameters coexist and compete on a
short length scale. Incommensurate magnetic order, which

sets in above T_c, becomes partially (or even fully) sup-
pressed below $T_c(p)$. At higher pressures, $p \gtrsim 1.0$ GPa,
$T_c(p)$ shows a tendency to rise again. The magnetic order
becomes commensurate and both bulk magnetism and bulk
superconductivity coexist within the whole sample
volume.

FeSe$_{1-x}$ samples with the nominal composition FeSe$_{0.94}$
and FeSe$_{0.98}$ were prepared by solid state reaction similar
to that described in Refs. [20–22]. Powders of minimum
purity 99.99% were mixed in appropriate ratios, pressed,
and sealed in a double-walled quartz ampoule. The pressed
rod was heated up to 700 °C followed by annealing at
400 °C [22].

The pressure was generated in a piston-cylinder type of
cell especially designed to perform muon-spin rotation
experiments under pressure [23]. As a pressure transmit-
ting medium 7373 Daphne oil was used. The pressure was
measured *in situ* by monitoring the pressure shift of the
superconducting transition temperature of Pb or/and In.
Two types of cells, the first one made from CuBe alloy
[maximum pressures p_{max}(300 K) $\simeq 1.4$ GPa and
p_{max}(7 K) $\simeq 1.1$ GPa] and the second one made from
MP35 alloy [p_{max}(300 K) $\simeq 1.7$ GPa and p_{max}(7 K) $\simeq$
1.4 GPa], were used.

ac susceptibility measurements were performed by us-
ing a home made ac magnetometer with a measuring field
$\mu_0 H_{ac} \sim 0.1$ mT and frequency $\nu = 96$ Hz. In order to
keep the position of the sample unchanged during the
series of ac susceptibility under pressure measurements,
the excitation and the two pickup coils were wound di-
rectly on the cell. To ensure that the ac signal was entirely
determined by the Meissner response of individual grains
and not by the Josephson type of weak links between them,
measurements of the ac susceptibility as a function of ν
($49 \leq \nu \leq 599$ Hz) and H_{ac} ($0.02 \leq \mu_0 H_{ac} \leq 0.5$ mT) at
$T = 2.5$ K on a standard Quantum Design PPMS instru-

ment were performed. The experiments reveal that the ac magnetization (M_{ac}) scales linearly with H_{ac} and is independent on ν as expected for a superconductor in the Meissner state.

The zero-field muon-spin rotation (ZF μSR) experiments were carried out at the μE1 beam line at the Paul Scherrer Institute, Switzerland for the temperatures ranging from 0.25 to 50 K. The typical counting statistics were $\sim 7 \times 10^6$ positron events for each particular data point.

The response of the superconducting state of FeSe$_{1-x}$ to pressure was studied in ac susceptibility (χ_{ac}) experiments, Fig. 1. The transition temperature T_c, Fig. 1(b), shows a nonmonotonic increase with a local minimum at $p \simeq 1.2$ GPa, similar to $T_c(p)$ reported in [19]. Figure 1(c) depicts $-\chi_{ac}(T)(1-N)$ at $T = 6$ K. Here N denotes the demagnetization factor which, assuming a spherical shape of the sample grains, was taken to be equal to 1/3. For temperatures lower than T_c, $|\chi_{ac}(T)(1-N)|$ is close, but slightly smaller than unity which could caused by penetration of the ac magnetic field on a distance λ from the surface of each individual grain (λ is the magnetic penetration depth). This reveals that within the pressure range studied the superconductivity is bulk by occupying close to 100% of the whole sample volume.

The magnetic response of FeSe$_{1-x}$ was studied in ZF μSR experiments, which is a well known technique to study magnetically ordered phases where the muon acts as a magnetic microprobe. The μSR experiments in Z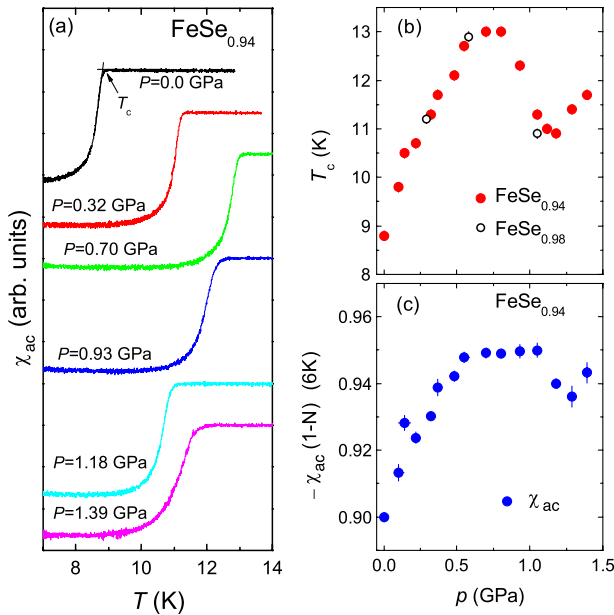F provide information on the internal magnetic field(s) [magnetic order parameter(s)] and on the magnetically ordered volume fraction [24]. In the following we discuss the ZF μSR data for the three different pressure regions.

In the low-pressure region, $0 \leq p \lesssim 0.8$ GPa, where T_c increases with increasing p, the ZF μSR time spectra prove the absence of long-range magnetic order for all temperatures as exemplified by the identical weakly damped spectra for $T = 0.24$ K, near $T_c(p)$ and 20 K, see $p = 0.0$ and $p = 0.76$ GPa data in Fig. 2(a). The solid lines in Fig. 2(a) correspond to a two-component fit:

$$A^{\mathrm{ZF}}(t) = A_S^{\mathrm{ZF}}(t) + A_{\mathrm{PS}}^{\mathrm{ZF}}(t) \quad (1)$$

with the first component describing the sample response and the second one representing the contribution of the pressure cell (ZF responses of the CuBe and MP35 cells are described in [23]). The sample contribution is well fitted to the single-exponential decay function:

$$A_S^{\mathrm{ZF}}(t) = A_{S,0}^{\mathrm{ZF}} e^{-\Lambda_0 t}, \quad (2)$$

(Λ_0 is the exponential relaxation rate), thus revealing that very diluted and randomly oriented magnetic moments exist in the sample volume which can be attributed to small traces of Fe impurities; see Ref. [25].
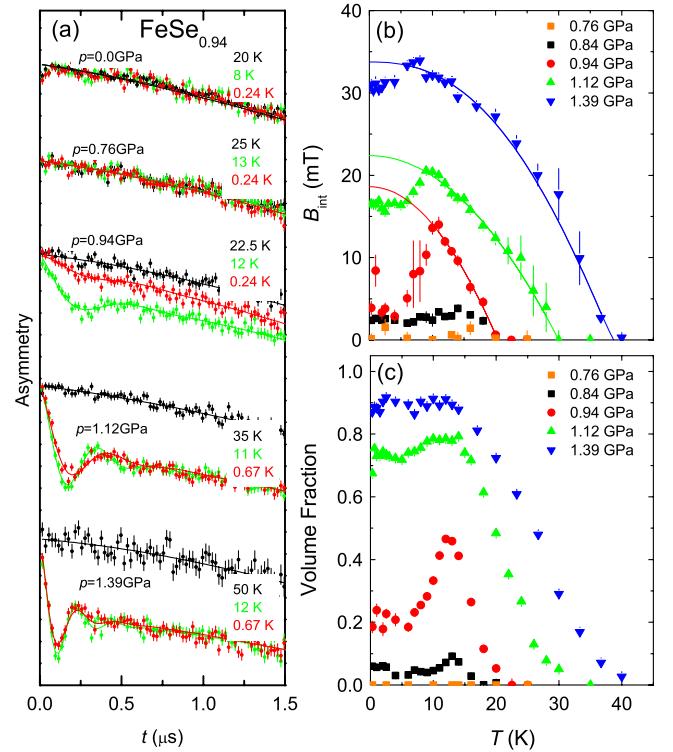

FIG. 1 (color online). (a) Temperature dependence of χ_{ac} of FeSe$_{0.94}$ measured at (from the top to the bottom) $p = 0.0$, 0.32, 0.7, 0.93, 1.18, and 1.39 GPa. The transition temperature T_c is determined from the intersection of straight line fits to the data above and below the transition. (b) Dependence of T_c on p of FeSe$_{0.94}$ and FeSe$_{0.98}$. (c) Pressure dependence of the normalized ac susceptibility $-\chi_{ac}(1-N)$ at $T = 6$ K.

FIG. 2 (color online). (a) Zero-field μSR time spectra of FeSe$_{0.94}$ measured at (from the top to the bottom) $p = 0.0$, 0.76, 0.94, 1.12, and 1.39 GPa. Dependence of the internal field at the muon stopping site B_{int} which is proportional to the magnetic order parameter (b), and the magnetic volume fraction (c), on temperature at various pressures. The solid lines in panel (b) are the fit of $B_{\mathrm{int}}(T)$ in the region $T_c(p) \leq T \leq T_N$ to $B_{\mathrm{int}}(T) = B_{\mathrm{int}}(0)[1 - (T/T_N)^\alpha]^\beta$ (α and β are the power exponents).

In the intermediate pressure region, $0.8 \lesssim p \lesssim 1.0$ GPa, the spontaneous muon-spin precession is clearly observed in the ZF μSR time spectra; see $p = 0.94$ GPa data in Fig. 2(a). Therefore, static magnetic order is established below the Néel temperature T_N. The analysis of the μSR data was made by accounting for the separation of the sample into magnetically ordered regions with muons experiencing a static local field and nonmagnetic (paramagnetic) regions:

$$A_S^{ZF}(t) = A_{S,0}^{ZF}[m(\tfrac{2}{3}j_0(\gamma_\mu B_{int}t)e^{-\Lambda_T t} + \tfrac{1}{3}e^{-\Lambda_L t})$$
$$+ (1-m)e^{-\Lambda_0 t}]. \qquad (3)$$

Here m is the magnetic volume fraction of the sample, j_0 is a zeroth order Bessel function, $\gamma = 2\pi 135.5$ MHz/T is the muon gyromagnetic ratio, and Λ_T and Λ_L are the exponential relaxation rates longitudinal and transverse to the initial muon-spin polarization. The oscillating part of the signal was found to be good described by a Bessel function, which is archetypical for incommensurate magnetic order [26]. The dependence of the internal field B_{int}, corresponding to the magnetic order parameter, and the magnetic volume fraction on temperature are shown in Figs. 2(b) and 2(c).

For pressures above 1.0 GPa we observe a further increase of the magnetic volume fraction and of the internal magnetic field B_{int}, Fig. 2. Additionally, we find that the μSR line shape is better described by a damped cosine with zero initial phase rather than by a Bessel function:

$$A_S^{ZF}(t) = A_{S,0}^{ZF}[m(\tfrac{2}{3}\cos(\gamma_\mu B_{int}t)e^{-\Lambda_T t} + \tfrac{1}{3}e^{-\Lambda_L t})$$
$$+ (1-m)e^{-\Lambda_0 t}]. \qquad (4)$$

This suggests that in the high pressure region the magnetic order becomes commensurate.

Figure 3 summarizes our results on the magnetism and superconductivity in an electronic phase diagram for FeSe$_{1-x}$. The magnetic order coexists and competes with superconductivity for $p \gtrsim 0.8$ GPa. Above this pressure long-range magnetic order is established below $T_N > T_c$ and bulk superconductivity sets in below T_c. The competition of the two ground states in this pressure range is evident from the following two observations: First, as a function of pressure T_c is weakened as soon as magnetic order appears, leading to the local maximum at $p \simeq 0.8$ GPa in $T_c(p)$; second, as a function of temperature B_{int}, as well as the magnetic volume fraction, decrease below T_c showing that the magnetism, which develops at higher temperatures, becomes partially (or even fully) suppressed by the onset of superconductivity. The superconducting volume fraction is close to 100% for all pressures, Fig. 1(c), while the magnetic fraction increases continuously and reaches $\simeq 90\%$ at the highest pressure investigated $p \simeq 1.39$ GPa, Fig. 2(c). In other words, both ground states coexist in the full sample volume at $p = 1.39$ GPa. Our data do not provide any indication for macroscopic phase separation into superconducting and magnetic clus-
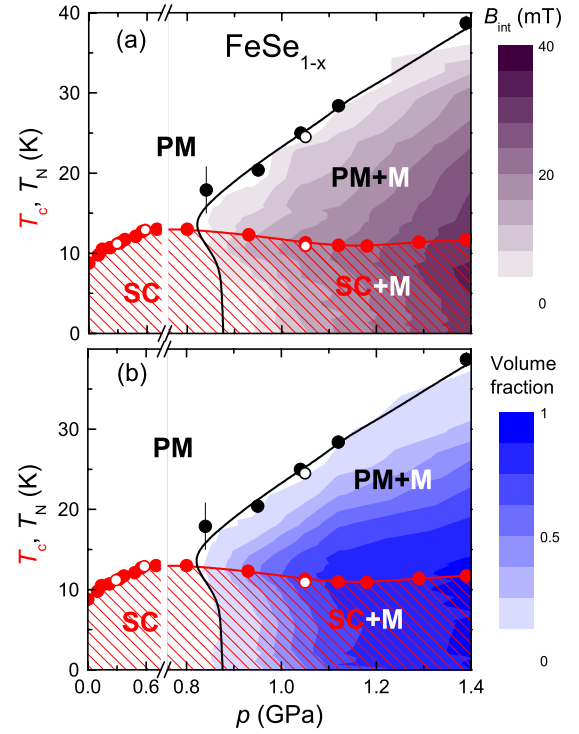

FIG. 3 (color online). (a) Pressure dependence of the superconducting transition temperature T_c, the magnetic ordering temperature T_N, and the internal field B_{int} (magnetic order parameter) obtained in ac susceptibility and muon-spin rotation experiments. (b) Pressure dependence of T_N, T_c, and the magnetic volume fraction. The $T_c(p)$ and $T_N(p)$ lines are guides for the eye. The closed and the open symbols refer to FeSe$_{0.94}$ and FeSe$_{0.98}$ sample. SC, M, and PM denote the superconducting, magnetic, and nonmagnetic (paramagnetic) states of the sample.

ters (bigger than a few nm in size), as observed, e.g., for Ba$_{1-x}$K$_x$Fe$_2$As$_2$ [27]. Actually, the data rather point to a coexistence of both order parameters on an *atomic* scale. This scenario is compatible with the itinerant two-band models of Fe-based HTS proposed recently by Vorontsov *et al.* [28] and Cvetkovic and Tesanovic [29]. According to these models the transition between the magnetic and the superconducting states may involve the formation of the intermediate phase, where both superconductivity and magnetism coexist.

In conclusion, the magnetic and superconducting properties of FeSe$_{1-x}$ were studied as a function of pressure up to 1.4 GPa by means of ac magnetization and μSR techniques. ac magnetization measurements show that within the pressure range studied the superconductivity is bulk by occupying close to 100% of the whole sample volume. μSR experiments reveal that above $\simeq 0.8$ GPa superconductivity coexists with magnetism with Néel temperatures $T_N > T_c$. In a narrow pressure range, where a local minimum in $T_c(p)$ is observed, superconductivity competes with magnetism in the sense that the magnetic volume fraction and the magnetic order parameter are suppressed below T_c. At the highest pressure investigated here superconductivity and static commensurate magnetism coexist

on short length scales in the full sample volume. Furthermore, both forms of order seem to be stabilized by pressure, since T_c as well as T_N and the magnetic order parameter simultaneously increase with increasing pressure. This exceptional observation provides a new challenge for theories describing the mechanism of high-temperature superconductivity.

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