Magnetic fluctuations and superconductivity in iron pnictides as probed by electron spin resonance

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(Received 22 December 2009; revised manuscript received 10 June 2010; published 30 August 2010)

The electron spin resonance (ESR) absorption spectrum of Eu2+ ions serves as a probe of the normal and superconducting state in Eu0.5K0.5Fe2As2. The spin-lattice relaxation rate 1/τcESR obtained from the ESR linewidth exhibits a Korringa-type linear increase with increasing temperature above Tc evidencing a normal Fermi-liquid behavior. Below 45 K deviations from the Korringa law occur which are ascribed to enhanced magnetic fluctuations within the FeAs layers upon approaching the superconducting transition. Below Tc the spin lattice relaxation rate 1/τcESR follows a T1.5 behavior without any appearance of a coherence peak.

DOI: 10.1103/PhysRevB.82.054525

PACS number(s): 76.30.–v, 74.70.Xa

I. INTRODUCTION

The recent discovery of superconductivity in Fe-based pnictides and chalcogenides1–4 has triggered enormous research efforts to understand the origin of superconductivity and its relation to the inherent magnetism of iron. One class of these materials are the ternary AFe2As2 systems with A = Ba, Sr, Ca, Eu (122-systems) and Tc values up to 38 K.5–7 The parent compounds exhibit a spin-density wave (SDW) anomaly accompanied by a structural distortion.3,5,6 Superconductivity (SC) appears, e.g., by substituting the A-site ions by K (Refs. 3 and 5) or Fe by Co.6,7 For underdoped Ba1−xKxFe2As2 and Co-doped BaFe2As2 a coexistence of the SDW state and superconductivity has been reported.9–14

A particularly interesting 122-system is EuFe2As2 with TSDW = 190 K15–17 the highest reported SDW transition temperature in the pnictides. This system is of special importance among the 122 iron pnictides since the antiferromagnetic ordering of local Eu3+ moments at TN = 19 K provides the opportunity to study the interplay between Eu and Fe magnetism and also the influence of Eu magnetism on SC (under hydrostatic pressure18 or doping19,20). The appearance of a SDW gap in EuFe2As2 was evidenced by optical spectroscopy17 and, recently, the opening of even two gaps with different characteristics was reported.21 Moreover, electron spin resonance (ESR) in single-crystalline EuFe2As2 revealed a drastic change in the magnetic properties of the Eu-spin system from a typical metalliclike behavior above TSDW to a behavior characteristic for a magnetic and insulating system in the SDW state.22

Here, we focus on Eu0.5K0.5Fe2As2 in which the iron SDW is completely suppressed by hole doping and SC is found below Tc = 32 K.5 The bulk nature of SC is confirmed by a clear specific-heat anomaly and diamagnetism found in dc-magnetization and ac-susceptibility measurements. After subtraction of the phonon contribution, a specific-heat jump height of about 70 mJ/mol K2 has been deduced.23 Mössbauer spectroscopy measurements have established the coexistence of Eu3+ short-range magnetic ordering with SC in Eu0.5K0.5Fe2As2 below 4.5 K.24 At the same temperature, a peak is found in the zero-field cooled magnetization, measured at low fields of 5 mT,5 and a corresponding minimum occurs in the magnetic penetration depth λ(T), determined by radio-frequency technique.25 Recently, the substitution of Fe by Co in EuFe2As2 reportedly leads to an incomplete superconducting transition in the electrical resistivity.20 SC has also been found in chemically pressurized EuFe2(As0.7P0.3)2 at Tc = 26 K, followed by ferromagnetic Eu ordering at 20 K.19

In this work we show that the ESR signal of Eu2+ can be used as probe of the superconducting properties in the 122-family of Fe pnictides. In a metallic system the linewidth of the ESR absorption is a direct measure of the spin-lattice relaxation rate 1/τcESR, thus providing information on the density of states at the Fermi energy and the opening of the SC gap. In polycrystalline Eu0.5K0.5Fe2As2 we observe a clear change of 1/τcESR from a normal Fermi-liquidlike behavior with a Korringa relaxation T1 above 45 K, the onset of magnetic fluctuations of the FeAs layers for Tc < T < 45 K, and a T1.5 law below Tc = 32 K.

II. EXPERIMENTAL DETAILS

Polycrystalline Eu0.5K0.5Fe2As2 was prepared using a sintering method described in Ref. 5 and characterized by energy-dispersive x-ray (EDX) analysis, x-ray, electrical resistivity, magnetic susceptibility, and specific-heat experiments.23 ESR measurements were performed in a Bruker ELEXYS S500 CW spectrometer at X-band frequencies (ν ≈ 9.36 GHz) equipped with a continuous He gas-flow cryostat in the temperature region 4.2 < T < 300 K. ESR detects the power P absorbed by the sample from the transverse magnetic microwave field as a function of the static magnetic field H. The signal-to-noise ratio of the spectra is improved by recording the derivative dP/dH using lock-in technique with field modulation. The sample was measured in the form of fine powder.

III. EXPERIMENTAL RESULTS AND DISCUSSION

Figure 1 shows ESR spectra of a powdered polycrystal of Eu0.5K0.5Fe2As2 for different temperatures. In all cases one
observes a single exchange-narrowed resonance line which is well described by a Dyson shape,\textsuperscript{26} i.e., a Lorentz line at resonance field $H_{\text{res}}$ with half-width at half maximum $\Delta H$ and a contribution of the dispersion to absorption $(D/A)$ ratio $0 \leq D/A \leq 1$, resulting in an asymmetry typical for metals where the skin effect drives electric and magnetic components of the microwave field out of phase. The $D/A$ ratio is determined as a fit parameter and depends on sample size, geometry, and skin depth. If the skin depth is small compared to the sample size, $D/A$ approaches 1. Focusing on the low-field regime, below the superconducting transition temperature $T_c$ the spectra as documented in Fig. 2 exhibit a diplike signal at low fields typical for the magnetic shielding below the lower critical field $H_{c1} = 100$ Oe,\textsuperscript{25} followed by a broad nonresonant microwave absorption feature due to the penetration of magnetic flux in the Shubnikov phase above $H_{c1}$ of the type-II superconductor.\textsuperscript{27}

Returning to the resonant absorption we determined the absolute value of the ESR spin susceptibility $\chi_{\text{ESR}}$ above $T_c$ by comparison of the double-integrated signal intensity with that of the reference compound Gd$_2$BaCuO$_4$—the so-called green phase—which exhibits an ESR signal with a similar linewidth. In Gd$_2$BaCuO$_4$ all Gd$^{3+}$ spins (with the same electron configuration 4$f^7$ and spin S=7/2 such as Eu$^{2+}$) contribute to the ESR signal and the corresponding susceptibility exhibits a Curie-Weiss law with $\Theta_{\text{CW}} = -23$ K.\textsuperscript{28} We find that about 50% of the Eu$^{2+}$ ions participate in the resonant absorption. Estimating the skin depth $\delta = (\rho/\mu_0\sigma)^{0.5}$ using the resistivity value $\rho = 0.04 \ \Omega\,\text{cm}$ at room temperature\textsuperscript{24} and the microwave frequency 9 GHz we find a skin depth of $\delta \approx 75 \ \mu m$. The typical grain size of powdered samples is of the same order of magnitude in agreement with the percentage of Eu$^{2+}$ spins contributing to the observed signal.

The temperature dependence of the double-integrated signal intensity $\chi_{\text{ESR}}$ is compared to the static susceptibility $\chi_{\text{dc}}$ in Fig. 3(a). Note the different scales due to the fact that only 50% of the Eu spins contribute to the resonant absorption. Starting from high temperatures the Curie-Weiss behavior of $\chi_{\text{ESR}}$ is interrupted just below $T_c$, where it abruptly decreases and again increases on further lowering the temperature, while the static susceptibility increases monotonously without any drop but only slightly deviating from the Curie-Weiss law at $T_c$. The temperature dependence of the $D/A$ ratio is shown in the inset of Fig. 3(a) together with the square root of the normalized conductivity $[\sigma/\sigma(T=T_c)]^{0.5}$ in the normal state taken from Ref. 5. In the normal state the two quantities can be scaled to fall on top of each other,
confirming that $D/A$ is proportional to the penetration depth of the microwave. The $D/A$ ratio drops by a factor of 3 when crossing $T_c$ with decreasing temperature. After the anticipated onset of enhanced magnetic fluctuations of the Eu ions at about 25 K it starts to increase again up to 8 K, below which $D/A$ decreases again. The drop of intensity on passing $T_c$ can be understood due to the fact that magnetic resonance is observed only from the volume fraction of the sample which is penetrated by the magnetic flux, i.e., the surface within the London penetration depth and—in superconductors of type II—the magnetic flux tubes with normal conductivity. The concomitant drop of the $D/A$ ratio is difficult to explain because the superconductivity strongly reduces the skin depth and, hence, is naively expected to increase the $D/A$ ratio. The observed decrease may presumably result from the change of the effective geometry of the normal-state regions, i.e., the flux tubes in the superconducting matrix instead of a homogeneously conducting state because the conductivity of these regions can be anticipated to be unchanged. Thus, the ratio of the skin depth to the diameter of the flux tubes is larger than the ratio of the skin depth to the full sample diameter, which can result in a decrease in the $D/A$ ratio. However, detailed electrodynamical considerations are necessary to clarify this observation. The consecutive increase of the $D/A$ ratio on decreasing temperature can be related to the reentrant Eu magnetism which leads to an increase in the normally conducting volume fraction. Finally, the peak at about 8 K marks the onset of short-range order.24,25

The temperature dependence of the $g$ value depicted in the lower frame of Fig. 3 is only slightly affected by the onset of superconductivity. The $g$ value is about 2 above $T_c$ and starts to increase strongly below 25 K. The inset compares the corresponding inverse shift of the resonance field from its value in an insulating environment determined by $g_{\text{ins}}=1.993$ (see Ref. 29) to the inverse static susceptibility. Both quantities approximately coincide showing that the resonance shift is dominated by demagnetization fields resulting from the large Eu magnetization similar to observations in systems such as Gd$_2$ or YBaMn$_2$O$_y$.30,31 Only the small kink at $T_c$ in both the reciprocal susceptibility and the resonance shift can be regarded as an effect of the superconducting state due to the opening of the excitation gap in the electronic density of states at the Fermi level and corresponding reduction in the Pauli contribution to the susceptibility. The $g$ shift at elevated temperature $\Delta g=g-g_{\text{ins}}=J_{\text{CE-Eu}}(0)N(E_F)=0.02$ results from the homogenous polarization of the conduction electrons in the external field (Pauli susceptibility) and is comparable to usual metals.32

Now we will turn to the temperature dependence of the ESR linewidth shown in Fig. 4. Note that in metallic systems the ESR linewidth is determined by the spin-lattice relaxation time $T_1$ (Ref. 26) and, hence, provides information complementary to NMR or nuclear quadrupole resonance (NQR) measurements. One can clearly identify a linear increase with temperature with a slope $b=5.1$ Oe/K and a residual zero-temperature width $\Delta H_0=374$ Oe. Upon entering the superconducting state, a pronounced drop of the linewidth can be recognized in the inset of Fig. 4. Below about 20 K the linewidth increases again due to growing magnetic fluctuations of the Eu spins on approaching short-range order.

The observed linewidth increase in the ESR signal can only be traced in a narrow temperature range below $T_c$ and indicates a normal three-dimensional Fermi-liquid state.26,32,33 In case of ferromagnetic correlations between the Eu ions (reading off the Curie-Weiss temperature from the inset in the lower panel of Fig. 3 gives $\Theta_{\text{cw}}=10$ K) the residual linewidth is expected to be negative $\Delta H_0=-b\Theta_{\text{cw}}=\approx 50$ Oe with $b$ being the derived Korringa slope.26 The larger positive value $\Delta H_0=374$ Oe is probably due to an inhomogeneous distribution of the Eu and K ions, a problem which is well known for the 122-systems. This may lead to strong fluctuations of the long-range dipolar fields while the narrowing effect of the short-range exchange narrowing is reduced.

In the inset of Fig. 4 we show the temperature dependence of the reciprocal electron spin-lattice relaxation time given by

$$1/T_1^{\text{ESR}} = \gamma (\Delta H - \Delta H_0),$$

where $\Delta H_0=374$ Oe is the residual zero-temperature linewidth obtained from the linear fit in the normal regime and $\gamma$ denotes the gyromagnetic ratio. The obtained power law in the normal state clearly confirms the Korringa law, but for the superconducting state we observe a behavior $\propto T^{1.5}$ without any indication of a coherence (Hebel-Slichter) peak, ruling out a conventional BCS scenario with an isotropic gap. Due to the onset of magnetic fluctuations the ESR power law can only be traced in a narrow temperature range below $T_c$ and we cannot exclude the possibility that $1/T_1^{\text{ESR}}$ may be influenced by the vicinity of the short-range Eu interactions. To examine closer the vicinity of $T_c$ we plot $1/(T_1^{\text{ESR}}T)$ as a function of temperature in Fig. 5. A clear increase from the
FIG. 5. (Color online) Temperature dependence of $1/(T^2_{\text{ESR}} T)$. The solid line indicates the linear Korringa law. Below $T^* = 45$ K a deviation from the linear behavior indicates the onset of magnetic fluctuations on approaching the superconducting transition.

constant high-temperature (Korringa) value occurs already below a temperature $T^* = 45$ K and leads to a maximum and a sharp drop just below $T_\text{c}$. A similar behavior of the spin-lattice relaxation time of $^{57}\text{Fe}$ and $^{75}\text{As}$ above $T_\text{c}$ has been reported by NMR in the related system Ba$_{0.6}$K$_{0.4}$Fe$_2$As$_2$ and attributed to spin fluctuations in the FeAs layers due to interband nesting.\textsuperscript{34}

A Korringa behavior in the normal state has also been found by ESR in pure and Co-doped EuFe$_2$As$_2$ (Refs. 22 and 35) and by NMR and NQR studies on other 122-compounds\textsuperscript{34,36} but in the superconducting state of Fe-based superconductors the temperature behavior of the nuclear spin-lattice relaxation time has revealed nonuniversal power laws $1/T_1^2 \propto T^\alpha$ with $\alpha$ ranging from 2.5–6.\textsuperscript{34,36–38} We want to point out that an NQR study of pure KFe$_2$As$_2$ revealed a power law $\propto T^{1.4}$ similar to our ESR results which was interpreted in terms of multigap superconductivity with line nodes\textsuperscript{36} and a recent NMR study suggested that this exponent may be universal for overdoped Ba$_{1-x}$K$_x$Fe$_2$As$_2$.\textsuperscript{39}

Given the narrow temperature range of the ESR power law, we refrain at the present stage from performing a fit of the data, as the above-mentioned NMR studies showed that very different power laws can be obtained by varying the gaps' sizes and symmetry. However, our data nicely show that local-moment ESR in iron pnictides is a highly efficient tool to shed light on the superconducting order parameters as a complementary method to nuclear spin resonance techniques.

IV. SUMMARY

In summary, we show that the ESR signal of Eu$^{2+}$ spins gives direct access to the superconducting state of the 122-class of pnictides. We identify a normal Fermi-liquid behavior above $T_\text{c}$ from the Korringa law of the ESR spin-lattice relaxation rate $1/T^2_{\text{ESR}}$. Just above $T_\text{c}$ we observe a deviation from the Korringa behavior which we assign to magnetic fluctuations in the FeAs layers on approaching the superconducting state. Below $T_\text{c}$ no Hebel-Slichter peak is observed, ruling out a simple isotropic BCS scenario, and the spin-lattice relaxation rate follows $1/T^2_{\text{ESR}} \propto T^{1.5}$.

ACKNOWLEDGMENTS

We thank S. Graser for fruitful discussions, and A. Pimenova and V. Tsurkan for experimental support. We acknowledge partial support by the Deutsche Forschungsgemeinschaft (DFG) under the Schwerpunktprogramm Grant No. SPP1458, the Collaborative Research Center TRR 80, and the Research Unit FOR 960 (Quantum phase transitions).

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