Progressive slowing down of spin fluctuations in underdoped $LaFeAsO_{1-x}F_x$

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The evolution of low-energy spin dynamics in the iron-based superconductor $LaFeAsO_{1-x}F_x$ was studied over a broad doping, temperature, and magnetic field range ($x = 0$–0.15, $T \leqslant 480$ K, $\mu_0 H \leqslant 30$ T) by means of ^{75}As nuclear magnetic resonance. An enhanced spin-lattice relaxation rate divided by temperature $(T_1T)^{-1}$ in underdoped superconducting samples ($x = 0.045$, 0.05, and 0.075) suggests the presence of antiferromagnetic spin fluctuations, which are strongly reduced in optimally doped ($x = 0.10$) and completely absent in overdoped ($x = 0.15$) samples. In contrast to previous analysis, Curie-Weiss fits are shown to be insufficient to describe the data over the whole temperature range. Instead, a Bloembergen-Purcell-Pound (BPP) model is used to describe the occurrence of a peak in $(T_1T)^{-1}$ clearly above the superconducting transition, reflecting a progressive slowing down of the spin fluctuations down to the superconducting phase transition.

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I. INTRODUCTION

Investigations of the role of spin fluctuations in iron-based superconductors are crucial for the understanding of the mechanism of superconductivity in these compounds. Standard electron-phonon modes have been found to be too weak to mediate superconductivity with the reported transition temperatures.[1,2] Instead, the vicinity to a magnetically ordered ground state and the topology of the multiband Fermi surface with quasinested electron and hole pockets already triggered at a very early stage of the pnictide research era theoretical considerations that spin fluctuations might be the pairing glue for Cooper pairs,[2–5] similar to the previous case of cuprate superconductors.

Nuclear magnetic resonance (NMR) is a versatile local probe technique to study the superconductivity as well as the static and dynamic magnetic properties of a material. The NMR spin-lattice relaxation rate T_1^{-1} is a very useful probe of the magnetic fluctuations since it is directly proportional to the wave-vector-$\vec{q}$-dependent dynamic spin susceptibility $\chi''(\vec{q},\omega)$. It is thus a key tool to investigate spin fluctuations on the border of magnetism and superconductivity in the iron-based superconductors. Indeed, an enhanced nuclear spin-lattice relaxation rate divided by temperature $(T_1T)^{-1}$has been observed in a number of nonmagnetic, superconducting iron pnictides, indicating the existence of strong antiferromagnetic spin fluctuations.[6–15] However, the role of these fluctuations in the occurrence of superconductivity is heavily debated. Some references still find pronounced spin fluctuations in optimally doped samples with the highest T_c,[6–12] concluding that these fluctuations promote superconductivity. Other references report that the highest T_c correlates with the complete suppression of previously existing spin fluctuations, which rather points towards a competition of superconductivity and magnetism.[13–17]

Here, we study the evolution of spin fluctuations as a function of doping, temperature, and magnetic field in $LaFeAsO_{1-x}F_x$, where superconductivity in the FeAs layers arises upon substituting oxygen with fluorine in the LaO layer.[18] This out-of-plane electron doping is expected to minimize the influence of the dopants on the FeAs planes, in contrast to in-plane cobalt dopants, for example, which additionally act as impurity scatterers.[19] Furthermore, the transition from the magnetically ordered state to the superconducting one is abrupt in $LaFeAsO_{1-x}F_x$.[12,20] No sign of coexistence of superconductivity and static magnetism has been observed in this compound, which is in contrast to other pnictide families, such as $CeFeAsO_{1-x}F_x$, $SmFeAsO_{1-x}F_x$, or Co-doped $Ba(Fe_{1-x}Co_x)_2As_2$.[21–24] This mutually exclusive superconducting or magnetic ordering enables us to study the role of fluctuations without the additional complication of contributions from overlapping magnetic order. Our measurements are largely consistent with previous NMR investigations of $LaFeAsO_{1-x}F_x$, which reported the absence of antiferromagnetic spin fluctuations for optimally doped ($x = 0.1$) and overdoped samples[13,16] and the presence of such fluctuations in underdoped samples,[13–15] pointing towards a competition of magnetism and superconductivity. We extend these previous investigations to higher temperatures, higher fields, and a broader range of doping levels. Note that a recent nuclear quadrupole resonance (NQR) study suggested a slightly different phase diagram, where significant spin fluctuations still appear in optimally doped (in this case $x = 0.06$) samples.[12]

This paper focuses on the presentation of an approach to quantitatively describe the relaxation data in the normal state of underdoped superconducting, nonmagnetic samples. To date, all published analyses of the enhancement of $(T_1T)^{-1}$ with decreasing temperature in such samples were based on a Curie-Weiss picture[8,10–13,15] or a combination of a Curie-Weiss term and an activated temperature dependence to account for the decrease of $(T_1T)^{-1}$ with decreasing temperature in the high-temperature regime.[9] The common use

of the Curie-Weiss model for the increase of $(T_1T)^{-1}$ follows from Moriya's self-consistent renormalization (SCR) theory for weakly itinerant two-dimensional (2D) antiferromagnets, which showed that the staggered susceptibility above T_N can be approximately described by a Curie-Weiss law.[25,26] However, in some of these studies there is a noticeable deviation from the Curie-Weiss law at low temperatures: $(T_1T)^{-1}$ decreases visibly already above the superconducting transition and forms a well-defined peak above T_c,[7,13] which cannot be expressed within the Curie-Weiss model or within the more correct SCR framework. This peak is also clearly not a Hebel-Slichter coherence peak[27] or related to flux-line lattice dynamics[28] since these are specific to $T < T_c$. We focus on the appearance of this peak, which is present for all our underdoped samples, and propose an analysis based on the Bloembergen-Purcell-Pound (BPP) model,[29,30] which can be used to describe the progressive slowing down of spin fluctuations. Our studies of the doping and field dependence of the peak in $(T_1T)^{-1}$ as well as selected measurements of the spin-spin relaxation rate T_2^{-1} corroborate the choice of the BPP model and help rule out other possible origins of such a peak in $(T_1T)^{-1}$, such as spin diffusion effects[31,32] or a field-induced anisotropy in the spin fluctuations.[33]

II. SAMPLE PREPARATION AND EXPERIMENTAL DETAILS

Polycrystalline samples of $LaFeAsO_{1-x}F_x$ with nominal doping levels $x = 0$, 0.035, 0.045, 0.05, 0.075, 0.1, and 0.15 have been prepared by following and improving the two-step solid-state-reaction approach of Zhu *et al.*[34,35] Detailed structural, thermodynamic, and transport characterization studies on the samples with $x = 0$, 0.05, 0.075, 0.1, and 0.15 can be found in previous publications.[20,35–39] The undoped sample ($x = 0$) shows a structural transition at $T_s = 156$ K, followed by a magnetic ordering at $T_N = 138$ K. Samples with $x > 0.04$ are superconducting, with $T_c = 20$, 22, 26.8, 10 K for $x =$ 0.05, 0.075, 0.1, 0.15, respectively. The presence of static magnetic order in these superconducting samples has been ruled out experimentally.[20,37] Two new samples with $x = 0.035$ and $x = 0.045$, residing directly at the boundary between the magnetically ordered and the superconducting ground state, have been prepared recently. The sample with $x = 0.035$ is not superconducting. The temperature dependence of its susceptibility resembles that of other magnetically ordered samples with $x < 0.04$.[39] Very slight changes of slope in the region between 80 and 140 K indicate possible structural and magnetic transitions around $T_s \approx 120$ K and $T_N \approx 100$ K. However, these anomalies in the susceptibility are too weak to determine the exact values of T_s and T_N. We will show that NMR T_1 measurements of this sample are able to determine the magnetic transition very precisely. The sample with $x = 0.045$, on the other hand, does not exhibit any magnetic or structural ordering but is superconducting, with $T_c \approx 19$ K, as probed by magnetization measurements in a magnetic field of 20 Oe.

TABLE I. T_c from *in situ* ac susceptibility measurements in 7 T and T_{max} of $(T_1T)^{-1}$ for all investigated doping levels.

	x				
	4.5%	5%	7.5%	10%	15%
T_c (K)	16	16	18	22	9
T_{max} (K)	27	28	40		

TABLE II. $T_c(H)$ of the sample with $x = 0.045$ from *in situ* ac susceptibility measurements in the different applied magnetic fields and $T_{max}(H)$ of $(T_1T)^{-1}$ for the same sample.

	$\mu_0 H$					
	0 T	3 T	7 T	16 T	23 T	30 T
T_c (K)	20	18	16	15	12	10
T_{max} (K)		25	27	36	38	42

For NMR measurements, the pellets were ground to a powder of 1–100-μm grain size. To protect the samples from moisture, they were put into quartz glass tubes which were sealed with Teflon thread tape.

^{75}As (nuclear spin $I = 3/2$) NMR measurements were carried out in a magnetic field of 7 T for all samples and additionally in 16 T for the sample with $x = 0.035$ and in 3, 16, 23, and 30 T for the sample with $x = 0.045$. Since the superconducting transition temperature decreases in an applied magnetic field and the knowledge of $T_c(H)$ was crucial for our analysis, we determined $T_c(H)$ by *in situ* ac susceptibility measurements by tracking the detuning of the NMR resonance circuit. The corresponding values for T_c(7 T) for all doping levels and $T_c(H)$ for the sample with $x = 0.045$ can be found in the first row of Tables I and II and are shown as gray symbols in the phase diagram (see Fig. 10 below). Due to the way T_c was determined, it should be noted that for $\mu_0 H > 0$ some corrections to $T_c(H)$ can be present due to the onset of vortex motions, which will, however, not impair our analysis. The nuclear spin-lattice relaxation rate T_1^{-1} was measured on the high-frequency peak of the quadrupolar-broadened NMR powder pattern of the central transition ($I_z = 1/2 \rightarrow I_z = -1/2$).[16] This peak corresponds to the field orientation $H||ab$, i.e., to the direction parallel to the iron planes.[16] The exact position of the peak was determined via frequency scans for each temperature to exclude possible frequency-dependent effects on T_1^{-1}. The inversion recovery method was used to determine T_1, and the recovery of the nuclear magnetization was fitted to the relaxation formula for the central transition of a nuclear spin $I = 3/2$:[40]

$$M_z(t) = M_0[1 - f(0.9e^{-(6t/T_1)^{\lambda}} + 0.1e^{-(t/T_1)^{\lambda}})], \quad (1)$$

where $M_z(t)$ is the nuclear magnetization recovered after a certain time t, M_0 is the saturation magnetization at thermal equilibrium, f is the inversion factor, which for a complete inversion equals 2, and T_1 is the nuclear spin-lattice relaxation time. A stretching exponent λ with $1 > \lambda \geqslant 0.45$ had to be used below 100 K to fit the recovery curves of all samples except for $x = 0$, $x = 0.1$, and $x = 0.15$. In these three cases, λ could be kept at 1 for all temperatures.

III. EXPERIMENTAL RESULTS AND ANALYSIS

Figure 1 shows the temperature evolution of the ^{75}As NMR spin-lattice relaxation rate divided by temperature $(T_1T)^{-1}$,

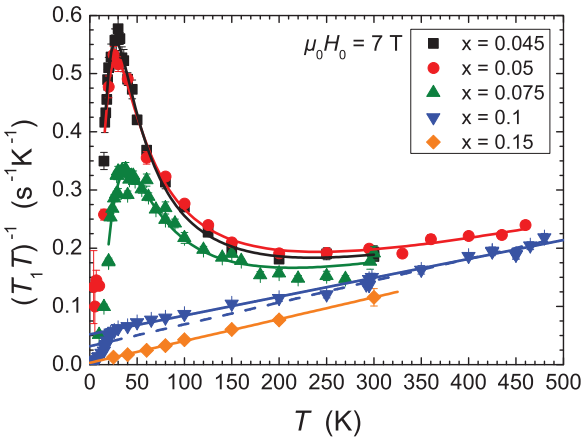

FIG. 1. (Color online) The spin-lattice relaxation rate divided by temperature $(T_1T)^{-1}$ vs temperature, measured in a magnetic field of 7 T, for different doping levels of superconducting samples. The lines are fits to our proposed BPP-like model, Eq. (5), for $0.045 \leqslant x \leqslant 0.075$ and linear fits for $x = 0.1$ and $x = 0.15$ (solid and dashed lines; see text for details).

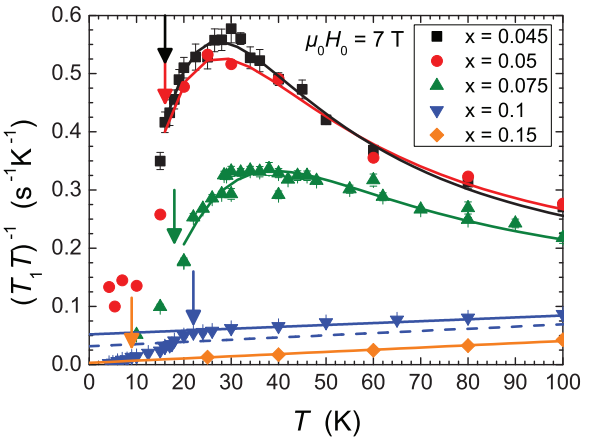

FIG. 2. (Color online) Enlargement of the low-temperature region of Fig. 1. Lines are fits to the data (symbols) with Eq. (5) for $0.045 \leqslant x \leqslant 0.075$ and linear fits for $x = 0.1$ and $x = 0.15$ (solid and dashed lines; see text for details). The superconducting transition temperatures T_c(7 T) are marked by arrows.

measured in a magnetic field of 7 T, for all superconducting samples ($x \geqslant 0.045$). For selected samples, the measurements have been extended up to 480 K ($x = 0.05$ and $x = 0.1$).

For the optimally doped ($x = 0.1$) and the overdoped ($x = 0.15$) samples, $(T_1T)^{-1}$ decreases monotonically with decreasing temperature. This behavior has been known since the beginning of the research on iron-based superconductors. At this early stage, it was compared to the pseudogap behavior in cuprates.[13,16] The NMR Knight shift, which is a direct measure of the intrinsic static spin susceptibility, $\chi(\vec{q} = 0, \omega = 0)$, shows a similar temperature dependence.[16,41] However, no pseudogap peak could be observed up to 480 K, and activated fits, as usually used to describe the opening of a pseudogap, fail to describe the data consistently over the whole temperature range, which renders the pseudogap scenario rather unlikely.[42,43] In contrast to the previously intended pseudogap fits, $(T_1T)^{-1}$ of $x = 0.1$ and $x = 0.15$ can be well fitted with a simple linear temperature dependence over the whole temperature range down to T_c (see Figs. 1 and 2). This agrees well with the static susceptibility measured by superconducting quantum interference device (SQUID) magnetization measurements, which also shows a linear temperature dependence in the high-temperature regime.[39] Several theoretical approaches have been made to discuss the linear decrease of the static uniform susceptibility with decreasing temperature, including the consideration of antiferromagnetic fluctuations[44–46] and of a large polarizability of the anions leading to attractive excitonic interactions and possibly to the preformation of Cooper pairs well above the superconducting transition.[47,48] A recent theoretical paper suggests peculiarities in the orbitally resolved density of states to be the reason for the decreasing susceptibility.[49] Another recent investigation suggests that average effective local iron spins S_{eff} result from a dynamical mixing of different iron spin states and that singlet correlations among these S_{eff} are causing the peculiar temperature dependence of the susceptibility.[50]

In the underdoped samples ($x = 0.045$, 0.05, and 0.075), at high temperatures, $(T_1T)^{-1}$ shows a decrease with decreasing temperature similar to the optimally doped and overdoped samples. But below 200 K, $(T_1T)^{-1}$ increases, indicating the presence of pronounced antiferromagnetic spin fluctuations. These fluctuations are only observable in $(T_1T)^{-1}$ and not in the macroscopic spin susceptibility or the NMR Knight shift.[39,42] This is because $(T_1T)^{-1}$ probes the $\vec{q}$-integrated imaginary part of the dynamical spin susceptibility $\chi''(q,\omega)$, whereas the macroscopic spin susceptibility or the Knight shift probe only at $\vec{q} = 0$. Upon increasing the doping level, the increase of $(T_1T)^{-1}$ is reduced. This behavior is quite common for underdoped samples of $LaFeAsO_{1-x}F_x$ and other pnictide families.[6–15]

Figure 3 shows Curie-Weiss fits of the form $(T_1T)^{-1} = C/(T + \theta)$ (dashed lines) for $x = 0.05$ and $x = 0.075$. Such fits have been widely used to describe the increase of spin fluctuations towards T_c.[8,10–13,15] However, as can be seen in Fig. 3, the fits are unable to describe the data for $T > 200$ K

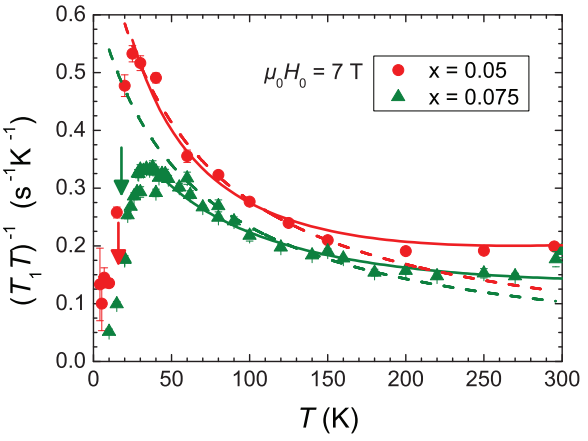

FIG. 3. (Color online) Examples of Curie-Weiss fits (dashed lines) and fits including a Curie-Weiss contribution and a linear temperature dependence (solid lines) to the $(T_1T)^{-1}$ data of the samples with $x = 0.05$ (red dots) and $x = 0.075$ (green triangles). The superconducting transition temperatures T_c(7 T) are marked by arrows.

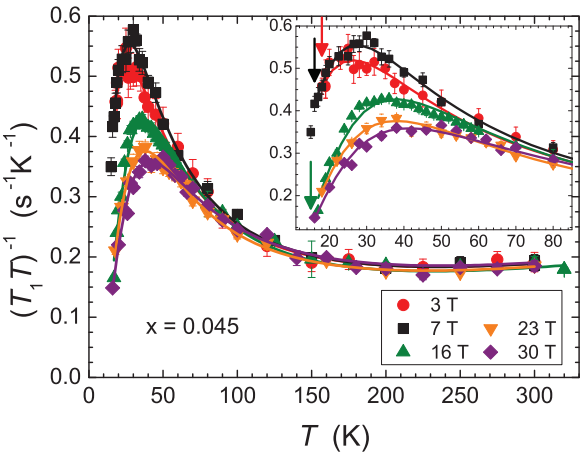

FIG. 4. (Color online) Temperature-dependent $(T_1T)^{-1}$ of $LaFeAsO_{0.955}F_{0.045}$, measured in magnetic fields of 3 T (red dots), 7 T (black squares), 16 T (green triangles), 23 T (orange triangles), and 30 T (purple diamonds). Solid lines are fits to our proposed BPP-like model; see Eq. (5). The inset depicts the relevant low-temperature region. Arrows mark $T_c(H)$.

and at low temperatures. The deviations at high temperatures can be addressed by adding a linear temperature dependence of $(T_1T)^{-1}$, as used for $x = 0.1$ and $x = 0.15$ (see solid lines in Fig. 3). However, much more important is the fact that $(T_1T)^{-1}$ decreases already above T_c and apparently forms a well-defined peak. This peak is visible in the $(T_1T)^{-1}$ data of all underdoped samples (see also Fig. 2), and it cannot be described with the depicted Curie-Weiss fit combinations. Table I compares the temperature of the maximum of $(T_1T)^{-1}$, T_{max}, to the corresponding T_c in the same field, measured by *in situ* ac susceptibility measurements. The maximum of $(T_1T)^{-1}$ occurs well above T_c (see also Fig. 10). Such a peak has already been observed in other iron-based (nonmagnetic) superconductors, such as underdoped $LaFeAsO_{0.96}F_{0.04}$ and FeSe under pressure.[7,14] It has been interpreted as a weak magnetic ordering,[14] which does not appear to be compatible with our data in light of previous experimental evidence,[12,20] or as a glassy spin freezing,[7] whose detailed analysis remains to be done.

Insight on the proper description of the relaxation data can be gained by measuring the evolution of this peak upon changing the external magnetic field. Measurements of $(T_1T)^{-1}$ on an underdoped sample with $x = 0.045$ in magnetic fields of 3, 7, 16, 23, and 30 T are shown in Fig. 4. While the high-temperature behavior of the spin-lattice relaxation rate remains unaffected by the application of higher fields, the position and the height of the peak in $(T_1T)^{-1}$ clearly change with field. Mainly, the temperature T_{max} where $(T_1T)^{-1}$ is maximal shifts to higher temperatures (from 25 K in 3 T to 42 K in 30 T) and thus is even more clear above the superconducting transition temperature T_c, which is itself reduced by the application of the external magnetic field, as expected (see also Table II and Fig. 10).

The field dependence of this peak is reminiscent of the characteristic field dependence of the BPP model,[29,30] which describes the behavior of the spin-lattice relaxation rate T_1^{-1} under the influence of local fluctuating magnetic fields $\vec{h}(t)$. In fact, T_1^{-1} probes the spectral density $J(\omega_L)$ of the fluctuating field components $h_\perp(t)$ perpendicular to the applied magnetic field at the Larmor frequency ω_L:

$$\frac{1}{T_1} = \frac{\gamma^2}{2}\int_{-\infty}^{\infty} \langle h_\perp(t)h_\perp(t+\tau)\rangle_t \exp(-i\omega_L\tau)d\tau\,, \quad (2)$$

with γ being the nuclear gyromagnetic ratio and $\langle h_\perp(t)h_\perp(t+\tau)\rangle_t$ being the autocorrelation function of the fluctuating magnetic field, which is assumed to decrease exponentially with the characteristic correlation time τ_c: $\langle h_\perp(t)h_\perp(t+\tau)\rangle_t = \langle h_\perp^2\rangle \exp(-|\tau|/\tau_c)$. This leads to

$$T_{1,BPP}^{-1}(T) = \gamma^2 h_\perp^2 \frac{\tau_c(T)}{1+\tau_c^2(T)\omega_L^2} \quad (3)$$

and thus to a peak in T_1^{-1} at the temperature where the effective correlation time of the spin fluctuations τ_c equals the inverse of the Larmor frequency ω_L. For a glassy spin freezing, the temperature dependence of the correlation time of the spin fluctuations can be described by an activated behavior:[51–53]

$$\tau_c(T) = \tau_0 \exp(E_a/k_BT)\,, \quad (4)$$

with the activation energy E_a and the correlation time at infinite temperature τ_0. Thus, upon applying higher magnetic fields, the peak in T_1^{-1} [and correspondingly a peak in $(T_1T)^{-1}$] should shift to higher temperatures, which is what we observe experimentally.

To analyze our data, we combine the BPP model for spin fluctuations with a linear temperature dependence of $(T_1T)^{-1}$ to account for the high-temperature behavior, which apparently has another origin since it is also visible in the optimally doped and overdoped samples, where the peak in $(T_1T)^{-1}$ has disappeared. In the end our fitting function reads

$$(T_1T)^{-1} = a + bT + \left(\frac{1}{T}\right) T_{1,BPP}^{-1}\,. \quad (5)$$

The constants a and b describe the linear temperature dependence. The last part is the BPP model [see Eq. (3)], multiplied with a prefactor $(1/T)$ to account for the fact that we actually fit the $(T_1T)^{-1}$ data. This formula is used to fit the data of the underdoped samples ($x = 0.045, 0.05, 0.075$) in 7 T over the whole temperature range down to the onset of superconductivity at T_c by fixing the slope b of the linear temperature dependence to the value found in the overdoped sample with $x = 0.15$. The constant term a was found to vary only slightly between the three fits. The data of $x = 0.1$ and $x = 0.15$ were only fitted with the linear contribution. All corresponding fitting curves are plotted in Fig. 1 and (in an enlarged scale) in Fig. 2 as solid lines. Note that if the linear fits were only applied to the high-temperature points for $x = 0.1$, the resulting slope b would be the same as that of the $x = 0.15$ sample (shown as dashed lines in Figs. 1 and 2). Thus, the deviation of the data from the linear dependence at low temperatures suggests that remnants of spin fluctuations remain even for this optimally doped sample.

The fact that a doping-independent slope b can be used to describe the linear temperature dependence of the dynamic susceptibility at high temperatures, as measured by $(T_1T)^{-1}$, agrees very well with the observed doping-independent high-T linear slope of the macroscopic susceptibility.[39] These

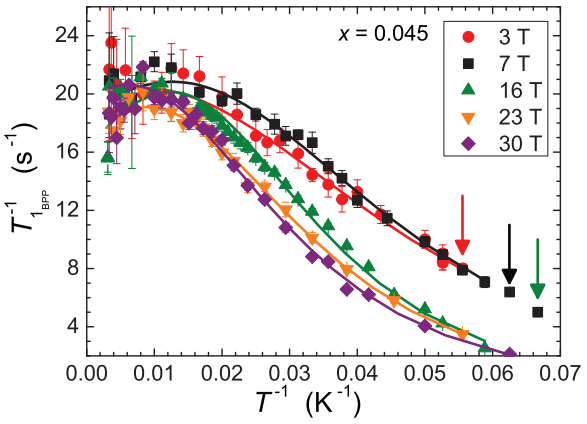

FIG. 5. (Color online) $T_{1,BPP}^{-1}$ of $LaFeAsO_{0.955}F_{0.045}$ vs inverse temperature, calculated by subtracting the linear contribution of Eq. (5) from the measured $(T_1T)^{-1}$. Arrows mark $T_c^{-1}(H)$. Solid lines denote the BPP part of our fits; see Eq. (3).

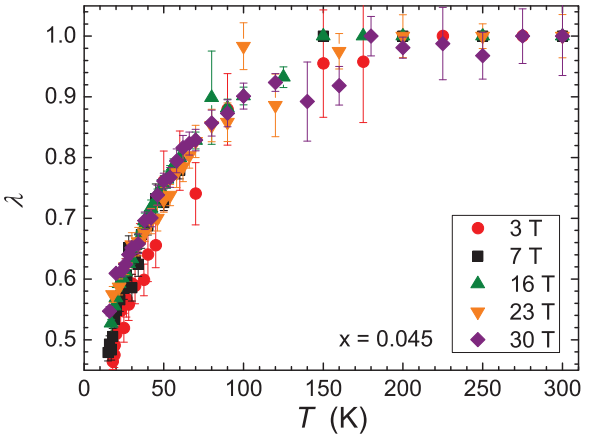

FIG. 6. (Color online) Temperature dependence of the stretching exponent λ of Eq. (1) for the field-dependent measurements on $LaFeAsO_{0.955}F_{0.045}$.

observations point towards a ground-state-independent origin, such as the recently suggested density-of-states effects.[49] Note that setting b as a free parameter during the fitting procedure did not significantly change the resulting BPP fit parameters. The doping dependence of the BPP fit parameters E_a, $h_\perp$, and τ_0 is plotted in a phase diagram of spin fluctuations in Fig. 10(a) together with the corresponding superconducting transition temperatures. Their absolute values and evolution upon doping will be discussed in Sec. IV.

Also the field-dependent data of the sample with $x = 0.045$ can be well fitted with the BPP-like model introduced in Eq. (5). Here again we fixed b to the value found for $x = 0.15$ in $H_0 = 7$ T. The fits are shown in Fig. 4 as solid lines [the corresponding BPP parameters are shown later, in Fig. 10(b), and analyzed in Sec. IV]. To isolate and illustrate the BPP contribution, Fig. 5 represents the field-dependent $T_{1,BPP}^{-1}$ data of $x = 0.045$ versus inverse temperature, the usual representation of the BPP model,[51,54] after the linear contribution from $(T_1T)^{-1}$is subtracted. Solid lines are the corresponding BPP parts of our fits [see Eq. (3)]. A clear field dependence is visible and corroborates our choice of the BPP model.

Figure 6 shows the temperature evolution of the stretching exponent λ used to fit the recovery of the nuclear magnetization [see Eq. (1)] for the field-dependent measurements on the sample with $x = 0.045$. A similar evolution was found for the doping-dependent measurements on all underdoped samples in 7 T (not shown). Starting from the temperature where $(T_1T)^{-1}$ begins to increase, a stretching exponent $\lambda < 1$ had to be used. This behavior, pointing towards a distribution of spin-lattice relaxation rates around a characteristic T_1^{-1}, is in good agreement with the suggested slowing down of spin fluctuations in this temperature range, resulting in a glassy spin freezing.[52,55] Note that, in principle, this distribution of spin-lattice relaxation rates could also stem from the presence of two different electronic environments on the nanoscale as observed by ^{75}As NQR.[56] However, these nanoscale regions are already present at room temperature, where the recovery of the nuclear magnetization is still well describable with $\lambda = 1$.

A further manifestation of the progressive slowdown of spin fluctuations in the underdoped samples is shown in Fig. 7, which compares the spin-spin relaxation rate T_2^{-1} of an underdoped sample ($x = 0.045$) with the one of the optimally doped sample ($x = 0.1$), both obtained in an external magnetic field of 7 T by fitting the decay of the spin echo after a $\frac{\pi}{2} - t - \pi$ pulse sequence to

$$M_{xy}(2t) = M_0 e^{-2t/T_2}. \quad (6)$$

While the spin-spin relaxation rate of the optimally doped sample decreases with decreasing temperature and levels off at a roughly constant value for $T \leqslant 100$ K, T_2^{-1} of the underdoped sample shows the same decrease at high temperatures but increases below $T \approx 60$ K. Connected with these observations is a broadening of the NMR linewidth for $x = 0.045$ with decreasing temperature, which is absent for $x = 0.1$. However, this broadening is difficult to quantify since the measurements for $x = 0.045$ have been done on a powder sample which also prevents a detailed analysis of T_2, such as a subtraction of the Redfield contribution, stemming from spin-lattice relaxation processes. Nevertheless,

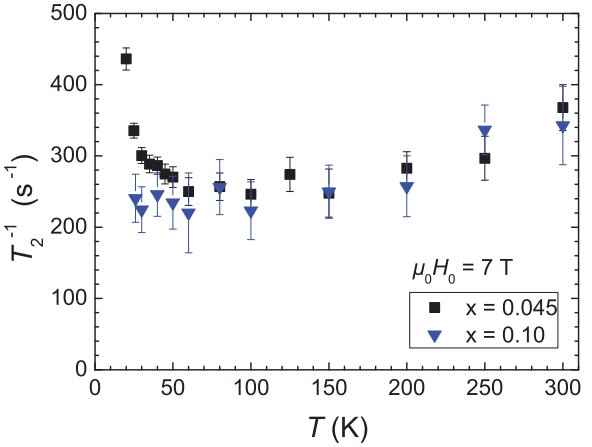

FIG. 7. (Color online) Spin-spin relaxation rate T_2^{-1} vs temperature, measured in a magnetic field of 7 T for $x = 0.045$ (black squares) and $x = 0.1$ (blue triangles).

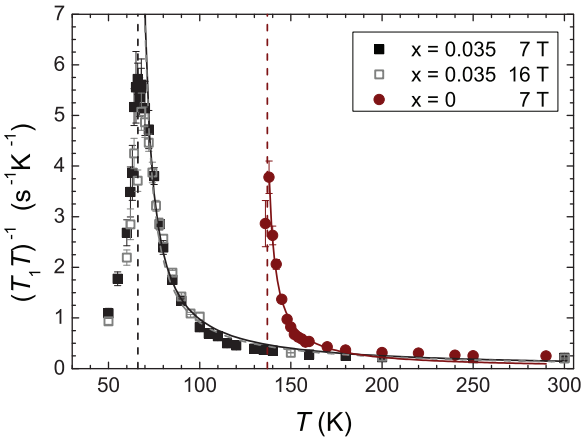

FIG. 8. (Color online) $(T_1T)^{-1}$ in the undoped (dots) and underdoped ($x = 0.035$, squares) samples, which become magnetic below $T_N = 137$ K and $T_N = 65$ K (dashed lines), respectively. Solid lines are Curie-Weiss fits to the data. For $x = 0.035$, measurements at 7 T (solid black squares) and at 16 T (open gray squares) are shown. No field dependence could be resolved.

the values of T_2 for $T > 50$ K are of the same order of magnitude as those found in $Ba(Fe_{1-x}Co_x)_2As_2$,[57] where they were argued to reflect a spin-motional narrowing, and as those reported for $Ba(Fe_{0.93}Rh_{0.07})_2As_2$.[58] The upturn of T_2^{-1} at low temperatures for $x = 0.045$ could either be caused directly by increased electronic spin fluctuations or by a reduction in the indirect interaction leading to spin-motional narrowing. On the basis of our measurements on powder samples we cannot distinguish between these two effects. Nevertheless, the lack of such an increase for $x = 0.1$ is consistent with our previous interpretation of the $(T_1T)^{-1}$ data. The fact that the increase of T_2^{-1} starts at a different temperature than that of $(T_1T)^{-1}$ suggests a slowing down of spin fluctuations over a broad temperature range, i.e., the lack of a well-defined transition, and thus refutes a scenario where the increase of $(T_1T)^{-1}$ is caused by a simple magnetic ordering.

As a final illustration of the specific character of the relaxation upturn seen in the underdoped superconducting samples, relaxation data for two magnetically ordered samples ($x = 0$ and $x = 0.035$) at different fields (7 and 16 T) are shown in Fig. 8. $(T_1T)^{-1}$ for these samples increases strongly towards the corresponding magnetic-ordering temperatures. The absolute values of $(T_1T)^{-1}$ at the maximum are about an order of magnitude higher than in the underdoped, superconducting samples. The data can be well fitted with a simple Curie-Weiss law $(T_1T)^{-1} = C/(T + \theta)$, where $\theta = -T_N$ yields the magnetic-ordering temperature T_N.[9,11,12] For the undoped sample we find $T_N = 137$ K, in nice agreement with earlier macroscopic susceptibility and muon spin rotation (μSR) measurements.[20,39] For the sample with $x = 0.035$ we find $T_N = 65$ K, which compares well with $T_N = 58$ K for a sample with a nominal fluorine content of $x = 0.03$, as recently reported for ^{75}As NQR measurements.[12]

The most essential point of the measurements is the fact that, in contrast to the peak observed in $(T_1T)^{-1}$ in the underdoped superconducting samples, the peak in $(T_1T)^{-1}$ of $x = 0.035$ does not shift with field. The measurements in 16 T yield the same temperature dependence of $(T_1T)^{-1}$ and a fit

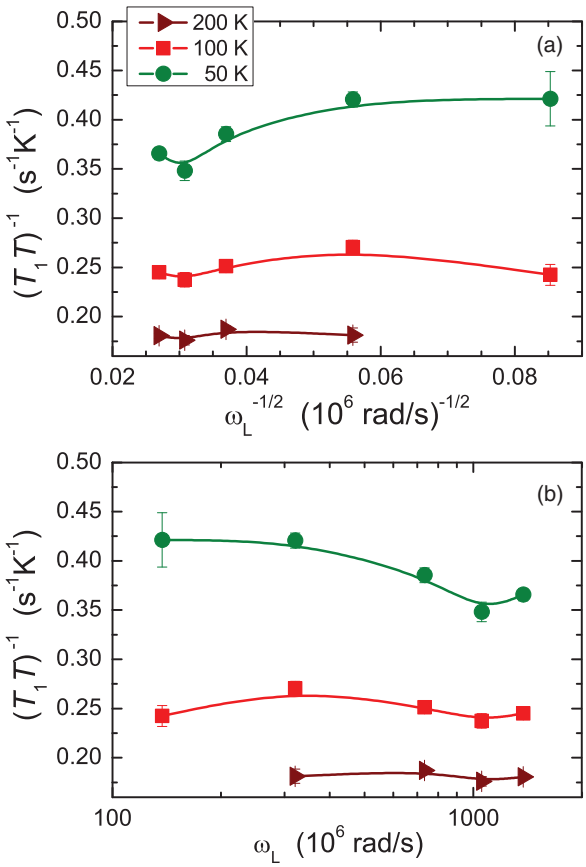

FIG. 9. (Color online) Tests for possible spin diffusion mechanism in (a) one and (b) two dimensions at three selected temperatures. (a) $(T_1T)^{-1}$ vs $\omega_L^{-1/2}$, which should result in a linear dependence if one-dimensional spin diffusion effects are at play. (b) $(T_1T)^{-1}$ vs ω_L on a semilogarithmic scale, testing for $(T_1T)^{-1} \propto \ln \omega_L^{-1}$, which is expected if 2D spin diffusion effects are at play. Lines are guides to the eyes.

to the data results in the same magnetic ordering temperature, $T_N = 65$ K. This behavior confirms that the peak in $(T_1T)^{-1}$ in the underdoped superconducting samples does not stem from a weak magnetic ordering, as suggested before,[14] but is indeed related to another effect, which we identify as a glassy spin freezing.

IV. DISCUSSION

Before discussing the doping and field dependence of the resulting BPP fitting parameters E_a, $h_\perp$. and τ_0, let us consider effects other than the BPP mechanism, which could also lead to a field-dependent peak in $(T_1T)^{-1}$but which could be ruled out for the present case. One such effect would be that the application of a magnetic field introduces some field-induced anisotropy in the spin fluctuations and thus a field dependence.[33] This is in disagreement with our measurements on the sample with $x = 0.035$, which in this case should exhibit some field dependence, as observed for $x = 0.045$. Another possible effect to be taken into consideration is electronic spin diffusion in low dimensions.[32] In fact, for electronic spin diffusion in one dimension, one expects a field dependence of the spin-lattice relaxation rate of the form

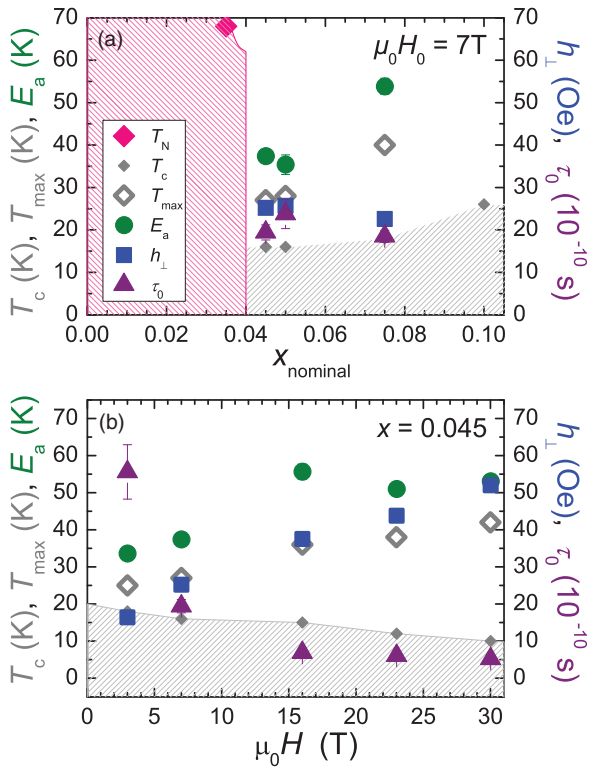

FIG. 10. (Color online) Fit parameters to our BPP-like model [Eq. (5)] (a) vs doping, obtained from the measurements in 7 T, and (b) vs field, obtained from the measurements on $x = 0.045$. Gray shaded areas denote the superconducting ground state, with solid gray diamonds marking $T_c(H)$. Open gray diamonds mark $T_{max}(x, 7\text{ T})$ in (a) and $T_{max}(0.045, H)$ in (b). The pink shaded area in (a) denotes the magnetically ordered ground state, with the pink diamond indicating $T_N = 65$ K for $x = 0.035$ as deduced from $(T_1T)^{-1}$ (see Fig. 8).

$(T_1T)^{-1} \propto \omega_L^{-1/2}$, while for 2D spin diffusion a dependence of the form $(T_1T)^{-1} \propto \ln \omega_L^{-1}$ is expected.[31,32,54,59] For our field-dependent measurements in magnetic fields up to 30 T we do not find either of these two dependencies (see Fig. 9). Even though the layered structure of $LaFeAsO_{1-x}F_x$ renders three-dimensional spin diffusion effects highly unlikely, let us note that also these can be excluded based on our measurements since they should result in a field-independent spin-lattice relaxation rate.[54,59] Thus, we can also exclude spin diffusion effects as the source of the observed field dependence of $(T_1T)^{-1}$. Finally, since the maximum of $(T_1T)^{-1}$ shifts to higher temperature upon increasing the magnetic field, a (pseudo) spin gap scenario such as discussed for cuprates[60] appears also very unlikely.

Let us now turn to the discussion of the obtained BPP fitting parameters. Figure 10 shows E_a, τ_0, and $h_\perp$ as a function of doping as deduced from measurements in 7 T [Fig. 10(a)] and as a function of magnetic field as deduced from measurements on the sample with $x = 0.045$ [Fig. 10(b)]. We first concentrate on the doping dependence [Fig. 10(a)]. The correlation time at infinite temperature and the value of the fluctuating magnetic field are essentially doping independent and amount to $\tau_0 = 2.3$ ns and $h_\perp = 25$ Oe. The rather long τ_0 is comparable to the value found in stripe-ordered $La_{1.65}Eu_{0.2}Sr_{0.15}CuO_4$, where Simovič *et al.* found $\tau_0 = 1.3$ ns by fitting the ^{139}La T_1^{-1} to the standard BPP model.[61] Also for the hole-doped cuprate superconductor $YBa_2Cu_3O_{6.45}$ τ_0 amounts to roughly 1 ns if an exponential dependence of $\tau_c(T)$ is assumed within the BPP model.[62,63] The absolute value of $h_\perp$ could be consistent with ZF-μSR and Mössbauer studies, where indications of low-T static disordered magnetism were found in underdoped samples with $0.05 \leqslant x \leqslant 0.075$, with internal fields being a factor of 20 smaller than in the magnetically ordered sample with $x = 0.04$, where $H_{int} \approx 1600$ Oe.[20,37] This leads to a rough estimation of the internal fields in these underdoped samples of about 80 Oe, which is of the same order of magnitude as our deduced $h_\perp$. Also longitudinal field (LF)-μSR measurements on a superconducting sample with a nominal fluorine content of $x = 0.06$ found evidence for very slowly fluctuating local spins and a spin-glass-like magnetic phase in 25% of the sample,[64] while no sign of such slow spin fluctuations was observed in optimally doped and overdoped $LaFeAsO_{1-x}F_x$.[65] However, while the general observation of very slow spin fluctuations in underdoped samples by means of μSR is consistent with our findings, the fact that the magnetism in the underdoped samples as seen by ZF- and LF-μSR is diluted or occurs only in a minor sample volume does not agree well with our finding of a glasslike transition of the spin fluctuations. In this context, LF-μSR on our samples could be of interest.

The activation energy E_a increases with increasing doping, from 33 K for $x = 0.045$ to 52 K for $x = 0.075$. *A priori* this would mean that the (thermal) energy that is needed to overcome the spin freezing increases when moving away from the magnetically ordered ground state, i.e., opposite to what one would naively expect. In stripe-ordered cuprates, such a doping dependence can be observed around 1/8 doping, where the temperature of the peak, and thus the activation energy, is maximal.[66] However, beyond the comparable order of magnitude of E_a in $LaFeAsO_{1-x}F_x$ and in such cuprates,[52,61] there is no ground to advocate such a scenario in pnictides. A more detailed investigation of the doping dependence may clarify this question.

We now turn to the field dependence of the BPP fit parameters for $x = 0.045$ [see Fig. 10(b)]. An increase of the fluctuating field $h_\perp$ and of the activation energy E_a upon increasing the magnetic field, together with a decrease of the correlation time τ_0 of the spin fluctuations at infinite temperatures with increasing magnetic field, suggests that spin fluctuations are enhanced upon applying an external magnetic field similar to what has been recently reported for $YBa_2Cu_3O_{6.45}$.[62] This observation is in agreement with transverse field (TF)-μSR measurements on underdoped samples in the superconducting state, which showed an increase of magnetic correlations upon increasing the applied magnetic field.[37] Note that, while the opposite field dependencies of T_{max} and T_c (see Table II) could suggest a competition between superconductivity and magnetic correlations, this could be explained by a direct reinforcement of the magnetism by the applied field, whereas the concomitant increase of T_{max}, E_a, and T_c with doping would rather indicate that superconductivity may be intimately related to very slow spin fluctuations. Let us finally note that the fact that the magnetic energy of 16 T is rather close to E_a may lead to a field dependence of the BPP parameter that is typically not observed.

Our data and interpretation agree well with resistivity measurements on underdoped $LaFeAsO_{1-x}F_x$ where at temperatures below ~60 K an upturn of the resistivity has been observed.[38] This upturn is indicative of charge-carrier localization and is visible in the underdoped superconducting samples up to $x = 0.075$. These observations suggest that a remnant feature of the spin density wave (SDW) order is still influencing the physics of the underdoped compounds, despite the absence of long-range magnetic order.

Note that our investigations are also in line with a recent NMR investigation on a sample with a nominal fluorine content of $x = 0.04$.[67] In this sample, static magnetism was observed at $T_N = 30$ K, along with a greatly reduced static magnetic field of $\mu_0 H < 100$ Oe, while a superconducting transition was observed at $T_c = 16.2$ K.[67] The very small value of the internal magnetic field, which was actually deduced from a line broadening (and not from a clear splitting) of the ^{139}La NMR spectrum, together with the reduced value of $(T_1T)^{-1}$ observed in this sample suggests that our slow spin-freezing scenario could bring insight into its physics. This sample seems to fit perfectly between our magnetically ordered sample with $x = 0.035$ and our superconducting sample with slow spin fluctuations with $x = 0.045$.

Finally, note that on the basis of the presented measurements, the true nature of the observed slowed-down spin fluctuations cannot be revealed. Apart from antiferromagnetically correlated spins, also charge, stripe, or domain-wall fluctuations could give rise to the enhancement in $(T_1T)^{-1}$. Further investigations are needed to clarify this point.

V. CONCLUSION

We have used ^{75}As NMR to investigate different samples of fluorine-doped $LaFeAsO_{1-x}F_x$. For underdoped samples with $0.045 \leqslant x \leqslant 0.075$, where the optimal T_c is still not reached, we find an enhancement of $(T_1T)^{-1}$ with decreasing temperature, followed by the formation of a well-defined peak in $(T_1T)^{-1}$ clearly above the superconducting transition temperature. We investigated the field dependence of this peak in magnetic fields up to 30 T and found a shift of the maximum of $(T_1T)^{-1}$ towards higher temperatures upon increasing the field. This behavior is consistent with the BPP model, describing a progressive slowing down of spin fluctuations. We fit our doping- and field-dependent data with a model combining the BPP dependence of T_1^{-1} with a linear temperature contribution to $(T_1T)^{-1}$, which is observed for the optimally doped and overdoped samples ($x = 0.1$ and $x = 0.15$) and seems to be doping independent, in nice agreement with the doping-independent slope of the macroscopic susceptibility. The combination of these two contributions is able to describe the doping- and field-dependent $(T_1T)^{-1}$ data of the underdoped samples over the whole temperature range, from 480 K down to T_c. Our model suggests the presence of very slow spin dynamics in underdoped, superconducting samples, which fully disappear beyond optimal doping. The field dependence of the BPP fitting parameters suggests that spin fluctuations are enhanced upon applying an external magnetic field. While this observation could suggest a competition between superconductivity and magnetic correlations, the doping dependence of the peak in $(T_1T)^{-1}$ and of the activation energy E_a would rather indicate that superconductivity may be intimately related to very slow spin fluctuations. In this regard, further investigating the nature of these fluctuations would be of interest, together with their connection or lack thereof to the magnetism of the parent compound.

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