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^{19}F NMR study of the coupling between 4*f* and itinerant electrons in the pnictide superconductors $SmFeAsO_{1-x}F_x$ ($0.15 \leq x \leq 0.2$)

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^{19}F NMR measurements in $SmFeAsO_{1-x}F_x$, for $0.15 \leq x \leq 0.2$, are presented. The nuclear spin-lattice relaxation rate $1/T_1$ increases upon cooling with a trend analogous to the one already observed in $CeCu_{5.2}Au_{0.8}$, a quasi-two-dimensional heavy-fermion intermetallic compound with an antiferromagnetic ground state. In particular, the behavior of the relaxation rate either in $SmFeAsO_{1-x}F_x$ or in $CeCu_{5.2}Au_{0.8}$ can be described in the framework of the self-consistent renormalization theory for weakly itinerant electron systems. Remarkably, no effect of the superconducting transition on ^{19}F $1/T_1$ is detected, a phenomenon which can hardly be explained within a single band model.

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Although magnetism and superconductivity are often mutually exclusive phenomena they are observed to occur simultaneously in several strongly correlated electron systems.[1] In the underdoped high-T_c superconductors the presence of both phenomena suggested the onset of a microscopic phase separation within the CuO_2 planes in magnetically ordered and superconducting regions.[2,3] In those compounds also rare-earth (RE) magnetism and superconductivity were found to coexist.[4] A similar scenario was recently found in Fe-based superconductors.[5] At variance with hole-doped cuprates but similarly to electron-doped ones,[6,7] in Fe-based superconductors RE *f* electrons do not appear to be decoupled from the Fermi sea. In fact, in superconductors of the so-called 1111 family, the reduction in the superconducting transition temperature T_c with pressure was explained in terms of a Kondo coupling between *f* and conduction electrons.[8] Also the relatively large magnetic ordering temperatures of the RE ions,[9] in some cases exceeding 10 K, can hardly be explained without invoking a hybridization between *f* and conduction electrons, namely, a Ruderman-Kittel-Kasuya-Yoshida (RKKY) coupling. Moreover, the magnitude of the hyperfine interaction between ^{75}As nuclei and *f* electrons in $NdFeAsO_{1-x}F_x$ (Ref. 10) suggests a non-negligible coupling between *f* and itinerant electrons. Even the magnitude of the Sommerfeld coefficient in the specific heat indicates that the hybridization of the conduction electron wave functions with RE *f* orbitals leads to a renormalization of the effective electron mass.[11] Thus, it is conceivable that the physics underlying the Fe-based superconductors of the 1111 family with a magnetic RE shares some similarities with that of intermetallic heavy fermion compounds.[12]

In the following the study of the static and dynamic properties of $SmFeAsO_{1-x}F_x$ superconductors involving *f* electrons will be discussed in the light of ^{19}F NMR spectroscopy and nuclear spin-lattice relaxation measurements. It will be shown that, remarkably, ^{19}F nuclear spin-lattice relaxation rate $1/T_1$ is not affected by the superconducting transition. On the other hand, $1/T_1$ can be suitably described in the framework of Moriya self-consistent renormalization (SCR) theory[13] for weakly itinerant two-dimensional (2D) antiferromagnets (AFs). In fact, within this model one can explain both the temperature (T) dependence of ^{19}F $1/T_1$ in $SmFeAsO_{1-x}F_x$ and of ^{63}Cu $1/T_1$ in $CeCu_{5.2}Au_{0.8}$, a 2D heavy fermion AF.[14] The static uniform spin susceptibility derived from the NMR shift follows a Curie-Weiss law, as expected, with a relatively large negative Curie-Weiss temperature.

Polycrystalline Sm-1111 samples were synthesized in sealed crucibles of tantalum.[15] This procedure reduces F losses since it avoids the partial reaction of fluorine with the quartz vessel so that it guarantees that the doping content strictly scales with the nominal one, x, which is intended both as an upper limit to the real content and as a sample label. The samples showed well defined superconducting transitions detected by means of a superconducting quantum interference device (SQUID) magnetometer (Fig. 1). μSR measurements performed in the $x=0.2$ sample show that the whole sample becomes superconducting below T_c.[16]

NMR measurements were performed by using standard radio-frequency (rf) pulse sequences. The intensity of the echo signal was maximized by a $\pi/2-\tau-\pi/2$ solid echo pulse sequence and ^{19}F NMR spectra were obtained from the Fourier transform of the second half of the echo. The spectra were characterized by a negative shift, with respect to ^{19}F NMR signal in PTFE (Fig. 2), which progressively increased upon cooling. The linewidth was found to be weakly T dependent above T_c, due to a small anisotropic dipolar hyperfine coupling. On the other hand, a broadening was evidenced in the superconducting phase due to the presence of the flux lines lattice field distribution. The magnitude of this distribution is similar to the one detected by means of ^{19}F NMR in $LaFeAsO_{1-x}F_x$,[17] however it appears to be significantly reduced with respect to the one detected by μSR on the same $SmFeAsO_{0.8}F_{0.2}$ sample. The origin of this discrepancy will be discussed elsewhere.

The T dependence of the NMR shift ΔK is directly related to the one of the static uniform spin susceptibility χ_s. In fact, one can write

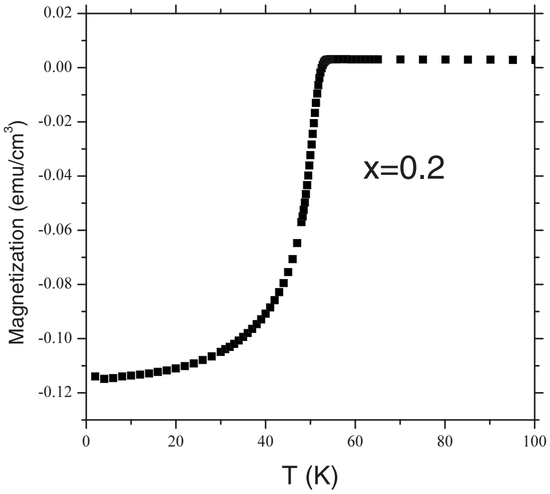

FIG. 1. T dependence of the field-cooled magnetization in $SmFeAsO_{0.8}F_{0.2}$ for a magnetic field $H \simeq 5$ Oe.

$$\Delta K = \frac{A\chi_s}{g\mu_B N_A} + \delta, \tag{1}$$

where A is ^{19}F hyperfine coupling with the f electrons, which dominates the response function, while δ is the chemical shift. Hence, by plotting ΔK vs χ_s estimated with a SQUID magnetometer, leaving T as an implicit parameter, one can estimate $A = -4.1 \pm 0.3$ kOe. The T dependence of ΔK indicates that χ_s follows a Curie-Weiss law with a Curie-Weiss temperature $\Theta = -11$ K. Remarkably Θ is an order of magnitude larger than the one of $SmBa_2Cu_3O_7$ (Ref. 4) but close to the one estimated for Sm_2CuO_4, where an indirect exchange coupling mechanism has been invoked.[6] In this latter electron-doped cuprate also the magnetic ordering temperature of Sm^{3+} moments is very close to the one found in $SmFeAsO_{1-x}F_x$. These observations indicate that the exchange coupling J among Sm^{3+} magnetic moments in

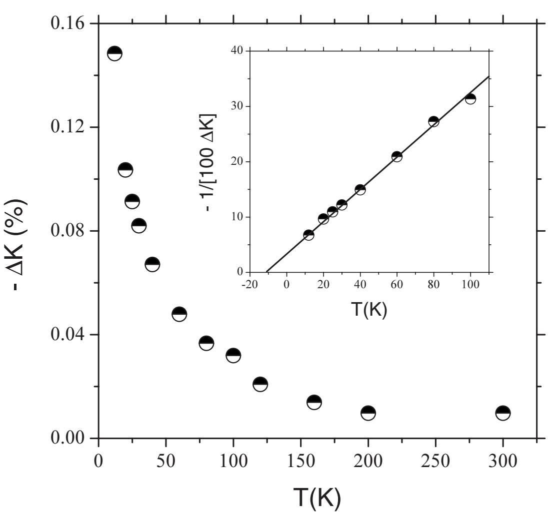

FIG. 2. T dependence of ^{19}F NMR shift in $SmFeAsO_{0.85}F_{0.15}$ for $H = 9$ T. In the inset the inverse of the shift is reported as a function of T in order to evidence the Curie-Weiss behavior of the spin susceptibility.

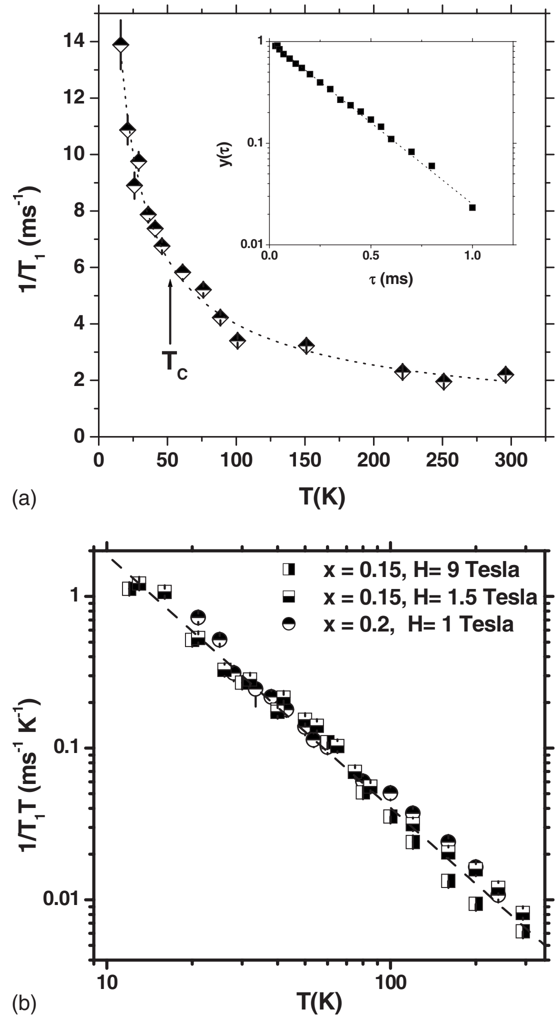

FIG. 3. (Top) T dependence of $1/T_1$ in $SmFeAsO_{0.8}F_{0.2}$ for $H = 1$ T. In the inset a typical recovery law for the nuclear magnetization is reported. (Bottom) T dependence of $1/T_1T$ in the $x = 0.15$ and $x = 0.2$ samples, showing no significant field or x dependence of $1/T_1$ in this doping range. The dashed line represents the empirical power law $1/T_1T \sim T^{-1.6}$.

$SmFeAsO_{1-x}F_x$ cannot be justified in terms of a direct exchange mechanism but rather suggests an indirect RKKY coupling.

$1/T_1$ was derived from the recovery of the nuclear magnetization $m(\tau)$, after $m(\tau)$ was set to zero by an appropriate excitation RF pulse sequence. The recovery of nuclear magnetization $y(\tau) = 1 - [m(\tau)/m(\infty)]$ was found to be a single exponential (Fig. 3), as expected for an ensemble of $I = 1/2$ nuclei with a common spin temperature. This confirms the good sample homogeneity and that the minor amount of SmOF which can be present[15] does not affect the recovery law. The T dependence of $1/T_1$, derived by fitting the recovery laws with $y(\tau) = \exp(-\tau/T_1)$, is reported in Fig. 3. One notices that $1/T_1$ increases with decreasing T and, eventually, below about 10 K, the short transverse relaxation time prevents the observation of ^{19}F NMR signal. Remarkably no anomaly in the ^{19}F spin-lattice relaxation is detected at T_c (see Fig. 3 at the top). The measurements performed at magnetic fields ranging from a few kG up to 9 T show that in the explored T range $1/T_1$ is field independent (Fig. 3).

Now we turn to the discussion of the T dependence of ^{19}F NMR $1/T_1$. First of all it is observed that ^{19}F spin-lattice relaxation rate in $SmFeAsO_{1-x}F_x$ is three orders of magnitude larger than in $LaFeAsO_{1-x}F_x$,[17] which clearly indicates that ^{19}F nuclei are probing low-energy excitations involving Sm^{3+} f electrons. Such an enhancement was recently observed also for ^{75}As $1/T_1$ in 1111 superconductors with Pr or Nd.[18] Since ^{19}F nuclei probe the correlated spin dynamics within weakly coupled SmO layers one can at first try to justify the T dependence of $1/T_1$ by considering the T dependence of the in-plane correlation length ξ for a 2D AF with localized spins. For a nuclear relaxation mechanism driven by spin fluctuations one can write

$$\frac{1}{T_1} = \frac{\gamma^2}{2} k_B T \frac{1}{N} \sum_{\vec{q}} |A_{\vec{q}}|^2 \frac{\chi''(\vec{q},\omega_R)}{\omega_R}, \tag{2}$$

with $\chi''(\vec{q},\omega_R)$ as the imaginary part of the dynamical spin susceptibility at the resonance frequency ω_R and $|A_{\vec{q}}|^2$ as the form factor describing the hyperfine coupling with the spin excitations at wave vector $\vec{q}$. In the assumption that $|A_{\vec{q}}|^2$ does not filter out critical fluctuations, by using 2D scaling arguments one finds $1/T_1 \propto \xi^z$.[19] For a 2D Heisenberg AF with localized spins one has $\xi \propto \exp(2\pi\rho_s/T)$, with $\rho_s \sim J$ the spin stiffness.[20] Since $J \sim \Theta \simeq -11$ K, it is difficult to justify within this model an increase in $1/T_1$ starting at $T \simeq 200$ K$\gg |\Theta|$. The even more rapid increase in ξ on cooling expected for 2D Ising or XY systems would not explain the experimental results.

One could also consider that the excitations probed by ^{19}F nuclei involve transitions among Sm^{3+} crystal-field levels characterized by three doublets at energies of $E_1=0$, $E_2=20$, and $E_3=45$ meV.[21] Then the relaxation processes would be Raman ones involving the exchange of energy $\hbar\omega_R$ between Sm^{3+} moments and the nuclei.[22] Accordingly the T dependence of $1/T_1$ is determined by the Boltzmann factors describing the variation in the population of the crystal-field levels.[23] Since in the explored T range $k_B T \ll E_3$ one can consider just the two low-energy doublets and one would find a T dependence characterized by an activated correlation time with an energy barrier E_2.[23] If one tries to fit the data within this approach one would find a barrier one order of magnitude smaller than E_2, showing that crystal-field excitations cannot explain the spin dynamics.

On the other hand, as it was pointed out in the previous paragraphs, the presence of an indirect RKKY exchange coupling would indicate a non-negligible hybridization between f orbitals and the conduction band, a scenario typically found in heavy fermion intermetallic compounds. Since no anomaly in $1/T_1$ is detected at T_c these conduction electrons should not be or only weakly be involved in the pairing mechanism. This would be possible only if different bands cross the Fermi surface, as it is the case here.[8,24] Hence, the enhancement of T_c caused by Sm in the 1111 superconductors should be associated with a size effect only and not to a direct involvement of f electrons in the pairing mechanism.

It is interesting to notice that if one tries to fit the increase in $1/T_1T$ with a power law one finds $1/T_1T \sim T^{-1.6\pm0.1}$ (Fig. 3). This power law is nearly identical to the one found in CeFePO,[25] a compound with the same structure of SmFeAsO, where ^{31}P $1/T_1T \sim T^{-1.5}$. In that compound the behavior of $1/T_1$ is consistent with the one of a weakly itinerant metal with a Fermi liquid ground state.[25] Therefore, it is conceivable to analyze $1/T_1$ results for $SmFeAsO_{1-x}F_x$ in the framework of the SCR theory developed by Moriya to describe weakly itinerant systems. Following Ishikagi and Moriya[26] one can write the dynamical spin susceptibility in terms of two characteristic parameters T_0 and T_A which characterize the width of the spin excitations spectrum in frequency and $\vec{q}$ ranges, respectively. For antiferromagnetic correlations, as suggested by the negative Curie-Weiss temperature, one has[26]

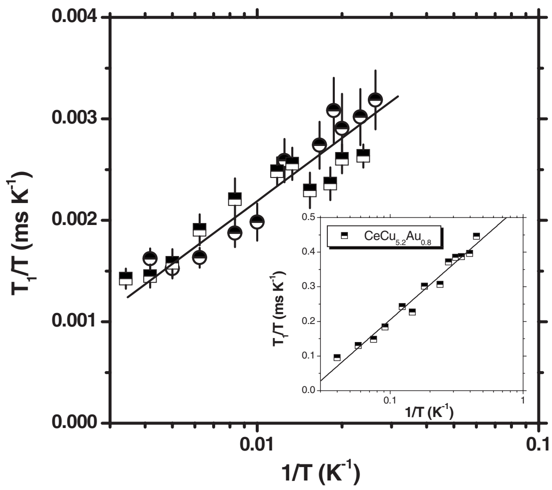

FIG. 4. Semilogarithmic plot of ^{19}F T_1/T vs T in $SmFeAsO_{1-x}F_x$ for $x=0.15$ (squares) and $x=0.2$ (circles). The solid line shows the best fit according to Eq. (7). In the inset the same type of plot is shown for ^{63}Cu NQR T_1/T vs T in $CeCu_{5.2}Au_{0.8}$ (data from Ref. 28).

$$\chi(q,\omega) = \frac{\pi T_0}{\alpha_Q T_A} \frac{1}{k_B 2\pi T_0 (y+x^2) - i\omega\hbar}, \tag{3}$$

where $x=q/q_D$, with q_D as a Debye-like cut-off wave vector, α_Q a dimensionless interaction constant and $y=1/2\alpha_Q k_B T_A \chi(0,0)$. Here $\chi(0,0)$ is the susceptibility per spin in $4\mu_B^2$ units, with dimensions of the inverse of energy, while T_A and T_0 are in Kelvin. From the previous expression one can derive $\chi''(\vec{q},\omega_R)/\omega_R$ by taking the limit $\omega_R \to 0$ since $\hbar\omega_R$ is well below the characteristic energy of spin fluctuations. One can assume that the form factor $|A_{\vec{q}}|^2 \simeq A^2$ is almost q independent as expected for delocalized electrons. Then, by integrating $\chi''(\vec{q},\omega_R)/\omega_R$ over $\vec{q}$ in 2D, over a circle of radius q_D centered at the AF wave vector Q_{AF}, one derives

$$\frac{1}{T_1} = \frac{\gamma^2 A^2}{2} T \frac{\hbar}{4\pi k_B T_A T_0 \alpha_Q} \frac{1}{y(1+y)}. \tag{4}$$

Now, for correlated electron spins[26] $y \ll 1$ and by resorting to the expression for y reported in the paragraph above, one can simplify Eq. (4) in the form

$$\frac{1}{T_1} \simeq \frac{\gamma^2 A^2}{4\pi}\left(\frac{T}{T_0}\right)\hbar\chi(Q_{AF}). \tag{5}$$

The T dependence of $1/T_1$ in the previous equation is determined by the one of $\chi(Q_{AF})$, which can be written in terms of the in-plane correlation length ξ. Taking into account the appropriate scaling and sum rules,[19] one has

$$\chi(Q_{AF}) = \frac{S(S+1)4\pi\xi^2}{3k_B T \ln[4\pi\xi^2+1]}. \tag{6}$$

Since for $T \ll T_0$ the in-plane correlation length of this weakly itinerant metal should scale as $\xi \sim \sqrt{T_0/T}$,[27] by substituting this expression in Eq. (6) and then in Eq. (5) one has

$$\frac{1}{T_1} \simeq \frac{\gamma^2 A \Delta K}{2}\frac{\hbar}{\mu_B}\frac{1}{\ln[4\pi T_0/T]}. \tag{7}$$

Finally, since for $T \gg \Theta$ the shift $\Delta K \propto 1/T$ one finds $(T_1/T) \sim \ln[4\pi T_0/T]$. In order to check the validity of this expression we have first considered the T dependence of $1/T_1$ in $CeCu_{5.2}Au_{0.8}$, a heavy fermion intermetallic compound with 2D antiferromagnetic correlations which give rise to a magnetic ground-state. In the inset of Fig. 4 we report ^{63}Cu T_1/T for this compound.[28] One notices that Eq. (7) nicely fits the data, with $T_0 = 3.2 \pm 0.3$ K. In Fig. 4 we report the same plot for ^{19}F nuclei in $SmFeAsO_{1-x}F_x$ for $x=0.2$ and $x=0.15$. In spite of the more significant scattering in the data one notices that also in $SmFeAsO_{1-x}F_x$ the same logarithmic divergence of T_1/T is observed with $T_0 = 76 \pm 15$ K.

In conclusion we have shown that in $SmFeAsO_{1-x}F_x$ the T dependence of ^{19}F $1/T_1$, driven by f electrons, can be explained by considering the low-energy excitations in SmO(F) layers as those of a 2D weakly itinerant AF. This observation brings further support to a non-negligible coupling between f and conduction electrons in the superconductors of the 1111 family and to an active role of f electrons in determining the electronic properties. The absence of any anomaly in $1/T_1$ at T_c suggests the presence of different bands crossing the Fermi surface, not all of them significantly involved in the pairing mechanism.

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