Tuning of competing magnetic and superconducting phase volumes in LaFeAsO$_{0.945}$F$_{0.055}$ by hydrostatic pressure


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The interplay between magnetism and superconductivity in LaFeAsO$_{0.945}$F$_{0.055}$ was studied as a function of hydrostatic pressure up to $p \simeq 2.4$ GPa by means of muon-spin rotation ($\mu$SR) and magnetization measurements. The application of pressure leads to a substantial decrease of the magnetic ordering temperature, reduction of the magnetic phase volume and, at the same time, to a strong increase of the superconducting transition temperature and the diamagnetic susceptibility. From the volume-sensitive $\mu$SR measurements it can be concluded that the superconducting and the magnetic areas, coexisting in the same sample, are inclined toward spatial separation and compete for phase volume as a function of pressure.

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The interplay between superconductivity and magnetism in high-temperature superconductors (HTSs) remains an important open issue. In cuprate and Fe-based HTSs, such a transformation follows an almost common scenario. On increasing the doping level the antiferromagnetically ordered phase develops into a purely conducting area, which is at the border to the superconducting state but still magnetic. For some families of Fe-based HTSs, such as, e.g., SmFeAsO$_{1-x}$F$_x$, Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$, and FeSe$_{1-x}$Te$_x$, the magnetism is continuously suppressed and superconductivity is enhanced by changing the F, Co, or Se content. In the intermediate region, bulk magnetism and bulk superconductivity are coexisting in space. In Ba$_{1-x}$K$_x$Fe$_2$As$_2$ the magnetic and the superconducting areas are found to be separated microscopically as revealed, e.g., by atomic force microscopy and muon-spin rotation ($\mu$SR) experiments.

One of the most interesting cases is realized in the LaFeAsO$_{1-x}$F$_x$ family of Fe-based HTSs demonstrating an abrupt (first-order-like) transition between the magnetic and the superconducting phases. $\mu$SR and Mössbauer experiments show that above a certain $x$ the samples become purely superconducting without visible traces of magnetism. Such a behavior seems to be rather different from the one observed for the other structurally related families of Fe-based HTSs in which the La atom is replaced by Sm, Pr, Ce, etc. All of them demonstrate a coexistence between superconductivity and magnetism for a certain doping level. Consequently, the question if a similar coexistence is present in LaFeAsO$_{1-x}$F$_x$ but within a much narrower, up to now not detected, doping region or if an abrupt change between the superconductivity and magnetism is a unique property of this particular family of Fe-based HTS needs to be resolved.

Hydrostatic pressure experiments on LaFeAsO$_{0.945}$F$_{0.055}$, which is at the border to the superconducting state but still magnetic, were performed to distinguish between the two above-mentioned possibilities. This approach allows to follow the transformation of the material from the magnetic to the superconducting state in detail on one sample, i.e., without the necessity to synthesize a large number of samples with exactly defined stoichiometry near the phase boundary. Our measurements show that both the magnetic and superconducting states are most probably spatially separated in the crossover region of the phase diagram and compete for phase volume.

The sample with the nominal composition LaFeAsO$_{0.945}$F$_{0.055}$ was prepared in a cubic anvil high-pressure cell from the stoichiometric mixture of LaAs, FeAs, Fe$_2$O$_3$, Fe, and LaF$_3$. A pressure of $\simeq 3$ GPa was applied at room temperature. By keeping the pressure constant, the temperature was first ramped up to a maximum value of 1320 °C, kept constant for 5.5 h, and then quenched to room temperature within a few minutes. X-ray measurements confirm the single-phase nature of the sample as well as the absence of a suitable amount of impurities.

The superconducting properties of LaFeAsO$_{0.945}$F$_{0.055}$ were studied by magnetization experiments. The zero-field-cooled and field-cooled (FC and ZFC) dc magnetization measurements up to $p \simeq 1.1$ GPa were performed by using the commercial superconducting quantum interference device (SQUID) magnetometer (MPMS-XL7) and a piston-cylinder CuBe pressure cell (“EasyLab Mccell 10”). The ac experiments up to $p \simeq 2$ GPa were performed by using the cell made from MP35N alloy and a home-made ac magnetometer (ac frequency $\nu = 72$ Hz, ac field amplitude $\mu_0 H_{ac} \simeq 0.1$ mT). As the pressure transmitting medium “Daphne oil 7373” was used. This oil solidifies at $p \simeq 2.2$ GPa at room temperature. Since the pressure was always applied at room temperature and most of the experiments presented in this Rapid Communication were performed below 2.2 GPa, we may assume that the pressure conditions were always nearly hydrostatic.
LaFeAsO$_{0.945}$F$_{0.055}$ at various pressures. The magnetic ordering temperature $T_N$ is defined as the temperature where the magnetic fraction reaches 50% of its maximum low-temperature value. The insets show the ZF muon-time spectra at $p = 0.0$ and 2.36 GPa. The solid lines are fits by means of Eq. (1). The dotted lines represent the response of the pressure cell.

Here $A_S(0)$ and $A_{PC}(0)$ are the initial asymmetries and $P_S(t)$ and $P_{PC}(t)$ are the muon-spin polarizations belonging to the sample and the pressure cell, respectively. $P_{PC}(t)$ was measured in an independent experiment. The response of the sample was assumed to consist of a magnetic and a nonmagnetic contribution and is described as

$$P_S(t) = \omega \left[ \frac{1}{4} e^{-\Delta_{m,l} t} + \frac{3}{4} \left( \xi e^{-\Delta_{m,t} t} + (1 - \xi) e^{-\Delta_{m,O2} t} \right) \right] + (1 - \omega)e^{-\Delta_{pm} t}.$$ 

Here $\omega$ is the relative weight (volume) of the magnetic fraction. $\Lambda_{m,l}$, $\Lambda_{m,t}$, and $\Lambda_{pm}$ are the exponential depolarization rates representing the longitudinal (1/3) and the transversal (2/3) relaxing components within the parts of the sample being in the magnetic state. The two components within the curly brackets account for contributions of two different muon stopping sites with the relative weights $\xi$ and $(1 - \xi)$, respectively. As follows from Ref. 13, one site is located on the line connecting the La and As ions along the $c$ direction, while the second one is located near the oxygen ions. $\Lambda_{pm}$ is the relaxation within the parts of the sample remaining nonmagnetic. The exponential character of this relaxation, instead of the normally expected Kubo-Toyabe kind of behavior, is probably caused by the presence of the small amount of magnetic impurities, similar to the one observed in the so called “11” family of Fe-based HTS (see, e.g., Refs. 4 and 15). For each particular pressure the whole set of the data was fitted simultaneously with $A_S(0)$, $A_{PC}(0)$, $\xi$, and the ratio $\Lambda_{m,l}/\Lambda_{m,t}$ as common and $\omega$, $\Lambda_{m,l}$, $\Lambda_{m,t}$, and $\Lambda_{pm}$ as individual parameters for each temperature point. The solid lines in the insets of Fig. 2 represent the result of the fit. The contribution from the cell at $T = 5$ K is shown as a dotted line.

The main panel of Fig. 2 shows the dependence of the magnetic fraction $\omega$ on temperature for $p = 0.0, 0.5, 1.16, \text{and}$

$A(t) = A_S(0) P_S(t) + A_{PC}(0) P_{PC}(t).$  \hspace{1cm} (1)
Two important points need to be considered. First, the magnetic volume fraction at each particular temperature is lowered by the application of pressure. Most noteworthy, with increasing pressure an increasingly large part of the sample remains in the paramagnetic state down to the lowest temperatures. Second, the magnetic ordering temperature $T_N$, defined as the temperature where the magnetic fraction reaches 50% of its maximum low-temperature value, initially decreases with increasing pressure but then demonstrates a tendency to saturate. $\omega(T)$ curves at $p = 1.16, 1.92$ (not shown), and 2.36 GPa being normalized to their values at $T \simeq 5$ K become almost identical.

In order to compare the influence of the pressure on the superconducting and the magnetic properties of LaFeAsO$_{0.945}$F$_{0.055}$, the dependences of $T_N$, $T_c$, $\omega$, and $4\pi\chi$ as a function of $p$ are plotted in Fig. 3. The decrease of $T_N$ and $\omega$ is associated with the corresponding increase of $T_c$ and $4\pi\chi$. By applying a pressure of 2.36 GPa, $T_N$ decreases from 44 to 27 K, while $T_c$ more than doubles from 7 to 16 K upon the application of 2.02 GPa.

It should be noted here that the above presented data are pointing to a competition of superconductivity and magnetism, but alone do not allow to answer the question on how these two forms of order coexist within the LaFeAsO$_{0.945}$F$_{0.055}$ sample. There are three possible scenarios. The first one is the so-called phase separation scenario according to which the superconductivity develops just within the parts of the sample remaining nonmagnetic down to low temperatures. Such a phase-separated coexistence was observed, e.g., in Ba$_{1-x}$K$_x$Fe$_2$As$_2$. The second possibility is an atomic coexistence of the superconducting and magnetic order parameters, which is consistent with models proposed in Ref. 17 and most probably realized within the so-called “11” family of Fe-based HTSs. The third possibility is a nanoscale segregation into magnetic domains, similar to that reported for cuprate HTSs. In underdoped cuprate HTSs, static, short-range, striplike magnetic correlations are thought to exist in the superconducting state and are assumed not to affect the superconducting carriers. Muons are sensitive to dipolar fields at a distance of up to a few lattice spacings, so if nanoscale magnetic domains exist, then the fraction of muons experiencing static local magnetic fields could be significantly higher than the fraction of Fe sites carrying an ordered moment. Such a type of coexistence was found to be realized within the SmFeAsO$_{1-x}$F$_x$ and CeFeAsO$_{1-x}$F$_x$ families of Fe-based HTSs.

Since the muon is a local probe, the $\mu$SR signals from spatially different areas of the sample are not averaged but superimposed in the measured spectra. This feature allows to distinguish between the three above-mentioned scenarios. As discussed above, the ZF-$\mu$SR response of the magnetic areas of the sample is characterized by a fast relaxing signal visible at early times of the spectra, while a nonmagnetic volume shows slow relaxation, better visible at longer times, only. In Fig. 4 two ZF muon-time spectra taken at the same temperature ($T = 2.6$ K) and pressure ($p = 2.36$ GPa) with different magnetic histories are shown. The first muon-time spectrum was recorded after cooling the sample from $T \simeq 100$ to 2.6 K in zero magnetic field. By keeping the temperature constant, the second ZF spectrum was obtained after ramping the magnetic field up to $\mu_0H \simeq 0.1$ T and then setting it back.

![FIG. 3.](image-url) (Color online) (a) Dependence of the magnetic ordering temperature $T_N$ and the superconducting transition temperature $T_c$ on pressure. The closed and the open circles correspond to $T_c$ as obtained in ac and dc magnetization experiments, respectively. (b) The magnetic fraction at $T = 5$ K and ZFC diamagnetic susceptibility $-4\pi\chi$ at $T = 3.5$ K, $\mu_0H = 5$ mT as a function of pressure. The closed and the open circles refer to the data obtained in ac and dc magnetization experiments, respectively. The lines are a guide for the eye.

![FIG. 4.](image-url) (Color online) (a) The ZF-$\mu$SR time spectra obtained after cooling the sample in zero magnetic field from $T \simeq 100$ K down to 2.6 K (red/gray symbols) and after sweeping the magnetic field to 0.1 T and then setting it back. The solid lines are fits by means of Eq. (1).
TABLE I. Parameters as extracted from the fit of Eq. (1) to the 
muon-time spectra obtained after cooling the sample from $T \sim 100$ to 2.6 K in zero magnetic field (ZFC) and after ramping the magnetic 
field up to $H_{RF} \sim 0.1$ T and setting it back to zero (ZFC $\rightarrow$ 0.1 T $\rightarrow$ ZF). $A_S$, $A_{PC}$, $\zeta$, and $\omega$ were assumed to be the same for both spectra.

<table>
<thead>
<tr>
<th></th>
<th>$\Lambda_{m,1}$ ($\mu$s$^{-1}$)</th>
<th>$\Lambda_{m,2}$ ($\mu$s$^{-1}$)</th>
<th>$\Lambda_{pm}$ ($\mu$s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZFC</td>
<td>19.7(2.7)</td>
<td>1.28(14)</td>
<td>0.165(26)</td>
</tr>
<tr>
<td>ZFC $\rightarrow$ 0.1 T $\rightarrow$ ZF</td>
<td>18.4(3.5)</td>
<td>1.20(28)</td>
<td>1.20(36)</td>
</tr>
</tbody>
</table>

FIG. 4. 

Our results point to a strong difference between LaFeAsO$_{1-x}$F$_x$ and the structurally related families of Fe-based HTSs with the La atom substituted by other rare-earth elements such as Sm, Ce, Pr, Nd, etc. In these families bulk magnetism and bulk superconductivity are found to coexist on the nanoscale level. The magnetization and $\mu$SR experiments reveal that in LaFeAsO$_{1-x}$F$_x$, the magnetism and superconductivity are not coexisting over the whole sample volume, i.e., this system is inclined toward phase separation. The reduction of the magnetic interaction and the simultaneous appearance of superconductivity indicate a much stronger competition between the two ordered parameters.

In conclusion, the interplay between magnetism and superconductivity was studied in LaFeAsO$_{0.945}$F$_{0.055}$ by performing muon-spin rotation and magnetization experiments as a function of pressure up to $p \sim 2.4$ GPa. At ambient pressure the sample is purely magnetic, but at the border to the superconducting state of LaFeAsO$_{1-x}$F$_x$. The application of hydrostatic pressure leads to a substantial decrease of $T_N$ and a reduction of the magnetic phase volume and, at the same time, to a strong increase of $T_c$ and the diamagnetic susceptibility. Magnetic-history-dependent ZF-$\mu$SR measurements show that superconductivity most probably develops in the areas of the sample that are nonmagnetic down to the lowest temperatures. This shows that in LaFeAsO$_{1-x}$F$_x$ magnetism and superconductivity are competing order parameters.

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The sample used in the present work was grown under high pressure, which may lead to possible differences in the actual F content incorporated into the structure as compared with that in the Ref. 8.


