Evidence of a structural phase transition in superconducting SmFeAsO\textsubscript{1-\textit{x}}F\textit{x} from \textsuperscript{19}F NMR

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Abstract

We report resistivity, magnetization and \textsuperscript{19}F NMR results in a polycrystalline sample of SmFeAsO\textsubscript{0.86}F\textsubscript{0.14}. The resistivity and magnetization data show a sharp drop at 48 K indicating a superconducting transition. The nuclear spin–lattice rate (1/T\textsubscript{1}) and spin–spin relaxation rate (1/T\textsubscript{2}) clearly show the existence of a structural phase transition near 163 K in the sample, which also undergoes a superconducting transition. This finding creates interest in exploring whether this is unique for Sm based systems or is also present in other rare-earth based 1111 superconductors.

(Some figures may appear in colour only in the online journal)

1. Introduction

The existence of competition between structural, magnetic and superconducting (SC) transitions [1] in F-doped oxypnictides makes them unconventional. Such competing order parameters would lead to a complex phase diagram including several coexisting phases in the nanoscale range. The general belief is that the parent compound ReFeAsO (Re = rare-earth) shows a structural phase transition (SPT) from tetragonal (T) to orthorhombic (O) symmetry around \( T_s = 160 \text{ K} \), and then nearly 20 K below \( T_s \) there is a long range magnetic order (MO) with a spin density wave (SDW) type transition. As the F doping is increased, the transition temperatures for the SPT and MO gradually decrease, and at a particular concentration of F, the system undergoes an SC transition [2, 3].

Based on synchrotron powder x-ray diffraction and muon spin rotation studies, a new phase diagram for the SmFeAsO\textsubscript{1-\textit{x}}F\textit{x} system has been proposed, indicating that the SPT (T–O) in the range of 175–155 K survives up to the optimal F-doped sample [4]. The difficulty in determining the occurrence of the SPT is due to the decrease of O distortion with the increase of F content. The SPT can be magnetically driven, relieving the magnetic frustration resulting from AFM neighbor and next neighbor interactions between local Fe moments [5, 6]. It can also be related to the nematic ordering [7], defined as the spontaneously broken C\textsubscript{4} rotational symmetry of the square lattice due to either AFM spin-fluctuations or orbital ordering, as was found in cuprates [8] and in the 122 family [9]. Theoretical results also show that in the 1111 family, the SPT is driven by spin-fluctuations or orbital ordering [10]. Martinelli et al [4] claimed that the survival of the SPT even for the optimally doped superconducting sample is due to the orbital ordering mediated symmetry breaking force and not driven by magnetic fluctuations.

We intend to study SmFeAsO\textsubscript{0.86}F\textsubscript{0.14} using nuclear magnetic resonance (NMR), which is a very useful microscopic tool to probe the local magnetic and structural properties. NMR is expected to detect any role of the magnetic fluctuation on the SPT. It may be mentioned that the signature of neither the SC transition nor the SPT was detected from the \textsuperscript{19}F nuclear spin–lattice relaxation rate (1/T\textsubscript{1}) in SmFeAsO\textsubscript{0.85}F\textsubscript{0.15} [11].
temperature variation study was performed using a closed cryogen free magnet from M/S Cryogenics Limited. The lattice parameters, obtained from Rietveld refinement, are consistent with a doping level of 0.14, and the presence of a faint amount of SmOF is marked by $\chi^2 = \sum_i (y_i - y_i(\alpha))^2$, which is minimized in the Rietveld method [12], where $y_i = \text{profile intensity}$, $y_i(\alpha) = \text{calculated counts with} \alpha \text{as the parameter vector and}$ $w_i = 1/\sigma_i^2 \text{being the variance of the } y_i$. The quality of the agreement between the observed and calculated profiles is measured by the profile factor $R_{	ext{Bragg}}$ and is defined as $R_{	ext{Bragg}} = \frac{\sum_i \sqrt{y_iw_i} - \sum_i y_i}{\sum_i \sqrt{y_iw_i}}$.

2. Experimental details

The polycrystalline sample with nominal composition SmFeAsO$_{0.86}$F$_{0.14}$ was prepared through a solid state reaction route using Sm, As, FeF$_2$, Fe and Fe$_2$O$_3$ as starting materials. All handling was carried out in an Ar-filled glove box with less than 1 ppm O$_2$ and H$_2$O. SmAs alloy was first obtained by heating Sm and As under pure Ar in a closed silica tube at 900°C for 12 h. The single phase nature of the alloy was confirmed by x-ray diffraction. The SmAs was then carefully ground and sieved to less than 100 $\mu$m, and mixed in stoichiometric ratio with Fe, Fe$_3$O$_4$ and FeF$_2$, and the resulting powder was pressed into 2 $\times$ 3 $\times$ 12 mm$^3$ bars under 200 MPa. These bars were heated two times with intermediate grinding and pressing, at 1150°C for 48 h under argon in alumina crucibles sealed in closed silica tubes, with Ta pieces as getter. XRD patterns (figure 1) were recorded using a Philips X-Pert Pro diffractometer with an X-Celerator detector using Cu Kα$_1$ radiation in a 2$\theta$ range of 20°–80°. The XRD patterns were analyzed using the Rietveld method with the help of FullProf software [12].

It is very hard to determine the actual F content of 1111 compounds precisely, as F and O cannot be distinguished using XRD and as the quantification of these light elements precisely, as F and O cannot be distinguished using XRD and as the quantification of these light elements is challenging. However, we can say that the F content of 1111 is less than 1 ppm O$_2$.

The resistivity was measured using a four probe method by applying magnetic fields in the range of 0–8 T using a cryogen free magnet from M/S Cryogenics Limited. The temperature variation study was performed using a closed cycle refrigerator also from M/S Cryogenics Limited. The DC magnetization measurements were carried out in the range of 0.1–7 T in PPMS from M/S Quantum Design, Inc., USA.

The 19F NMR measurements were performed on the powder sample in a fluorine free probe and carried out using a conventional phase-coherent spectrometer (Thamway PROT 4103MR) with an $H_0 = 7.04$ T superconducting magnet (Bruker). The spectrum was recorded by changing the frequency step by step and recording the spin echo intensity by applying a $\pi/2 - \tau - \pi/2$ solid echo pulse sequence. The spin–lattice relaxation time ($T_1$) was measured using the saturation recovery method, applying a single $\pi/2$ pulse. The spin–spin relaxation time ($T_2$) was measured by applying $\pi/2 - \tau - \pi$ pulse sequence.

3. Results and discussion

3.1. Resistivity and magnetic susceptibility

Figure 2 shows the $T$ dependence of the resistivity ($\rho$) and the dc magnetic susceptibility ($\chi$). $\rho(T)$ at zero field shows a clear signature of an SC transition ($T_c$) at 48 K. The width of the transition ($T_c - T_{c1}$) is not as sharp as in the zero field case. $\rho$, above $T_c$, does not vary with $T^2$, as usually seen in the Fermi liquid case; instead it follows a linear behavior between $T_c$ and 160 K. Hess et al [14] ascribed the linear behavior of $\rho(T)$ above $T_c$ observed in SmFeAsO$_{1-x}$F$_x$ with $x$ up to 0.1 as a strange metallic behavior.
dependence of the Knight shift (spectrum. The vertical dashed line represents the resonance line position in a diamagnetic reference compound. (b) The temperature dependence of the Knight shift (K) for the 19F NMR line in SmFeAsO0.36F0.14. The variation of K(T) shows a deviation from the CW fit (→) below 160 K. Figure 3(a) shows 19F NMR spectra of SmFeAsO0.36F0.14 taken at 7.04 T. The continuous line represents the calculated spectrum. The vertical dashed line represents the resonance line position in a diamagnetic reference compound. (b) The temperature dependence of the Knight shift (K) for the 19F NMR line in SmFeAsO0.36F0.14. The variation of K(T) shows a deviation from the CW fit (→) below 160 K.

Figure 2(b) shows the variation of χ with T at 7 T with the inset showing the T dependence of M at different magnetic fields. A well defined SC transition was observed at 48 K, even at 7 T. At H ≥ 1 T, M is positive below Tc. This is because with the increase of field, the paramagnetic moment of Sm 4f (and/or Fe 3d) overcomes the diamagnetic response of the SC electrons.

The χ–T curve, in the range 160–300 K, follows χ = χ0 + C/(T + θ), with χ0 = 0.0019 emu mol−1 and θ = −11 K, where χ0 contains the contributions from Pauli paramagnetism, orbital paramagnetism and Landau diamagnetism of conduction electrons. From the Curie–Weiss (CW) constant (C), we found P eff = 0.79 μB, which is close to the free ion value (0.84 μB) of the Sm3+4f local moment. The deviation of χ(T) from the CW law may arise due to the development of short range magnetic correlation within the Fe 3d spins. A contribution from Sm 4f is ruled out, as the Sm 4f AFM ordering temperature is T N = 3.8 K (manifested as a peak in the χ–T curve, shown in figure 2(b)), which means that its contribution to χ is expected to follow the CW law near 160 K. This deviation may also result from the coupling between the Fe 3d spins/orbitals and the SPT, as observed by Martinelli et al [4]. It is to be noted that the only secondary phase we have observed in the sample is from a faint amount of SmOF, which is paramagnetic in the whole temperature range (see figure 1).

### 3.2. Nuclear magnetic resonance

Figure 3(a) shows 19F NMR spectra along with the calculated one at different temperatures. Below 10 K, the spectra could not be detected because of the excessive line broadening/shortening of the nuclear spin–spin and spin–lattice relaxation times, due to the development of short range correlations among the Sm 4f spins, as revealed in the magnetic susceptibility behavior. The almost symmetric (Lorentzian) spectrum indicates negligible anisotropy in the local magnetic field at the 19F site, as was also reported in (La/Sm)FeAsO1−xFε [15, 11]. The shift (K) of the resonance line (from the diamagnetic reference position) was either measured from the peak position of the spectrum or obtained from the theoretically fitted curve and is negative in sign (figure 3(b)) throughout the whole temperature range. In LaFeAsO0.9F0.1, 19F NMR showed a small positive shift ~100 ppm above Tc [15]. This indicates that in SmFeAsO0.36F0.14, the dominant contribution to the Knight shift arises from the Sm 4f spin over that of Fe 3d. Moreover, in the case of SmCoPO, where the phosphorous lies in the Co–P plane, it was shown from 31P NMR [16] that the major contribution to the Knight shift arises from the Sm 4f electrons.

The T dependence of the shift, K, is given by

$$K = K_0 + \left( \frac{H_{hf}}{N\mu_B} \right) \chi(T),$$

where K0 is the T independent contribution arising from the Pauli paramagnetic and orbital parts of the conduction electrons, and the transferred Van Vleck susceptibility from the rare-earth ion. Hhf represents the hyperfine coupling constant between the 19F nuclear spin and the Fe 3d and Sm 4f electron spins, N and μB are the Avogadro number and Bohr magneton respectively. The K–T curve in the range of 160–300 K, fitted (figure 3(b), solid line) using the CW formula for χ(T), gives K0 = 0.016%, θ = −11 K, and the product of the C and Hhf. Using C from the χ–T curve, we have Hhf = −3.93 ± 0.06 kOe/μB. The negative hyperfine coupling arises due to the dominant contribution of Sm 4f over that of Fe 3d, as the 19F Hhf is positive in F-doped LaFeAsO [15]. In this connection it may be mentioned that the 19F Knight shift data are not available in F-doped PrFeAsO.

### 3.3. Nuclear spin–spin (1/T2) and spin–lattice (1/T1) relaxation rates

Figure 4 shows the 19F NMR transverse relaxation rate, 1/T2 (which gives the intrinsic width of the resonance line), and the longitudinal relaxation rate, 1/T1, as a function of
In the temperature range of 10–300 K, except between a narrow range of 160–170 K, $T_1$ was determined from the recovery of the longitudinal component of the nuclear magnetization $M(\tau)$ as a function of the delay time $\tau$ using $M(\tau) = M(\infty)(1 - \exp(-\tau/T_1))$. In the latter range we used a stretched exponential ($M(\tau) = M(\infty)(1 - \exp(-\tau/T_1)^{\beta})$) to fit the recovery curve with the exponent $\beta = 0.75$ (figure 5). The recovery of the transverse magnetization was found to be a single exponential at all temperatures. $T_2$ was obtained by fitting the decay curve with the equation $M(2\tau) = M_0 \exp(-2\tau/T_2)$, where $M_0$ is the initial magnetization.

Above 180 K, $1/T_1$ remains constant while $1/T_2$ shows continuous increment. The values of $1/T_1$ are almost the same as those reported by Prando et al [11] and three orders of magnitude larger than in LaFeAsO$_{1-x}$F$_x$ [15]. This implies a dominant contribution of localized Sm 4f spin-fluctuation to the $1/T_1$ and $1/T_2$ processes [17, 18]. At around 163 K, both the $1/T_1$ and $1/T_2$ data show clear peaks. We associate these with the SPT as reported by Martinelli et al [4]. We believe that this observation is the first evidence of the SPT in SmFeAsO$_{0.86}$O$_{0.14}$ using any microscopic tool. We shall discuss the nature of this SPT in section 3.4.

Below the SPT, down to 50 K, both $1/T_1$ and $1/T_2$ show slow enhancement. However, in the range 30 K < $T < T_c$, $1/T_1$ shows a small but clear decrement which may be associated with the enhanced contribution from 4f local spin ordering superimposed on the decreasing trend of the diamagnetic contribution of the superconducting electrons. It is to be mentioned that the magnitude of the $^{19}$F NMR $1/T_1$ in the normal state of PrFeAsO$_{0.89}$F$_{0.11}$ is very close to that in LaFeAsO$_{0.89}$F$_{0.11}$, indicating a negligible contribution of Pr 4f spin over Fe 3d [19]. Moreover, an effect of Pr 4f spin ordering on the $T$ dependence of $1/T_1$ (as well as on the Knight shift) was not observed. This makes it possible to observe a large drop in $1/T_1$ at $T_c$ in PrFeAsO$_{0.89}$F$_{0.11}$.

Finally, the sharp increase of $1/T_1$ and $1/T_2$ in the range of 10–25 K should be due to the development of Sm 4f spin short range correlation (which was also reflected in the behavior of the bulk susceptibility) as the system approaches $T_N$ (3.8 K) [20].

3.4. The nature of the structural transition

We have shown the existence of an anomaly (possibly due to the SPT) near 160 K in the temperature variation of the resistivity, the susceptibility and the $^{19}$F NMR Knight shift in SmFeAsO$_{0.86}$O$_{0.14}$. However, the most direct evidence of the SPT has come from $1/T_1$ and $1/T_2$ measurement. The occurrence of the SPT will be reflected in the $^{19}$F ($I = \frac{1}{2}$) NMR $1/T_1$ through a change in the electron-nuclear dipolar and hyperfine contribution to the fluctuating local magnetic field ($H_{\text{local}}$) produced at the $^{19}$F site by the Fe 3d and Sm 4f spins. On the other hand, $1/T_2$ is governed by the contributions from (i) the dipolar interaction of the $^{19}$F nuclear spins with like and unlike nuclear spins, which is temperature and field independent ($1/T_2\text{static}$), and (ii) the dipolar and hyperfine interactions of the $^{19}$F nuclei with the longitudinal component of the fluctuating magnetic field produced by the neighboring Fe$^{2+}$ 3d-spins and Sm 4f spins ($1/T_2\text{dynamic}$). For localized spins, the latter contribution shows a Curie–Weiss behavior in its $T$ dependence [18].
Close to the magnetic ordering temperature, it shows strong $T$ dependence, as the fluctuation frequency of $H_{\text{local}}$ reduces and becomes comparable to the nuclear resonance frequency due to the development of short range magnetic correlation. Near the SPT ($T_S$), as the atomic positions are altered, it should change both $1/T_1|_{\text{static}}$ and $1/T_2|_{\text{dynamic}}$. The magnitude of the drop in both $1/T_1$ and $1/T_2$ (clearly revealed from the change in the nature of the decay curves (figure 5)) below $T_S$ is small, indicating a weak tetragonal to orthorhombic distortion, as also pointed out by Martinelli et al from structural study. Nevertheless, the effect of this small orthorhombic distortion is reflected in both the $1/T_1$ and $1/T_2$ data. As pointed out earlier, the $T$ independent behavior of $1/T_1$ in the range of 180–300 K indicates faster fluctuations of $H_{\text{local}}$ than the NMR resonance frequency ($\nu_R$). The enhancement of $1/T_1$ in the range of 163–175 K is a clear signature of the slowing down of the fluctuation of $H_{\text{local}}$, so that its frequency is comparable to $\nu_R$, contributing to the relaxation process. Such slowing down of the fluctuation of $H_{\text{local}}$ can arise due to several reasons. (1) It may be due to the development of a short range magnetic correlation of the Fe 3d spins (as the Sm 4f spins order magnetically at 3.8 K ($T_S$), the short range correlation among the 4f spins would occur close to $T_S$, so its temperature dependent contribution to $1/T_1$ would arise far below 175 K). This is supported by the fact that the $\chi$ and $K$ versus $T$ curves deviate from the CW law below 160 K (figures 2(b) and 3(b)), with $\theta = -11$ K implying AFM correlations. Thus, a role of AFM correlated spin-fluctuations (maybe secondary) in driving the SPT cannot be ruled out. (2) The effect of slowing down of the orbital fluctuations near $T_S$ may also have a contribution (through spin–orbital coupling), if the SPT is driven by 3d orbital ordering as proposed theoretically [21] and from synchrotron powder diffraction data [4]. (3) Softening of a lattice vibrational mode near $T_S$ can also enhance $1/T_1$ provided it can reduce the fluctuation frequency of $H_{\text{local}}$ through a coupling with the spin/orbital motions of the electrons, as the contribution of the phonon modes to $1/T_1$ is much less compared to that of the fluctuations of $H_{\text{local}}$.

We have shown that within a short interval of 170–160 K, the recovery curves of $T_1$ (figure 5(a)) follow a stretched exponential, $M(\tau) = M(\infty)(1 - \exp(-\tau/T_1)\beta)$, with the exponent $\beta \approx 0.75 \pm 0.03$, indicating a distribution of $1/T_1$. The spatial distribution of the SPT temperature can induce a stretched exponential in the recovery curve, but the clear sharp peak in $1/T_1$ (figure 4(b)) eliminates this possibility. However, the SPT related disorder may induce a distribution of $T_1$ over a certain temperature range above $T_S$, resulting in the necessity of a stretched exponential. At the final stage of preparation of this paper, we noticed the work of Martinelli et al [22], where it was shown that on cooling, microstrain along the tetragonal $hh0$ direction appears and increases as the temperature is decreased. Just above the structural transition, the microstrain reaches its maximum value and then is abruptly suppressed by symmetry breaking. The microstrain reflects a distribution of the lattice parameters in the tetragonal phase and hence explains the occurrence of a stretched exponential in the recovery curves of $T_1$.

In conclusion, we report resistivity, magnetization and $^{19}$F NMR results in superconducting SmFeAsO$_{1-x}$F$_x$. Both the resistivity and the magnetization data clearly show the signature of the superconducting transition at 48 K. The behavior of $1/T_1$ and $1/T_2$ confirms, for the first time from a microscopic tool like NMR, the existence of a structural phase transition at 163 K, as in the non-superconducting parent compound, in a sample that undergoes a superconducting transition at 48 K. This finding creates interest in exploring whether this is unique for Sm based Fe–As systems or is also present in other rare-earth based 1111 superconductors.

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